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by

T. D. Reilly
M. L. Evans

los alamos
scientific laboratory
of the University of California
LOS ALAMOS, NEW MEXICO 87545

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MEASUREMENT RELIABILITY FOR
NUCLEAR MATERIAL ASSAY

BY

T. D. REILLY AND M. L. EVANS
NUCLEAR SAFEGUARDS RESEARCH GROUP, R-1
LOS ALAMOS SCIENTIFIC LABORATORY
LOS ALAMOS, NEW MEXICO 87545

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ABSTRACT

This report discusses the reliability of nuclear material assay (including analytical chemistry, calorimetry, and nondestructive nuclear methods). The assay of feed, product, scrap, and waste is considered. Ranges of accuracy and precision are given.

CHAPTER 1

INTRODUCTION

SCOPE

This report is designed to be a source book for reliability data relevant to nondestructive assay measurements. Comparing data from any plant with data given here permits evaluation of an assay system's performance. The data of this report would also be invaluable in designing any facility handling or processing nuclear material. Simulation studies using accuracy and precision data given here can predict how well safeguards and accountability systems detect diversion of nuclear materials in a given process or at an entire plant.

Generic types of materials are discussed (including feed, product, scrap, and waste), but not all materials encountered in the various fuel cycles are considered. A basic premise of this report is that only typical reliability data should be presented, because the limits of reliability must be determined on a plant-by-plant basis by means of a comprehensive measurement-control program. Reliability can range from the best that can be achieved under optimum conditions, to routinely obtainable values, to poor results caused by careless procedures or inadequate control. Consequently, this report gives ranges of values to be used in assessing total system reliability.

DEFINITION OF TERMS

The term "precision" describes the reproducibility of measurements by a given method at a given plant. Measurement precision may be determined by subdividing a sample and performing replicate assays, or, with nondestructive methods, by assaying the same sample again.

The term "bias" describes systematic errors encountered in a given method at a given plant. Biases are caused, for example, by calibration errors, nonrepresentative standards, or improper operating procedures. Measurement bias is normally determined by assay of a known standard, but, in the absence of an appropriate standard, the term can also describe differences between assay results for the same sample at different plants or laboratories. (In such a case, the results of one of the assays are taken as the "true" or accepted values.) If the bias in a given assay method for a known standard is small, the method is accurate.

Instruments or methods that consistently yield accurate and precise results are "reliable." Statements of reliability usually include values for precision and accuracy; when such are not available, subjective evaluations which rely on individual experience with the methods are given.

Unless otherwise stated, all values of precision are expressed as percentages and refer to one relative standard deviation (RSD). Where biases and other uncertainties (e.g., deviations) are provided, numerical values involve estimates and should be interpreted as approximate values.

Calculation of the mean and standard deviation (sigma) for a statistical distribution (e.g., relative differences between two measurements) is performed in the usual manner. That is, for a distribution consisting of N measurements X_i, i = 1, 2, 3, ..., N, the mean and standard deviation of the distribution are estimated by

$$\text{Mean} = \frac{1}{N} \sum_{i=1}^{N} X_i \equiv \overline{X} \quad ,$$

and

$$\text{Sigma} = \sqrt{\frac{1}{N-1} \sum_{i=1}^{N} (X_i - \overline{X})^2} \quad .$$

CHAPTER 2

OVERVIEW OF NUCLEAR MATERIAL ASSAY

DEVELOPMENT OF MEASUREMENT METHODS

The evolution of a method of measurement has many stages. Development begins with initial measurement theory--the recognition of a signature. After initial testing, the first studies attempt to identify the parameters that influence measurement, the interferences, the limits of applicability, and the standards required. When applicable standards already exist, the method can be tested against them. It can also be tested against other proven methods if such exist. Samples are then circulated among laboratories to test methods and standards for agreement (consistency). Standard procedures are documented and physical standards are developed. These are made available through recognized standards agencies such as the National Bureau of Standards (NBS) and the International Atomic Energy Agency (IAEA). Quality-control programs are developed within individual laboratories. Sample exchange programs may be set up to monitor measurement performance on a routine basis. Even after widespread application of the method, continuing measurement research refines procedures and standards and evaluates new methods.

STATUS OF ANALYTICAL CHEMISTRY ASSAY

Analytical chemistry measurements of product- and feed-grade materials have evolved as outlined above. Standard uranium and plutonium samples are available from NBS for calibration purposes in the determination of elemental concentration using titrimetry and coulometry and for isotopic determinations using mass spectrometry.

Standard measurement procedures have been issued through the American Society for Testing and Materials (ASTM) and the American National Standards Institute (ANSI) for the assay of product-grade uranium and plutonium metals, oxides, and nitrate solutions. ASTM-ANSI standard procedures also exist for UF_6, UF_4, and mixed-oxide materials. A comprehensive book of measurement methods[1] (detailed procedures) was published in 1963 and revised[2] in 1972. Both editions describe methods for sample preparation and for the analysis of certain scrap, waste, and product-grade materials.

Numerous domestic and foreign round robins and sample-exchange programs were initiated in the mid-1960s and some are still being conducted. In general, they demonstrate the range of measurement reliability that occurs in practice. The results of some laboratories consistently deviate from the average. Round robins have frequently improved performance in such laboratories by pointing out deficiencies in measurement methods and procedures.

Most chemical methods require considerable operator skill and care to achieve reliable results. Because of information exchange, analytical chemistry measurements have become highly developed and well documented. The definition and control of measurement accuracy have permitted reasonable agreement to be achieved concerning the use and appropriateness of reference materials and standard procedures.

STATUS OF NONDESTRUCTIVE ASSAY

Nondestructive assay (NDA) measurement is of more recent origin than chemical analysis. Most NDA methods have been developed within the last ten years, many within the last five. Developed independently at various laboratories, they are inadequately standardized and documented. Most NDA methods require special physical standards, yet there is no set procedure for producing or procuring them.

NDA methods are now used to assay product materials such as fuel rods, oxide powders, and process solutions. These methods are similar to analytical chemistry techniques in that standards for powder and solution measurements can be constructed quite readily from (or calibrated against) standard reference samples. For measurement of waste and scrap, where NDA is the major technique, more representative standards are required, and fabrication methods are still under development.

Very few sample-exchange programs using NDA methods have been undertaken. There are no common standards upon which to base comparisons. Data describing the accuracy and precision presently attainable with these methods are based on measurements of synthetic counting standards or on comparisons with analytical chemistry determinations.

With the exception of calorimetry, no NDA standard procedures have been written, although some are now under development. NDA methods have reached the stage of development at which consideration should be given to the implementation of common physical standards, standard procedures, and interlaboratory exchange programs so that measurement reliability can be better defined and controlled. These considerations would also provide impetus for much-needed container standardization. Benefits from such administrative and organizational improvements are as important as those to be derived from further technical experimentation and development.

MEASUREMENT CONTROL PROGRAM RECOMMENDATIONS

Each plant or laboratory should maintain an internal measurement control program. Such a program should include:

- Training and periodic requalification of measurement equipment operators.
- Routine procedures to establish and calibrate equipment operation.
- Occasional analysis of samples to check against biases between techniques.

- Occasional analysis of blind samples.
- Supervision of the control program by a statistician or scientist having some autonomy over laboratory operation.

CHAPTER 3

ANALYTICAL CHEMISTRY

Analytical chemistry methods are usually applied to relatively pure materials, especially process feed and product. Uranium and plutonium concentrations are determined by coulometry or a variety of titration methods. Isotopic concentrations of ^{235}U and ^{239}Pu are determined by mass spectrometry. Under optimum conditions, uranium and plutonium concentration measurements have a precision of 0.1% or better. In routine analysis this precision may be worse by a factor of two or more. Calibrations are usually performed using a standard derived from NBS standard reference material, and thus should have no significant bias.

PRECISION UNDER OPTIMUM CONDITIONS

Many different methods for determining uranium and plutonium concentration are in use (see Refs. 2-6). For very pure materials, gravimetric determinations may be made. The uranium (Ref. 2, p. 70) or plutonium (Ref. 3, p. 377) is burned to U_3O_8 or PuO_2 and accurately weighed. Nonvolatile impurities are determined spectrographically and the results are corrected accordingly. There are many titration procedures. Generally, uranium (Ref. 2, p. 74) or plutonium (Ref. 2, p. 274) is first reduced to U(IV) or Pu(III) with a substance such as zinc amalgam. It is then oxidized to U(VI) or Pu(IV) with potassium dichromate or ceric sulfate. The titration end-point is often determined potentiometrically. In controlled-potential coulometry, U(IV) or Pu(III) is oxidized to U(VI) or Pu(IV) at a platinum electrode of fixed potential chosen to eliminate interfering electrode reactions. The current is integrated to the oxidation end-point to determine the uranium or plutonium concentation. Some methods may require a uranium or plutonium separation beforehand. Reliability suffers when this is necessary.

During the development or testing of a method, the optimum performance is usually determined. All steps are performed with extreme care by a senior scientist who is well acquainted with controlled test procedures. The test materials are relatively pure; sometimes NBS standard reference materials are used for the tests. Table I shows the precision achievable under these conditions. The bias is assumed to be zero.

Figure 1 (compiled from Refs. 6, 7, 9, and 25) shows the precision obtainable by mass spectrometry for different plutonium isotopes. A similar curve applies to uranium isotopic determinations. The figure demonstrates the better precisions obtained for well-characterized, relatively pure material (a solution of NBS standard reference material) as compared with process and product solutions. It also shows that ^{238}Pu determination by α-spectroscopy (following ^{241}Am separation) is more precise than mass spectrometric determination for ^{238}Pu concentrations less than about 0.7%.

ACCURACY FROM INTERLABORATORY EXCHANGE PROGRAMS

These programs are carried out under conditions simulating those found in routine analysis situations, except that they usually involve relatively pure product-like material and the analysts often know that the samples are part of a test. Typical results exhibit an RSD larger than that obtained under optimum conditions. Often one or two laboratories exhibit good precision but vary 0.5% or more from the mean of other laboratories.

Many such exchange programs have been conducted. Some, like the SALE Program,[7] are continuing exchanges that have been conducted for many years. Others are one-time exchanges conducted for a specific purpose, such as testing a new measurement method.

TABLE I

DESTRUCTIVE ANALYSIS PRECISION UNDER OPTIMUM CONDITIONS

Method	Concentration Measured	Precision (RSD, %)	Reference
Gravimetry	Uranium	0.05	Ref. 2, p. 73
Redox titration	Uranium	0.02	Ref. 2, p. 83
Coulometry	Uranium	0.05	Ref. 4, p. 720
Mass spectrometry	^{235}U (2%)	0.014	Ref. 2, p. 118
	^{235}U (92%)	0.028	---
Gravimetry	Plutonium	0.05	Ref. 3, p. 377
Redox titration	Plutonium	0.04	Ref. 2, p. 285
Coulometry	Plutonium	0.04	Ref. 5, p. 93
Mass spectrometry	^{239}Pu (60-40%)	0.02	Ref. 5, p. 142

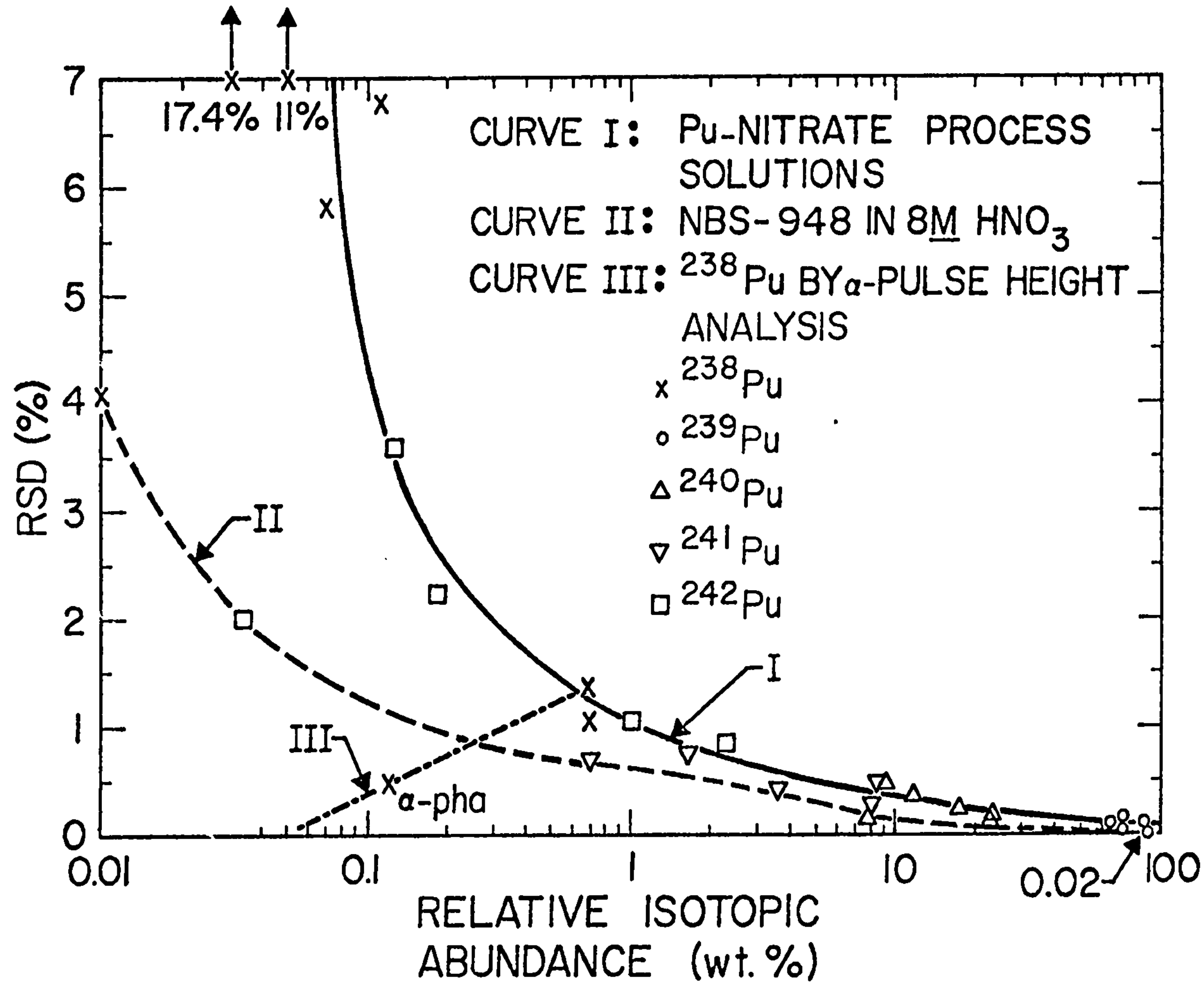

Fig. 1. Precision of plutonium isotopic measurement.

The Umpire Laboratory Program[8] began in 1968 with the aim of qualifying US and foreign laboratories to analyze uranium and plutonium materials for the Atomic Energy Commission (AEC)*. The program used samples prepared from very pure, well-characterized, source materials. Various impurities were added to simulate process and product materials. The impurity levels ranged from 0.04% for uranyl nitrate to 0.5% for plutonium dioxide. The samples were analyzed by four AEC laboratories and by others that wished to participate. The AEC laboratories were given five samples in each category and instructed to perform multiple analyses with as much diversity of analysts, equipment setups, and time of analysis as possible. Uranium nitrate, oxide, and hexafluoride as well as plutonium nitrate, oxide, and metal were tested. Materials were analyzed by all participating groups for uranium or plutonium concentration, major isotope concentration, and impurity levels, and a questionnaire was used to provide such information as analyst personnel histories, available equipment, quality control program, and statistical services. The results were analyzed to determine the significant components of the variance (between laboratories, analysts, setups, times of analysis, and replicate samples). Results were then compared with the ERDA measurement performance to determine measurement precision and bias.

The AEC laboratories defined the qualifying standard to which other laboratories were compared. Results from some laboratories were rejected because their measurement accuracy or precision was significantly worse than the standard. Even the RSD between AEC laboratories was usually a significant component of the total measurement variance — in some cases, 0.5% or more.

The SALE Program was an outgrowth of the Umpire Laboratory Program. It involves a continuing exchange (every 2 months) of uranium and plutonium samples to examine measurement variance.

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*Now the Energy Research and Development Administration (ERDA).

Reports are issued with measurement results and statistical analyses. These reports include control charts of laboratory performance that some smaller laboratories use as their main quality-control program. The first report compiled and pooled data from the Umpire Program to give typical error components in the analysis of uranium and plutonium materials. Table II shows the RSD for a single measurement as determined by this study. The table exhibits averages of interlaboratory deviations among 8 AEC laboratories and 19 other participating laboratories. Because each laboratory used the most accurate and precise method that was readily available, this study may reflect better performance than can be expected from routine analysis. Comparison of Table II with Table I shows the difference in precision between optimum conditions and exchange programs.

JEX (70) was a Joint Integral Safeguards experiment carried out at the Eurochemic Reprocessing Plant in Mol, Belgium.[9] This experiment had many goals, such as closing a material balance around a large reprocessing campaign at the plant, examining the applicability of Minor Isotope Safeguard Techniques (MIST) to a reprocessing plant, taking a physical inventory, and conducting an interlaboratory exchange program to determine the reliability of relevant analytical methods. By far the largest part of the effort was devoted to the last goal. Tests for uranium and plutonium concentration and isotope distribution were carred out on uranium and plutonium product solutions and hot dissolver solutions from the plant. Eight laboratories from the US, West Germany, Belgium, Italy, Austria, and France were involved. Samples were taken from actual feed and product materials, as contrasted to the Umpire Laboratory Program for which synthetic samples were prepared. An analysis of variance was performed to examine sampling error, interlaboratory deviation, and precision. The results show significant differences between intralaboratory and interlaboratory deviations.

TABLE II

RSD FOR A SINGLE MEASUREMENT, SALE PROGRAM[a]

	Concentration Measurement		^{235}U or ^{239}Pu Abundance Level		
Material	Volumetric[b] (%)	Gravimetric (%)	Surface Ionization (%)	Gas Source (%)	Corresponding Isotopic Level (at.%)
Uranyl nitrate	0.2	0.1	0.4	0.09	1
Uranium hexafluoride	0.2	0.09	0.4	0.03	5
Uranium oxide	0.15	0.05	0.2	---	12
Plutonium nitrate	0.7	---	0.04	---	90
Plutonium oxide	0.5	---	0.07	---	86
Plutonium metal	0.2	---	0.04	---	93

---

[a] See Ref. 7, p. 12.

[b] The terms volumetric measurement and titration refer to the same chemical procedure.

The Analytical Chemistry Program[10] was set up to test the adequacy of analytical methods on Liquid Metal Fast Breeder Reactor/Fast Fuel Test Facility (LMFBR/FFTF) mixed-oxide (plutonium-uranium) fuel. Well-characterized FFTF pellets and special blends of uranium-plutonium oxide material and impurities were distributed to seven laboratories that used essentially the same procedures and standards. The recommended method for measurement of uranium and plutonium concentration was controlled-potential coulometry. Interlaboratory variance was small because of this use of a common standard and measurement procedure; nevertheless, results from two of the laboratories had to be omitted (one from analysis of variance in uranium concentration and the other from analysis of variance in plutonium concentration) because the results were approximately 0.5% below the overall average.

A study[11-17] of shipper and receiver measurements of PuO_2 and $Pu(NO_3)_4$ shipments analyzed the differences with respect to net weight, plutonium weight, and plutonium isotopic abundances for nearly 300 different items. The study was done to provide information on actual measurement performance for use in safeguards systems studies.

Tables III-VI present data obtained from various interlaboratory exchange programs. Results from these studies vary considerably. Demonstrated precisions range from slightly below optimum (Table I) to 1% or larger. Precisions of 1% or more are seldom obtained and should not be taken as indicative of typical performance. They do show, however, that actual performance can be significantly worse than optimum, particularly if the internal measurement control program is inadequate. However, assuming good controls are maintained, a laboratory should be able to assay product materials to 0.2% or better.

JEX (70) also included an interlaboratory comparison of hot-feed solution by isotope dilution mass spectrometry analysis.[18] The solution is spiked with known amounts of ^{233}U and ^{242}Pu, and the other peaks in the mass spectrum are adjusted by

TABLE III

RELIABILITY OF URANIUM CONCENTRATION MEASUREMENTS IN INTERLABORATORY EXCHANGE PROGRAMS

Program	Material	Method	Average Precision (RSD, %)	Average Interlaboratory Deviations (RSD, %)	Average Bias[a] (%)
Umpire	Uranyl nitrate[b]	Titration (AEC)	0.03	0.08	---
	UF_6[c]	Titration (AEC)	0.08	0.18	---
	U_3O_8[d]	Titration (AEC)	0.05	0.09	---
	All[e]	Titration (all laboratories[f])	0.01-0.24[g]	---	---
SALE[h]	Uranyl nitrate	Titration	0.19	0.04	0.06
	Uranyl nitrate	Gravimetry	0.07	0.02	0.02
	Uranyl nitrate	All methods[i]	0.22	0.06	0.05
	Range (all methods)		0.03-0.79	---	0.004-0.55
	UO_2	Titration	0.17	0.03	0.03
	UO_2	Gravimetry	0.08	0.06	0.03
	UO_2	All methods[i]	0.17	0.16	0.02
	Range (all methods)		0.02-1.42	---	0.01-1.08
JEX (70)[j]	Uranyl nitrate	All chemical methods[k]	0.11	0.20	---
LMFBR/FFTF[l]	Mixed oxide	Coulometry	0.27	0.03[i]	---
Average over all programs, methods, and materials			0.13	0.09	0.04
Range for all programs, methods, and materials			0.01-1.42	0.02-0.20	0.004-1.08

---

[a] In SALE, the sample concentration is presumed known by the fabricator. The average relative deviation from this is the average bias.

[b] See Ref. 12.

[c] The results from one laboratory were omitted because they were 0.58% low relative to the average.

[d] See Ref. 14.

[e] All signifies uranyl nitrate, UF_6, and U_3O_8.

[f] AEC and other participating laboratories.

[g] This excludes two laboratories that exhibited a precision for uranyl nitrate measurement of about 1.9%.

[h] See Ref. 7.

[i] This includes titration, gravimetry, coulometry, x-ray fluorescence and mass spectrometry. See Ref. 7.

[j] See Ref. 9, pp. 7-29.

[k] This includes oxydimetry, coulometry, gravimetry, and x-ray fluorescence.

[l] See Ref. 10, pp. 10-12.

TABLE IV

RELIABILITY OF ^{235}U CONCENTRATION MEASUREMENTS IN INTERLABORATORY EXCHANGE PROGRAMS

Program	Material	^{235}U (%)	Average Precision (RSD, %)	Average Interlaboratory Deviations (RSD, %)	Average Bias[a] (%)
Umpire (AEC)	Uranyl nitrate[b]	6	0.07	0.03	---
Umpire (AEC)	UF_6[c]	6	0.18	0.16	---
Umpire (AEC)	U_3O_8[d]	12	0.09	0.19	---
Umpire (all laboratories[e])	All[f]	---	0.01-0.57	---	---
SALE[g]	Uranyl nitrate	---	0.21	0.10	0.01
SALE[g]	Range	---	0.03-0.49	---	0.001-0.55
SALE[g]	UO_2	---	0.44	0.13	0.07
SALE[g]	Range	---	0.07-2.01	---	0.02-1.29
JEX (70)[h]	Uranyl nitrate	0.35	0.9	1.2	---
Average over all programs and materials			0.32	0.30	0.04
Range for all programs and materials			0.01-2.01	0.03-1.2	0.001-1.29

---

[a] In SALE, ^{235}U concentration is assumed known by the fabricator. The average relative deviation from this is the average bias.

[b] See Ref. 12, pp. 19-21.

[c] See Ref. 13, pp. 25-27.

[d] See Ref. 14, pp. 21-25.

[e] AEC and other participating laboratories.

[f] All signifies uranyl nitrate, UF_6, and U_3O_8.

[g] See Ref. 7. The data quoted are for all methods (thermal ion and gas source mass spectrometry, and gamma spectroscopy).

[h] See Ref. 9, pp. 7-73.

TABLE V

RELIABILITY OF PLUTONIUM CONCENTRATION MEASUREMENTS IN INTERLABORATORY EXCHANGE PROGRAMS

Program	Material	Method	Average Precision (RSD, %)	Average Interlaboratory Deviations (RSD, %)	Average Bias[a] (%)
Umpire (AEC)	$Pu(NO_3)_4$[b]	Titration	0.14	0.67	---
Umpire (AEC)	PuO_2[c]	Titration	0.09	0.48[d]	---
Umpire (AEC)	Metal[e]	Titration	0.03	0.17	---
Umpire (all laboratories[f])	All[g]	Titration	0.56	---	---
SALE[h]	$Pu(NO_3)_4$	Titration (potentiometric)	0.29	0.13	0.11
SALE[h]	$Pu(NO_3)_4$	All methods[i]	0.64	0.19	0.10
SALE[h]	Range (all methods)		0.07-1.44	---	0.02-1.04
SALE[h]	PuO_2	Titration (potentiometric)	0.25	0.23	0.20
SALE[h]	PuO_2	All methods[i]	0.35	0.13	0.11
SALE[h]	Range (all methods)	---	0.09-0.86	---	0.0-0.35
JEX (70)	$Pu(NO_3)_4$[j]	Titration	0.24	0.25	---
LMFBR/FFTF	Mixed oxide[k]	Coulometry	0.14	0.07[l]	---
BNWL-1682	$Pu(NO_3)_4$[m]	---	0.49	---	0.21
BNWL-1682	Range	---	0.16-0.61	---	---
BNWL-1682	PuO_2	---	0.10	---	0.29
BNWL-1682	Range	---	0.04-0.28	---	---
Average over all programs, materials, and methods			0.25	0.26	0.17
Range over all programs, materials, and methods			0.0-1.44	0.07-0.67	0.0-1.04

---

[a] In SALE, the sample concentration is assumed known by the fabricator. The average relative deviation from this is the average bias.

[b] See Ref. 15.

[c] See Ref. 16.

[d] Two of the samples were measured at different times. The first sample gave an RSD (interlaboratory) = 0.67%; the second gave 0.06%; pooled RSD = 0.46%.

[e] See Ref. 17.

[f] AEC and other participating laboratories.

[g] All signifies $Pu(NO_3)_4$, PuO_2, and plutonium metal.

[h] See Ref. 7.

[i] This includes titration, coulometry, and x-ray fluorescence.

[j] See Ref. 9, pp. 7-54.

[k] See Ref. 10, pp. 8-9.

[l] The results of one laboratory were omitted because they were 0.49% low relative to the average.

[m] See Ref. 21.

TABLE VI

RELIABILITY OF ^{239}Pu CONCENTRATION MEASUREMENTS IN INTERLABORATORY EXCHANGE PROGRAMS

Program	Material	Average Precision (RSD, %)	Average Interlaboratory Deviations (RSD, %)	Average Bias (%)
Umpire (AEC)	$Pu(NO_3)_4$[a]	0.03	0.03	---
Umpire (AEC)	PuO_2[b]	0.03	0.07	---
Umpire (AEC)	Metal[c]	0.02	0.03	---
Umpire (all laboratories[d])	All[e]	0.01-0.08	---	---
SALE[f]	$Pu(NO_3)_4$	0.06	0.03	0.01
SALE[f]	Range	0.04-0.12	---	0.001-0.08
SALE[f]	PuO_2	0.09	0.11	0.08
SALE[f]	Range	0.02-0.16	---	0.01-0.19
JEX (70)	$Pu(NO_3)_4$[g]	0.2	0.1	---
BNWL-1682	$Pu(NO_3)_4$[h]	0.08	---	0.04
BNWL-1682	Range	0.07-0.13	---	---
Average over all programs and materials		0.07	0.06	0.04
Range for all programs and materials		0.01-0.2	0.03-0.11	0.001-0.19

[a] See Ref. 15, pp. 20-23.

[b] See Ref. 16, pp. 19-21.

[c] See Ref. 17, pp. 18-20.

[d] AEC and other participating laboratories.

[e] All signifies $Pu(NO_3)_4$, PuO_2, and plutonium metal.

[f] See Ref. 7. The data were taken using only one method--thermal ion mass spectrometry.

[g] See Ref. 9, pp. 7-80 to 7-103. The value for average precision (average interlaboratory deviation) was obtained by propagating scan errors of the isotopic ratios (interlaboratory deviations in the isotopic ratios) through the appropriate expression relating the amount of ^{239}Pu to the isotopic ratios.

[h] See Ref. 11, p. 3.

the appropriate ratios to obtain absolute masses. For this test, the relative deviations were found to be as follows.

	Precision (RSD)	Interlaboratory Deviation
U	1.1%	1.4%
Pu	0.6%	2.7%

These results illustrate the decline in measurement reliability that occurs when the samples contain substantial impurities.

CHAPTER 4

CALORIMETRY

Plutonium calorimetry involves the measurement of heat generated by the radioactive decay of plutonium and americium. All but a negligible portion of the decay energy is transformed into heat when the decay particles (alpha, beta, and low-energy gamma) are absorbed by the sample and calorimeter walls. The heat generated by a plutonium sample can be measured very accurately by calorimetry. The heat determination can be traced to primary NBS electrical standards, thereby obviating the need for accurate plutonium standards.

The plutonium isotopic composition and ^{241}Am content must be known or determined if the amount of plutonium is to be inferred from the measured heat. Uncertainties in composition are usually the largest errors in the measurement. There are also uncertainties in specific powers, heat determination, heat distribution, and heat produced by interfering reactions such as radiolysis. A good description of plutonium calorimetry is given in Refs. 19 and 20. For the contributing isotopes, Table VII (see Ref. 2, pp. 9, 21) gives the half-lives, specific powers (W/g), and the RSD in the determination of the specific powers.

Calorimetry measurements are usually somewhat time-consuming because the sample and calorimeter must come to thermal equilibrium before the heat determination can be made. For PuO_2 feed or scrap samples, equilibrium times may be as long as 8-10 h. For well-controlled geometry and small sample size, the time may be less than 1 h. A calorimeter has been built for measuring small ZPPR fuel rods (1 cm in diameter by 15 cm long, 13-26 g plutonium) in about 20 min.[21] Efforts are under way to shorten the time required for calorimetry measurements by means of isothermal

TABLE VII

SPECIFIC POWERS OF PLUTONIUM AND AMERICIUM

Isotope	Half-Life (yr)	Specific Power (W/g)	Specific Power (RSD, %)
^{238}Pu	87.79	5.6716×10^{-1}	0.10
^{239}Pu	24 082	1.9293×10^{-3}	0.27
^{240}Pu	6 537	7.098×10^{-3}	0.2
^{241}Pu	14.35	3.390×10^{-3}	0.06
^{242}Pu	379 000	1.146×10^{-4}	---
^{241}Am	434.1	1.1423×10^{-1}	0.14

calorimetry, computer control, and equilibrium end-point prediction.[22]

EXPECTED MEASUREMENT RELIABILITY

The typical precision of a plutonium heat determination is 0.25%. In some calorimeters the precision can be as low as 0.01%, but this usually applies only for very small samples and is not required in view of the large errors in isotopic abundances. The error caused by uncertainties in the specific powers is usually 0.1-0.2%. The heat distribution error (that error owing to position within the calorimeter) is usually 0.1% or less. The major component of error is the uncertainty in the plutonium isotopic composition and americium content, which must be known in computing the effective power P_{eff} (W/g) of the plutonium in the sample.*

Precisions vary for plutonium mass spectrometry. The precision shown in Fig. 1 will be used here for the purpose of illustration. The lower curve (for a well-characterized NBS sample) represents a high-precision case, and the upper curve (for a process solution) represents a low-precision extreme. The lower curve is similar to that used by the analytical chemistry group at the Los Alamos Scientific Laboratory (LASL).[23] The upper curve is similar to that reported by the New Brunswick Laboratory (NBL).[24] These reported isotopic precisions are used to compute the uncertainty in P_{eff} for the range of plutonium isotopic compositions given in Table VIII.[25]

For this illustration, the americium ingrowth is assumed to be for 1 yr (^{241}Am = 0.047 ^{241}Pu). The best americium precision is assumed to be 2%, the worst precision 10%. Tables IX-XIV give details of the calculations for each plutonium composition of Table II, and the results (calorimetric plutonium measurement precision) are summarized in Table XV. The gamma spectrometry values are optimal. They are obtained using predictions of Gunnink's simulation code (Fig. 2) for the analysis of the 95- to

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*The total power (W_s) of a plutonium sample as measured by calorimetry is given by summing the power produced by the n constituent isotopes contributing to the sample heat:

$$W_s = \sum_{i=1}^{n} M_i P_i = M \sum_{i=1}^{n} R_i P_i = M\, P_{eff} \quad ,$$

where M_i = mass of the i^{th} isotope,
M = total mass of plutonium,
P_i = specific power of the i^{th} isotope,
R_i = ratio of the mass of the i^{th} isotope to the total plutonium mass (isotopic abundance), and
P_{eff} = effective specific power of the sample.

Thus, the mass of the plutonium in a sample can be calculated from the sample's power and effective specific power:

$$M = W_s / P_{eff} \quad .$$

The relative error in the determination of plutonium mass is given by

$$\left(\frac{\sigma M}{M}\right)^2 = \left(\frac{\sigma W_s}{W_s}\right)^2 + \sum_{i=1}^{n} \left(F_i \frac{\sigma P_i}{P_i}\right)^2 + \sum_{i=1}^{n} \left(F_i \frac{\sigma R_i}{R_i}\right)^2 \quad ,$$

where $F_i = R_i P_i / P_{eff}$. The first term in the above equation is the uncertainty in the heat determination and the second term derives from uncertainties in the specific powers. The third term, related to uncertainties in the isotopic abundances (mass ratios), is the major component of error in the plutonium determination.

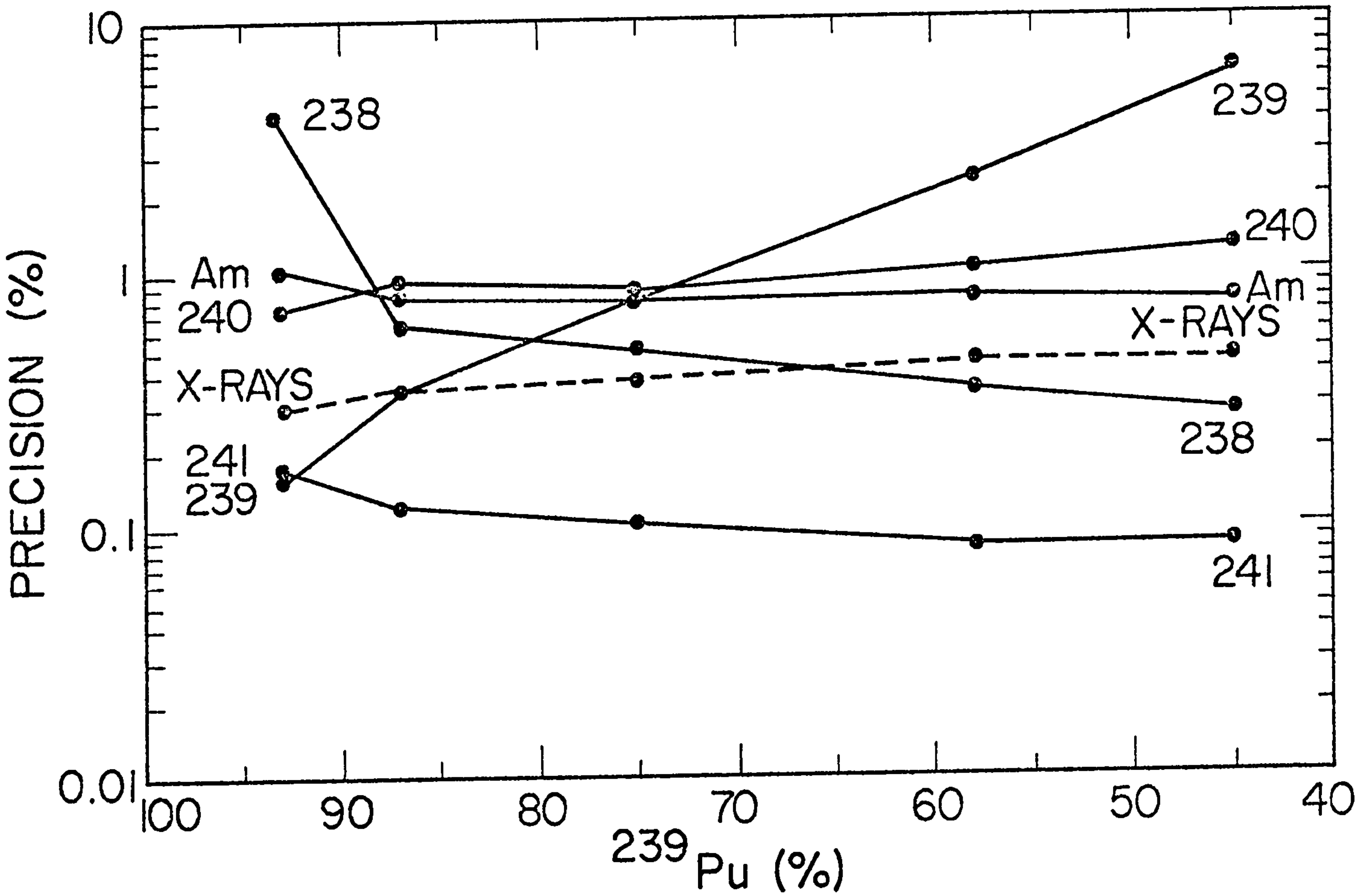

Fig. 2. Optimum precision of gamma-ray isotopic determination for the range of isotopic distributions given in Table XXIII.

TABLE VIII

TYPICAL PLUTONIUM ISOTOPIC COMPOSITIONS

Burnup (1000 MWD/t)	Description	Isotopic Abundance (%)				
		^{238}Pu	^{239}Pu	^{240}Pu	^{241}Pu	^{242}Pu
Low	Low-burnup plutonium	0.01	93.6	5.9	0.38	0.015
8-10	FFTF feed	0.08	86.1	11.7	1.89	0.21
16-18	---	0.25	75.0	18.0	4.5	1.0
25-27	Spent LWR	1.1	61.6	20.9	12.6	3.8
38-40	Saturated LWR recycle	3.3	41.1	27.6	17.6	10.4
---	Spent LMFBR	0.94	59.9	27.0	7.5	4.7

TABLE IX

PRECISION OF CALORIMETRIC MEASUREMENT FOR LOW-BURNUP PLUTONIUM

Isotope	Isotopic Abundance (%)	Fractional Specific Power	Isotopic Uncertainty σ_{R_i}/R_i (%) Mass Spectrometry High Precision	Mass Spectrometry Low Precision	Gamma Spectroscopy
^{238}Pu	0.01	0.0245	2.5	12	4.2
^{239}Pu	93.6	0.7802	0.02	0.07	0.14
^{240}Pu	5.9	0.1809	0.28	0.48	0.7
^{241}Pu	0.38	0.0056	0.75	1.75	0.17
^{242}Pu	0.015	---	---	---	---
^{241}Am	0.018	0.0088	2	10	1.0

Total specific power, $P_{eff} = 2.315 \times 10^{-3}$ W/g

Plutonium precision (high) = 0.08% RSD

Plutonium precision (low) = 0.31% RSD

Plutonium precision (gamma) = 0.20% RSD

TABLE X

PRECISION OF CALORIMETRIC MEASUREMENT FOR FFTF FEED

Isotope	Isotopic Abundance (%)	Fractional Specific Power	Isotopic Uncertainty σ_{R_i}/R_i (%) Mass Spectrometry High Precision	Mass Spectrometry Low Precision	Gamma Spectroscopy
^{238}Pu	0.08	0.1458	1.4	5.7	0.62
^{239}Pu	86.1	0.5338	0.02	0.1	0.33
^{240}Pu	11.7	0.2669	0.1	0.35	0.92
^{241}Pu	1.89	0.0206	0.41	0.78	0.12
^{242}Pu	0.21	---	---	---	---
^{241}Am	0.089	0.0327	2	10	0.8

Total specific power, $P_{eff} = 3.112 \times 10^{-3}$ W/g

Plutonium precision (high) = 0.22% RSD

Plutonium precision (low) = 0.9% RSD

Plutonium precision (gamma) = 0.32% RSD

TABLE XI

PRECISION OF CALORIMETRIC MEASUREMENT FOR 18000 MWD/t BURNUP

Isotope	Isotopic Abundance (%)	Fractional Specific Power	Isotopic Uncertainty σ_{R_i}/R_i (%) Mass Spectrometry High Precision	Mass Spectrometry Low Precision	Gamma Spectroscopy
^{238}Pu	0.25	0.3125	0.75	2.20	0.5
^{239}Pu	75.0	0.3189	0.04	0.1	0.75
^{240}Pu	18.0	0.2816	0.16	0.3	0.85
^{241}Pu	4.5	0.0336	0.3	0.53	0.1
^{242}Pu	1.0	---	---	---	---
^{241}Am	0.212	0.0534	2	10	0.8

Total specific power, $P_{eff} = 4.538 \times 10^{-3}$ W/g

Plutonium precision (high) = 0.25% RSD

Plutonium precision (low) = 0.88% RSD

Plutonium precision (gamma) = 0.38% RSD

TABLE XII

PRECISION OF CALORIMETRIC MEASUREMENT FOR SPENT LWR

Isotope	Isotopic Abundance (%)	Fractional Specific Power	Isotopic Uncertainty σ_{R_i}/R_i (%) — Mass Spectrometry: High Precision	Isotopic Uncertainty σ_{R_i}/R_i (%) — Mass Spectrometry: Low Precision	Isotopic Uncertainty σ_{R_i}/R_i (%) — Gamma Spectroscopy
^{238}Pu	1.1	0.6225	0.5	1.0	0.32
^{239}Pu	61.6	0.1185	0.05	0.12	2.2
^{240}Pu	20.9	0.1480	0.16	0.28	1.0
^{241}Pu	12.6	0.0426	0.2	0.35	0.08
^{242}Pu	3.8	---	---	---	---
^{241}Am	0.595	0.0678	2	10	0.8

Total specific power, $P_{eff} = 1.002 \times 10^{-2}$ W/g

Plutonium precision (high) = 0.34% RSD

Plutonium precision (low) = 0.92% RSD

Plutonium precision (gamma) = 0.36% RSD

TABLE XIII

PRECISION OF CALORIMETRIC MEASUREMENT FOR SATURATED LWR RECYCLE

			Isotopic Uncertainty $^{\sigma}R_i / R_i$ (%)		
			Mass Spectrometry		
Isotope	Isotopic Abundance (%)	Fractional Specific Power	High Precision	Low Precision	Gamma Spectroscopy
^{238}Pu	3.3	0.8130	0.35	0.6	0.17
^{239}Pu	41.1	0.0344	0.1	0.18	6.2
^{240}Pu	27.6	0.0851	0.14	0.22	1.2
^{241}Pu	17.6	0.0259	0.18	0.3	0.085
^{242}Pu	10.4	---	---	---	---
^{241}Am	0.831	0.0412	2	10	0.75

Total specific power, $P_{eff} = 2.303 \times 10^{-2}$ W/g

Plutonium precision (high) = 0.3% RSD

Plutonium precision (low) = 0.64% RSD

Plutonium precision (gamma) = 0.28% RSD

TABLE XIV

PRECISION OF CALORIMETRIC MEASUREMENT FOR SPENT LMFBR

			Isotopic Uncertainty σ_{R_i}/R_i (%)		
			Mass Spectrometry		
Isotope	Isotopic Abundance (%)	Fractional Specific Power	High Precision	Low Precision	Gamma Spectroscopy[a]
^{238}Pu	0.94	0.5879	0.5	1.0	---
^{239}Pu	59.9	0.1275	0.08	0.12	---
^{240}Pu	27.0	0.2113	0.14	0.23	---
^{241}Pu	7.5	0.0280	0.23	0.43	---
^{242}Pu	4.7	---	---	---	---
^{241}Am	0.354	0.0446	2	10	---

Total specific power, $P_{eff} = 9.068 \times 10^{-3}$ W/g

Plutonium precision (high) = 0.3% RSD

Plutonium precision (low) = 0.74% RSD

Plutonium precision (gamma) = 0.36% RSD

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[a] Similar to that for spent LWR (see Table XII).

TABLE XV

CALORIMETRIC PLUTONIUM MEASUREMENT PRECISION

			Error Component (RSD, %)			
				Isotopic Ratios		
				Mass Spectrometry[b]		
Description	^{239}Pu (%)	P_{eff} (W/g)	Specific Powers[a]	High Precision	Low Precision	Gamma Spectroscopy[c]
Low-burnup plutonium	93.6	2.315×10^{-3}	0.21	0.08	0.31	0.20
FFTF feed	86.1	3.112×10^{-3}	0.15	0.22	0.9	0.32
16-18 000 MWD/t	75.0	4.538×10^{-3}	0.11	0.25	0.88	0.38
Spend LWR	61.6	1.002×10^{-2}	0.08	0.34	0.92	0.36
Saturated LWR recycle	41.1	2.303×10^{-2}	0.08	0.3	0.64	0.28
Spent LMFBR	59.9	9.068×10^{-3}	0.08	0.3	0.74	---

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[a] These values were computed from the data of Tables VII and VIII using the expression $[\Sigma^{n}_{i=1} (F_i \ \sigma P_i/P_i)]^{\frac{1}{2}}$, where $\sigma P_i/P_i$ is the relative error in the determination of the specific power of the i^{th} isotope.

[b] These values were computed from the data of Fig. 1 and Table VII using the expression $[\Sigma^{n}_{i=1} (F_i \ \sigma R_i/R_i)]^{\frac{1}{2}}$, where $\sigma R_i/R_i$ is the relative error in the determination of the abundance of the i^{th} isotope.

[c] These values were computed from the data of Fig. 2 and Table VII with the expression in (b) above.

105-keV complex for a 1-h count on 1 kg PuO_2. These values, admittedly optimistic, have yet to be confirmed by experiment.

Table XV shows the high precision obtainable from plutonium calorimetry. It also shows that this precision varies little with changes in isotopic composition. The high-precision values result in uncertainties of about 0.3%, the low-precision just under 1%. The largest source of error is caused by uncertainties in the ^{238}Pu concentration. This isotope produces as much as 80% of the total heat (see Tables IX-XIV*) and must be measured carefully. In mass spectrometry determinations, ^{238}U from the source filament or from incomplete uranium separation can bias the ^{238}Pu determination. This can be especially troublesome at low ^{238}Pu concentrations (less than 0.1%).

The mass spectrometry determination requires sampling the plutonium container. Heterogeneous samples especially can produce large sampling errors, because isotopically inhomogeneous scrap materials have been noted.[25]

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*In Tables IX-XIV, the precision of plutonium determination is calculated from the expression

$$\left[\sum_{i=1}^{n}\left(F_i\,\frac{\sigma R_i}{R_i}\right)^2\right]^{1/2}$$

where $F_i = R_iP_i/P_{eff}$ is the fractional specific power owing to the i^{th} isotope. This expression includes uncertainty owing only to imprecision of the isotopic determination — the chief source of error in calorimetric plutonium measurement.

The contribution of ^{242}Pu to the total specific power is negligible in the example compositions of Tables IX-XIV, and has been omitted in the calculation of plutonium calorimetric precision.

CALORIMETRIC PRECISION: INTERLABORATORY COMPARISON

The heat determination of calorimetric measurement should show a precision of about 0.25%. A good demonstration is provided by the following experiment. Thirty small cans of plutonium-contaminated incinerator ash were sent to Mound Laboratory for calorimetric measurement as part of a LASL inventory verification program.[26] Small samples of these materials were also sent for mass spectrometry and gamma spectroscopy isotopic determinations. After Mound Laboratory's measurements were completed, the cans were returned to LASL and were calorimetered. The two measurements were performed nearly 6 months apart with different calorimeters operated by different personnel. The results of these two measurements are given in Table XVI. The same isotopic composition and values of specific heat were assumed for both measurements (corrected for radioactive decay and americium ingrowth) so that the table is a comparison of the two heat determinations. Table XVI exhibits excellent agreement between the two measurements. Assuming each measurement has a precision of about 0.25%, the standard deviation of the relative differences should be about 0.35% (adding errors in quadrature), in good agreement with the measured value of 0.39%.

These samples were ill-suited to mass spectrometric isotopic determination because of large isotopic inhomogeneities. Gamma scans of the containers indicated ^{240}Pu differences as large as a factor of two in a single can. However, a crude gamma isotopic measurement was attempted by LASL. Using that isotopic distribution, the mean and standard deviation of the values (LASL-Mound)/Mound, were -0.015 and 0.022 respectively. The samples cans were also gamma-scanned for total ^{239}Pu content; those measurements are discussed in Chap. 5.

Data from another interlaboratory comparison are presented in Table XVII.[27] The data are for a series of plutonium scrap materials calorimetered at two laboratories. Since the materials from the originating plant had a relatively constant isotopic

TABLE XVI

INTERLABORATORY CALORIMETRY COMPARISON

	Plutonium Mass (g)		
Sample	LASL	Mound	Relative Difference[a]
154A	29.36	29.4	-0.0014
154B	46.98	46.7	0.0060
292A	40.78	40.8	-0.0005
292B	32.76	32.6	0.0049
328A	84.17	84.0	0.0020
328B	68.06	68.2	-0.0021
338A	80.96	80.7	0.0032
338B	6.78	6.8	-0.0029
401A	36.89	37.1	-0.0057
401B	36.86	36.8	0.0016
430A	88.24	87.9	0.0039
430B	57.28	57.3	-0.0003
433A	50.71	50.4	0.0062
433B	44.54	44.7	-0.0036
508A	63.63	63.9	-0.0042
508B	53.51	53.8	-0.0054
650A	38.45	38.7	-0.0065
650B	36.33	36.4	-0.0019
811A	52.78	52.7	0.0015
811B	45.47	45.4	0.0015
814A	44.03	44.2	-0.0038
814B	43.37	43.3	0.0016
610A	63.88	64.5	-0.0096
610B	43.16	43.3	-0.0032
627A	71.29	71.2	0.0013
627B	87.85	87.7	0.0017
628A	36.42	36.5	-0.0022
628B	34.27	34.2	0.0020
633A	14.81	14.6	0.0144[b]
633B	72.74	72.5	0.0033

Mean = -0.00043 = -0.043%
Sigma = 0.0039 = 0.39%

---

[a] Relative differences are with respect to the Mound values.

[b] Sample 633A has been omitted in the calculation of the mean and standard deviation.

TABLE XVII

INTERLABORATORY COMPARISON OF CALORIMETRIC PLUTONIUM SCRAP MEASUREMENTS

Sample	Plutonium Mass (g)		Relative Difference[a]
	Laboratory 1	Laboratory 2	
F-1	195	201	-0.0299
F-2	8	13	-0.385[b]
F-3	223	231	-0.0346
F-4	423	424	-0.0024
F-5	52	25	1.08[b]
F-6	490	476	0.0294
F-7	153	144	0.0625
F-8	555	545	0.0183
F-9	837	821	0.0195
F-10	9	14	-0.357[b]
F-11	369	355	0.0394
F-12	195	191	0.0209
F-13	733	724	0.0124
F-14	93	95	-0.0211
F-15	310	304	0.0197
F-16	522	502	0.0398
0-7	450	450	0.0

Mean = 0.0124
Sigma = 0.028

---

[a] Relative differences are with respect to Laboratory 2.

[b] Samples F-2, F-5, and F-10 were omitted from the calculation of the mean and standard deviation for reasons explained in the text.

composition, the stream-average composition was used to calculate P_{eff} for both measurements. Here the agreement between the two measurements is not as good as for the previous comparison. The measurment of sample F-5 shows an obvious nonrandom error (chemcal recovery later found 23.7 g plutonium). Samples F-2 and F-10 contain amounts of plutonium near the sensitivity threshold of the calorimeters, hence the large relative differences. Even with these cases removed, the standard deviation (sigma) of the relative differences of these two measurements is about 3%.

COMPARISON OF CALORIMETRY WITH CHEMICAL ANALYSIS OR RECOVERY

Results of two experiments are presented below that compare calorimetry measurements with chemical analysis and total chemical recovery. Table XVIII presents data taken from measurements on PuO_2 feed material standards from a pilot mixed-oxide fabrication plant.[28] This material is well characterized with respect to americium content and plutonium isotopic composition. The agreement between the assay methods is comparable to the expected precision of the individual measurements.

Another test involved 65 samples chosen from a plutonium inventory and sent to several laboratories to compare a variety of NDA techniques. One laboratory (Mound) calorimetered the samples and computed total plutonium from the stream average ^{239}Pu and ^{240}Pu concentrations and gamma spectrometric ^{238}Pu, ^{241}Pu, and americium values. These samples were of a variety of material types: metal buttons, dirty oxide, green cake, fluoride, and incinerator ash. A sampling of each category was chosen for destructive analysis by the LASL Analytical Chemistry Group CMB-1. With the exception of the metal buttons, a total dissolution and plutonium recovery was attempted (a very large effort). The results of this experiment (unpublished) are presented in Table XIX. The calorimetry results were based on the stream average plutonium isotopic composition except for the ash samples, where the gamma correction was used for the larger

TABLE XVIII

COMPARISON OF FEED MATERIAL BY CALORIMETRY AND CHEMICAL ANALYSIS

	Plutonium Mass (g)		
Sample	Calorimetry	Chemical	Relative Difference[a]
A	486.48	487.46	-0.0020
B	586.56	581.58	0.0086
C	819.33	821.10	-0.0022
D	979.17	973.52	0.0058
E	991.86	984.92	0.0070
F	1 020.88	1 019.74	0.0011
AA	12.94	12.9	0.0031
BB	786.9	788.7	-0.0023
CC	843.78	845.6	-0.0022
DD	802.9	804.8	-0.0024

Mean = 0.0015
Sigma = 0.0044

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[a] Relative differences are with respect to the chemical values.

TABLE XIX

COMPARISON OF CALORIMETRY AND ANALYTICAL CHEMISTRY MEASUREMENTS FOR A VARIETY OF MATERIAL TYPES

	Plutonium Mass (g)		
Sample Sample	Mound Calorimetry	LASL Chemical Assay	Relative Difference[a]
M-2	1 780	1 798.1 ± 0.9	-0.0101
M-6	637	642.9 ± 0.6	-0.0092
M-10	1 411	1 423.6 ± 1.1	-0.0089
M-4	1 741	1 754.1 ± 0.9	-0.0075
M-9	2 261	2 222.3 ± 1.1	0.0174
O-4	786	798.3 ± 2	-0.0154
O-6	108	105.4 ± 0.5	0.0247
O-8	1 365	1 350.2 ± 3.5	0.0110
F-4	424	423.3 ± 0.8	0.0017
F-5	24.7	23.68 ± 0.12	0.0431[b]
F-9	821	825.6 ± 1.2	-0.0056
G-2	922	927.4 ± 1.3	-0.0058
G-4	644	648.6 ± 0.9	-0.0071
A-1	204	205.3 ± 0.2	-0.0063
A-8	369	357.7 ± 0.3	0.0316
A-11	39.4	40.8 ± 0.2	-0.0343

Mean = -0.0016
Sigma = 0.0167

---

[a] Relative differences are with respect to the chemical values.

[b] Sample F-5 has been omitted from the calculation of the mean and standard deviation.

ingrowth of americium. The materials studied were mostly scrap and were not well characterized. The chemical recovery was time-consuming and tedious, involving many individual analyses; a description of this process, along with other measurements (gamma and neutron NDA) of this material, appears in Chap. 7.

CHAPTER 5

PLUTONIUM ISOTOPIC MEASUREMENT BY GAMMA-RAY SPECTROSCOPY

The most common method for determining the isotopic composition of plutonium materials is surface-ionization mass spectrometry, often supplemented by alpha-spectroscopy to determine low levels of ^{238}Pu. These methods are described in Chap. 3. Gamma-ray spectroscopy is a good alternative to mass spectrometry because it is nondestructive, is instrumentally simpler, and has different sources of interferences. Americium-241 and the plutonium isotopes with masses 239 through 241 all have characteristic gamma-rays; ^{242}Pu does not. Plutonium-239 and 241 have relatively strong lines with little interference. Plutonium-238 has a clean line (152.8 keV) that is quite weak. All gamma rays from ^{240}Pu have rather severe interferences.

Two main approaches to gamma-ray spectroscopy have been tried: careful spectrum fitting of complex peak groupings,[29] and simpler spectrum analysis using correlations with clean lines to subtract interferences.[30-32] There is a wide range of material types to investigate, from small, well-characterized solution samples to the heterogeneous scrap samples.[33-34] Each has different characteristics and may require different measurement techniques. Only a few of these material types have been adequately measured. The material type for which the technique is best developed is a small sample of dilute solution (0.5-10 g/ℓ) of low-burnup plutonium. Gamma-ray spectroscopy has not been extensively used on reactor-grade plutonium solutions, concentrated solutions, and arbitrary solid samples. Gunnink[29] has carried out computer simulation studies that give some guidance for the general problem of measuring solid, bulk samples.

LIQUID SAMPLES

The first work on plutonium solutions, reported by Cline[35,36] involved gamma-ray measurements on 13-cm-diam, 10-liter, polyethylene L-10 bottles of plutonium nitrate solution. On 15 bottles, he reported a measurement precision of 5% for ^{239}Pu, 7% for ^{240}Pu, and 3% for ^{241}Pu. Plutonium-238 was not reported in these first measurements. For these bulk samples, attenuation corrections were based on internal line ratios of ^{239}Pu or ^{241}Pu.

The most thorough work on this problem has been done by Gunnink[29,34] at the Lawrence Livermore Laboratory (LLL). His system is now in routine use at LLL and the duPont Savannah River Laboratory (SRL)[37] for measuring samples of dilute solutions of low burnup plutonium (about 6% ^{240}Pu). Two sample types have been encountered: recently reprocessed material that is nearly americium-free, and aged material with significant levels of americium. The americium-free material has negligible 60-keV activity, which permits intense clean lines (38-52 keV) from ^{238}Pu, ^{239}Pu, and ^{240}Pu to be used for analysis. A 10-mℓ sample of solution is placed in a precision-made vial and measured with a small, high-resolution intrinsic germanium detector. Table XX summarizes results obtained from 91 solution samples (1-h count time, 0.5-2 g/ℓ concentrations), listing the gamma measurement precision and values of the mean relative difference between gamma-ray and mass spectrometry measurements. The differences are small, but are statistically significant. The bias in a calorimetric determination resulting from this difference would be 0.15%. Metal samples were dissolved to 30-50 g/ℓ concentrations and show similar results.

Aged plutonium solutions could be measured using the same gamma-ray techniques by first stripping the americium in an ion-exchange column; but this gives rise to other problems, such as complex sample preparation and an imperfect recovery from the column. Older samples with americium ingrowth are usually measured by analyzing the complex gamma-ray multiplet at 95-105 keV.

TABLE XX

RESULTS ON RECENTLY REPROCESSED DILUTE PLUTONIUM SOLUTIONS COMPARING GAMMA SPECTROSCOPY AND MASS SPECTROMETRY (MS) FOR DETERMINATION OF ISOTOPIC CONCENTRATION[a]

Plutonium Isotope	Isotopic Abundance (wt%)	Gamma Precision (RSD, %)	MS Precision (RSD, %)	Relative Difference[b] (%)
238	0.01	2.0	---[c]	1.5[d]
239	93.0	0.03	0.05	-0.004
240	6.0	0.4	0.5	0.72
241	0.6	0.04	1.0	-2.1

---

[a] See Ref. 37, p. 11.

[b] Mean relative difference between gamma spectroscopic and mass spectrometric isotope abundance values (taken with respect to the MS values).

[c] Not obtainable by mass spectrometry.

[d] Isotopic abundances determined by alpha counting and gamma spectroscopy.

This requires much more sophisticated analysis routines, very stable detector electronics, and carefully determined peak shape parameters. Table XXI presents results from 105 comparisons of gamma and mass spectrometric measurements of aged plutonium solutions (count time 30 min). These results are similar to those obtained from the simpler, americium-free material. The gamma measurement of this material (low-burnup plutonium) shows a reliability similar to that of mass spectrometry (compare with Fig. 1). This technique is well developed and is routinely used in at least two laboratories, where the gamma spectroscopy measurements are occasionally verified by mass spectrometry.

These techniques may be equally applicable to other material types (higher burnup, solid samples), but at present, there has been insufficient testing to make a definitive statement. Some liquid samples of reactor-grade plutonium have been measured. Table XXII summarizes isotopic concentration determinations of 25 samples ranging from 1 to 50 g/ℓ concentration. Deviations from the mass spectrometry values are slightly larger than those shown for the low-burnup case. The differences shown in the table could result in a bias of about 3% in a calorimeter measurement.

SOLID SAMPLES: EXPERIMENTS AND SIMULATION STUDIES

Relatively little has been reported on gamma-spectrometry isotopic measurements of solid plutonium materials. In an early report,[38] Gunnink described a series of measurements on a set of six small plutonium fuel rods. He reported the following precision:

TABLE XXI

COMPARISON OF GAMMA SPECTROSCOPY AND MASS SPECTROMETRY (MS) RESULTS FROM AGED PLUTONIUM SOLUTION SAMPLES FOR DETERMINATION OF ISOTOPIC CONCENTRATION[a]

Isotope	Isotopic Abundance (wt%)	Gamma Precision (RSD, %)	MS Precision (RSD, %)	Relative Difference[b] (%)
^{238}Pu	0.015	0.6	---[c]	---
^{239}Pu	90.0	0.09	0.05	-0.003
^{240}Pu	8.0	0.9	0.5	0.43
^{241}Pu	0.6	0.6	1.0	0.50
^{241}Am	---	0.3	---	-1.6

---

[a] See Ref. 37, p. 12.

[b] Mean relative difference between gamma spectroscopic and mass spectrometric isotope abundance values (taken with respect to the MS values).

[c] Not obtainable by mass spectrometry.

TABLE XXII

PRELIMINARY RESULTS ON REACTOR-GRADE PLUTONIUM ANALYSIS COMPARING GAMMA SPECTROSCOPY AND MASS SPECTROMETRY FOR DETERMINATION OF ISOTOPIC CONCENTRATION[a]

Plutonium Isotope	Isotopic Abundance (wt%)	Relative Difference[b] (%)
238	0.4	6.8
239	72.0	0.026
240	21.3	0.24
241	5.0	-1.8

---

[a] See Ref. 37, p. 12.

[b] Relative difference between gamma spectroscopic and mass spectrometric isotope abundance values (taken with respect to the MS values).

Fuel Rod	Precision (%)
^{238}Pu	20
^{239}Pu	2
^{240}Pu	5
^{241}Pu	2
^{241}Am	2

Such measurements are not precise enough for calorimetric determinations; however, analysis procedures have been improved considerably since those early results. LASL reported measurements on a series of solid samples ranging from (U-Pu)O_2 fuel pellets to synthetic incinerator ash (see Ref. 37, p. 16). The measurements used clean gamma-ray lines or simple multiplets and nearby clean lines to subtract interferences. The average relative differences between the gamma measurements and the known values were as follows.

Fuel Rod	Precision (%)
^{238}Pu	3.2
^{239}Pu	0.6
^{240}Pu	0.03
^{241}Pu	0.11

As a first step in solving the general problem of the isotopic determination of solid samples, Gunnink (with calorimetry in mind) wrote a simulation code to study the various gamma-ray groupings and to predict the optimum performance of the gamma-ray method. This study of precision assumed the major source of error to be counting statistics. It permitted study of the different material types without the need for a large number of expensive standards. Input parameters to the code were the isotopic composition, count rate and count time, detector parameters, isotope decay rates, and gamma-ray branching ratios. The spectrum generated by the simulation code served as input to the standard analysis code for isotopic determination. The different gamma-ray groups were investigated to see where they might be applied to the analysis of materials of varying composition. The study concluded that the complex 94-105 keV multiplet (containing all plutonium isotopes and americium) is the best region for general analysis. Figure 2 (see Ref. 10, p. 7) shows the optimum precision obtainable for the range of isotopic distributions given in Table XXIII (see Ref. 1, Part 1, p. 4). The experiment assumed a 1-h count of about 1 kg PuO_2. The detector was a 1-cm^3 intrinsic germanium crystal with a resolution of 550 eV at 122 keV. The precision shown in Fig. 2 is more than adequate for calorimetry. The simulation code showed that results obtained from gamma-ray measurements in this energy region are very sensitive to peak-shape parameters. The system must be very stable: a 1% change in peak position or peak width can produce a 1% change in the determination of certain isotopes.

The predictions of Fig. 2 are very encouraging and indicate that this technique may become more widely used. It may indeed become competitive with mass spectrometry, but only after a great deal of development and testing.

TABLE XXIII

RANGE OF EXPECTED PLUTONIUM ISOTOPIC DISTRIBUTIONS

	Isotopic Abundance (wt%)				
Burnup (1000 MWD/t)	^{238}Pu	^{239}Pu	^{240}Pu	^{241}Pu	^{242}Pu
Low	0.01	93	6	0.5	0.04
8-10	0.10	87	10	2.4	0.3
16-18	0.25	75	18	4.5	1.0
25-27	1.0	58	25	9.0	7.0
38-40	2.0	45	27	15.0	12.0

CHAPTER 6

FEED AND PRODUCT MATERIAL MEASUREMENT

Product and feed materials include uranium and plutonium liquids, powders, pellets, and fuel rods. Most product quality control and accountability programs now use a sampling plan in conjunction with analytical chemistry methods. With few exceptions, nondestructive measurements have not demonstrated the accuracy and precision attainable with analytical chemistry. Because feed and product constitute the largest part of a plant's inventory, the most reliable measurements are required for their determination. A drawback of sampling is that it does not test the entire inventory. Nondestructive measurements are being added to accountability systems to facilitate measurement of the entire product inventory. A common use of NDA has been in quality control and accountability of product fuel rods. This section will discuss nondestructive measurement techniques for product and feed liquids, powders, and fuel rods.

LIQUID MEASUREMENT

A common product of a reprocessing plant is plutonium nitrate solution (in the future it may be PuO_2). The solution is stored and shipped in 10-liter plastic bottles (13 cm in diameter by 90 cm high) placed inside large shipping drums. Gamma spectroscopy measurements have been attempted on whole bottles removed from the shipping containers.[35,36] The intensities ratio of the 129-keV and 414-keV gamma rays of ^{239}Pu was used to measure the plutonium concentration. Total ^{239}Pu content was determined from the intensity of the 414-keV gamma ray. Attempts were made to measure the ^{238}Pu and ^{240}Pu concentrations from the

153-keV and 160-keV gamma-ray intensities. The results gave an accuracy of 5% for ^{239}Pu, ^{241}Pu, and total plutonium content. Better reliability should be attainable but has not been demonstrated.

Gunnink's gamma spectroscopy system for the measurement of plutonium solution samples is used routinely for measuring 10-m samples of dilute (less than 5 g/ℓ) solution from a reprocessing plant. Samples of dissolved plutonium metal are also measured with this system. The precision is approximately 0.5% for total plutonium content and 0.1-0.2% for ^{239}Pu content. Biases are not fully discussed, but are expected to be less than 0.2%.

Gamma-ray densitometry has been used to measure plutonium concentration in solution in both flow cells and sample containers. This promising technique is currently undergoing development. There are, however, very limited reliability data for the method at present. The British Nuclear Fuel Laboratory (BNFL) Windscale has had an in-line plutonium densitometer in routine operation for over 10 yr. It uses an ^{241}Am transmission source and a xenon-filled ionization chamber detector.[40] This instrument is accurate to better than 5.0%, but is sensitive to heavy-metal contamination in the sample. The applicability of absorption-edge densitometry to plutonium solutions[41] has been investigated. Precisions of 1-2% and biases of less than 1% are readily obtainable, but no routine system has yet been put into operation.

An in-line liquid monitor has been used for 3 yr to measure the ^{235}U enrichment of the final UF_6 product at an enrichment plant. The system measures ^{235}U enrichment by counting 185.7-keV gamma rays, and ^{234}U enrichment by counting neutrons from $^{19}F(\alpha,n)^{22}Na$ in UF_6. A NaI detector is used for the gamma measurement, and ^{3}He detectors are used for the neutron measurement. An arithmetic-control module subtracts backgrounds and computes enrichment for display and teletype output. Table XXIV[42] presents data taken with the instrument. The instrument has a bias of less than 0.01% and a precision of about 0.16%, consistent

TABLE XXIV

COMPARISON OF GAMMA ISOTOPIC AND MASS SPECTROMETRIC ASSAY OF UF_6 ENRICHMENT

^{235}U Enrichment (%)		
Sample (MS)[a]	Gamma	Relative Difference[b] (%)
2.869	2.871	0.07
3.013	3.009	-0.13
2.790	2.789	-0.04
2.898	2.900	0.07
2.911	2.910	-0.03
2.919	2.921	0.07
2.946	2.940	-0.20
2.969	2.974	0.17
2.964	2.965	0.03
2.817	2.813	-0.14
2.819	2.825	0.21
2.833	2.824	-0.32
2.870	2.862	-0.28
2.888	2.891	0.10
2.905	2.904	-0.03
3.176	3.181	0.16
3.072	3.079	0.23
3.073	3.076	0.10
		Mean = 0.002%
		Sigma = 0.16%

---

[a] MS denotes mass spectrometric assay values.

[b] Relative difference is calculated with respect to the mass spectrometry values. The relative differences have been recomputed and, in general, are different from those of Ref. 42.

with counting statistics. These are among the most reliable NDA measurements yet demonstrated. The system can run unattended for long periods of time and maintain a precision of about 0.5% (95% confidence level) with a bias of less than 0.1%. The ^{234}U measurement displays a bias of about 0.3% and a precision of about 1.3%. The system measures ^{235}U concentration in a liquid stream; similar reliability should be achievable for other uranium solutions, but much development remains to be done.

A similar NaI system has been used to measure samples of uranium solutions (1-400 g/ℓ concentration) from a uranium recovery plant.[43] The uranium has a relatively constant, high enrichment. Samples are placed in a counting cell that spreads the solution into a thin layer to minimize variations in attenuation caused by differing uranium concentrations. A NaI detector measures the 185.7-keV gamma rays from ^{235}U. There is no transmission correction. Uranium is assumed to be the only cause of attenuation variations, so that the concentration is determined by the count rate. Table XXV presents data taken with the system for prepared solution standards. Two other standards of 10 and 400 g/ℓ concentration were used to calibrate the instrument. The system has been used routinely in place of alpha-particle counting techniques to provide process accountability information.

A new system has recently been installed to replace the NaI system. It uses a GeLi detector to measure the 186-keV gamma rays for solutions with concentrations of less than 50 g/ℓ. A transmission measurement reduces biases arising from different solution densities. In addition, a K-edge transmission measurement is made on solutions with concentrations of 100-400 g/ℓ to determine the total uranium concentration.[41] The system is computer-controlled and is part of a real-time inventory control experiment being conducted at the uranium recovery facility.[44] The accuracy of the uranium determination should be 1% or better, but system evaluation is not yet complete. Other uranium densitometry systems have been developed and put into use,

TABLE XXV

URANIUM SOLUTION MEASUREMENTS[a]

Known Concentration (g/ℓ)	Measured Concentration (g/ℓ)	Relative Difference[b] (%)
25	24.94	-0.24
50	50.07	0.14
50	49.88	-0.24
50	50.05	0.10
100	100.63	0.63
200	201.14	0.57
		Mean = 0.16% Sigma = 0.38%

---

[a] Unpublished data.

[b] Relative differences are computed with respect to the known concentrations.

but only sparse reliability data for the systems are available at present (Ref. 40, p. 95).

There is considerable potential for the gamma-ray measurement of uranium and plutonium solutions by gamma counting and transmission densitometry methods. L-10 plutonium nitrate bottles have been measured with accuracies of about 5% for ^{239}Pu, ^{241}Pu, and total plutonium concentrations. Precisions of 0.5% for total plutonium and 0.2% for ^{239}Pu have been obtained on small samples, with biases of less than 0.2%. A highly reliable system for in-line UF_6 enrichment measurement has been developed with precisions of 0.25% and biases of less than 0.1%. This level of reliability has not been demonstrated generally, and at present, the bias is estimated to be more than 1%. As these techniques are developed further, they will undoubtedly receive widespread use as in-line and at-line process solution measurement systems.

POWDER AND PELLET ASSAY

The assay of powder and pellets usually involves small samples of feed and product material, although sometimes bulk samples are also measured. NDA methods supplement chemical analysis because of advantages in speed and economy. Eventually, the NDA methods will also be used in analytical laboratories. This section describes only uranium powder and pellet measurements, although some of the same techniques apply to plutonium.

A hybrid neutron and gamma assay system has been developed to measure the UO_2 input to a light-water reactor (LWR) fuel fabrication plant.[245] It combines a NaI gamma enrichment measurement with a neutron (usually gross neutron rate, but coincidence counting is also possible) measurement for ^{238}U. The material is contained in 20-liter cans. Table XXVI shows data obtained with an early version of the system. A newer version exhibits better reliability, but performance data have not yet been published. The NDA measurements display a bias of less than 1% and a precision of about 2%.

TABLE XXVI

MEASUREMENT OF 20-ℓ CANS OF UO_2 FEED[a]

^{235}U Content (%)			Total Uranium Mass (g)		
Emission Spectroscopy[b]	NDA	Relative Difference[c] (%)	Emission Spectroscopy[b]	NDA	Relative Difference[c] (%)
0.22 ± 0.01	0.21	-4.5	29 948	29 899	-0.2
0.72 ± 0.01	0.71	-1.4	30 677	30 877	0.7
1.37 ± 0.03	1.40	2.2	18 782	18 383	-2.1
1.54 ± 0.04	1.56	1.3	19 204	18 915	-1.5
2.48 ± 0.04	2.47	-0.4	15 950	16 364	2.6
2.91 ± 0.05	2.94	1.0	16 222	16 566	2.1
4.45 ± 0.04	4.35	-2.2	11 182	10 799	-3.4
		mean = -0.6% sigma = 2.33%			mean = -0.3% sigma = 2.2%

---

[a] See Ref. 45, p. 20.

[b] Emission spectroscopy is based on the isotopic line shift at 4224 Å and is generally less accurate than mass spectrometry.

[c] Relative differences are calculated with respect to the emission spectroscopy values.

Another example of powder measurement involves the active assay of an inventory of highly enriched UAl_x powder similar to that used in material testing reactor (MTR) fuels.[46] Ninety cans contained approximately 320 kg of 93% enriched uranium. The fuel was in the form of a uranium-aluminum alloy (69 ± 3% uranium by weight). The material was assayed by measuring delayed neutrons from fissions induced by 14-MeV neutrons. For the complete inventory, the sampling/chemical assay value was 298 214 g ^{235}U and the value determined by NDA was 298 307 g. The difference of 93 g (0.03%) is insignificant. Table XXVII presents results of a resampling/chemical assay performed on 13 of the cans after the NDA determination had been done. It shows an assay precision of about 1% and a negligible bias between the two determinations. The precision of the sampling/analytical assay is considerably better than that described later for scrap materials. Although these measurements were made with an accelerator, similar reliability should be obtainable with instruments such as the Isotopic Source Assay System (ISAS) and Random Driver.

A Random Driver assay system has been evaluated as an accountability instrument for high-temperature gas-cooled reactor (HTGR) fuel materials.[47] Measurements were made on HTGR fuel particles consisting of highly enriched uranium-thorium carbide beads (100-300 μm in diameter) coated with graphite and SiC in various stages of coating. The fuel was contained in 2- to 4-liter plastic and aluminum cans. For 62 different batches containing a total of about 17.7 kg ^{235}U, the NDA measurement was only 30 g (-0.17%) lower than the chemical assay. A linear regression analysis indicated a bias of 0.64% ± 1.28% (95% confidence level) for an individual measurement. Table XXVIII summarizes the results for the different fuel categories. The table shows no significant bias between the two measurements, although biases below about 1% would not necessarily be evident from these tests. The dissolution of these materials was a problem for

TABLE XXVII

ACTIVE ASSAY OF UAl_x FUEL MATERIAL[a]

^{235}U Mass (g)			
Sampling/Chemical			
Original	Resampling	NDA	Relative Difference[b] (%)
3 236.42	3 231	3 231	0[c]
4 540.63	4 534	4 572	0.838
3 217.57	3 208	3 228	0.623
3 391.54	3 380	3 425	1.331
4 286.00	4 287	4 252	-0.816
4 540.00	4 541	4 468	-1.608
2 226.26	2 219	2 204	-0.676
2 503.06	2 500	2 498	-0.080
3 437.65	3 445	3 489	1.277
3 705.51	3 724	3 712	-0.322
3 799.56	3 791	3 806	0.396
801.02	801	750	-6.367[d]
3 206.39	3 216	3 192	-0.746

Mean = 0.020%
Sigma = 0.950%

---

[a] See Ref. 46, p. 3.

[b] Relative differences are computed with respect to the resampled chemical values.

[c] This can was used as the calibration standard for the NDA measurements.

[d] This measurement and that of footnote c have been omitted from the calculation of the mean and standard deviation.

TABLE XXVIII

RANDOM DRIVER ASSAY OF HTGR FUEL BEADS[a]

Category	Total ^{235}U Mass (g) Chemical	Random Driver	Relative Bias ± 2σ[b] (%)
Inner carbon-coated particles (large kernels)	5 298	5 368	1.30 ± 0.88
SiC-coated particles (small kernels)	4 795	4 751	-0.92 ± 0.88
SiC-coated particles (large kernels)	5 440	5 408	-0.59 ± 1.10
Outer carbon-coated particles (small kernels)	692.1	687.8	-0.63 ± 5.5
Outer carbon-coated particles (large kernels)	1 522	1 502	-1.31 ± 1.20

---

[a] See Ref. 47, p. 99.

[b] Relative biases are computed with respect to the chemical values.

chemical analysis. As a result, other techniques such as delayed neutron activation analysis using a small research reactor or a Van de Graaff accelerator and gamma-ray assay have been investigated as possible alternatives for measurements on these fuels.

An ISAS instrument was used to measure bottles of uranium powders and pellets for various experimental reactors at the National Reactor Testing Station.[48] Results of these measurements are presented in Table XXIX. Materials were also measured by bremsstrahlung interrogation using a mobile (trailer-mounted laboratory) LINAC assay system called GAMAS. The GAMAS measurements were part of an inventory verification inspection. The precision of the ISAS and GAMAS measurements is better than 1%, and biases between analytical chemistry and NDA are 1% or less.

Systems have been developed to measure small samples (e.g., small vials, 1-3 dram capacity) of special nuclear material (SNM) that are used as inventory verification samples. In the past, such samples taken for process and quality control have often been assayed by analytical chemistry procedures. Systems have now been constructed that automate the destructive analysis procedures for the routine assay of quality-control samples.[49] These systems have included titrimetry, coulometry, and spectrophotometry. The automated procedures greatly increase the throughput of assay samples. Several nuclear measurement systems have been developed for small samples. A Small Sample Assay System (SSAS) has been built using a ^{252}Cf source (thermal or epithermal irradiation) to induce fissions in the SNM and employing a NaI detector to count delayed gamma rays from the fissions.[50] After irradiation, the sample is transferred from the source to the NaI detector. For UO_2 pellet samples (0.7-3.3% ^{235}U concentration) the instrument gives a precision of 0.5% and for oxide powder samples 0.8%.

As an example of the reliability achievable with NDA small-sample assay techniques, 25 samples of Rover fuel bead material

TABLE XXIX

ASSAY OF URANIUM FUEL MATERIALS AT NRTS[a]

Material	System	Uranium Mass[b] (g) Chemical Assay	 NDA	Relative Difference[c] (%)	Random Error (%)	Systematic Error (%)
UO_2 powder in 2-ℓ bottle 18.5% ^{235}U	GAMAS	143 739	143 612	-0.09	0.25	1.0
	ISAS	16 231	16 236	0.03	0.25	---
PBF pellets in 2-ℓ bottle	GAMAS	39 810	40 256	1.1	0.67	1.2
	ISAS	5 373	5 362	-0.2	0.60	---
UAl_x in 4-ℓ can	GAMAS	288 823	288 395	-0.15	0.26	---

---

[a] See Ref. 48, pp. 33 and 45.

[b] The GAMAS measurements are of total uranium content, whereas the ISAS values reflect ^{235}U content.

[c] Relative differences are calculated with respect to the chemical values.

(highly enriched uranium) were obtained as part of an inventory inspection. They were measured before chemical analysis by a Van de Graaff delayed-neutron assay procedure, a GeLi gamma assay procedure, and a ^{252}Cf system similar to that described above.[51,52] After the nondestructive assay, the samples were sent to the New Brunswick Laboratory. Results for six of the samples are presented in Table XXX. The accelerator measurements show a bias and precision comparable to good analytical chemistry measurements. Independent chemistry values were available from the originating plant. For the entire sample batch, the mean relative deviation of the two chemistry determinations was 0.078%, and the standard deviation of the relative differences was 0.46%. By comparison, the Van de Graaff measurements showed a mean relative deviation with respect to the chemistry measurements of -0.057% and a standard deviation of relative differences of 0.34%. The average precision owing to counting statistics was about 0.25%. These results are consistent with zero bias between the two measurements. The ^{252}Cf and gamma measurements show precisions of about 1%, consistent with counting statistics. Further development of these techniques will be required to assure sufficiently low measurement bias. The Van de Graaff accelerator has also been used for the assay of other materials. For small samples of UAl_x, the observed bias between chemistry and NDA was 0.19% ± 0.1% and the precision was 0.5%.

In summary, the measurements presented here exhibit biases of 1% or less and precisions of 0.3-2%. An optimistic estimate of achievable reliability would be a bias of 0.1% or less and a precision of 1%. A more conservative estimate would be a bias of 1%. Measurements of UO_2 feed in bulk are capable of a 2% precision and a bias of less than 1%. HTGR fuel material can be measured with an instrument of the Random Driver type with a bias of less than 1%. Active delayed-neutron measurements of bulk quantities of uranium-aluminum fuel material can also be bias-free. Measurements of bulk oxide fuel materials should be similarly bias-free. The development of radioactive-source assay systems for this type of material is promising. Small

TABLE XXX

URANIUM SMALL SAMPLE ASSAY[a]

^{235}U Mass (g)						
Chemical	Van de Graaff	^{252}Cf	Gamma	Relative Difference[b] (%) VDG vs Chem.	Relative Difference[b] (%) ^{252}Cf vs Chem.	Relative Difference[b] (%) Gamma vs Chem.
3.3473	3.3578 ± 0.0077	3.25	3.400	0.31	-2.91	1.57
2.7357	2.7206 ± 0.0068	2.76	2.739	-0.55	0.89	0.12
3.1107	3.1123 ± 0.0075	3.10	3.147	0.05	-0.34	1.17
3.2566	3.2579 ± 0.0078	3.235	3.280	0.04	-0.66	0.72
3.0252	3.0215 ± 0.0075	3.02	2.988	-0.12	-0.17	-1.23
3.1534	3.1557 ± 0.0077	3.14	3.123	0.07	-0.42	-0.96
				Mean = -0.033% Sigma = 0.288%	Mean = -0.60% Sigma = 1.25%	Mean = 0.23% Sigma = 1.14%

---

[a] See Ref. 51, p. 8.

[b] All relative differences are computed with respect to the chemical assay values.

sample measurements can be made bias-free with precisions less than 0.5% in some cases, and hence, can be quite competitive with destructive analysis.

FUEL RODS

Nondestructive analysis permits accountability and quality control measurements for entire inventories of product rods. Total fissile content and pellet-to-pellet variation can be measured. The latter can be important in checking for "rogue" pellets in the rod. The first measurements involved passive gamma scanning of rods; later, active systems have developed that have increased throughput and, at least for uranium, much smaller absorption corrections.

Probably the best example of what is achievable for breeder-type fuel rods is a system developed for routine quality control and accountability for FFTF fuel rods.[53] This involves irradiation with ^{252}Cf neutrons and measurements of delayed-fission gamma rays with two NaI detectors for determination of the total fissile content. Passive gamma radiations from the pins are also measured to monitor pellet-to-pellet variations. This system has been used for acceptance testing of all FFTF fuel pins. In addition, the routine quality-control procedure calls for destructively analyzing 1 pin out of about 120. Table XXXI shows a comparison between the nondestructive pin scan and the destructive analysis.[54] The differences between shipper and receiver chemistry measurements are as large as the difference between chemistry and NDA measurements. There is no significant bias between the two methods. None of the differences is statistically significant. For 18 fuel batches containing a total of 504 kg of fissile plutonium, the difference between the two chemistry measurements was 78 g or 0.02%. The difference between the NDA and chemical measurements was 998 g or 0.20%. This difference could indicate a small bias between the two measurements.

TABLE XXXI

COMPARISON OF DESTRUCTIVE AND NONDESTRUCTIVE FFTF PIN ASSAY

	Chemical Assay of Plutonium Mass (g)			Difference (g)	
	Vendor	HEDL	HEDL NDA (g)	Vendor - HEDL	NDA - HEDL
INNER CORE 15 PINS					
Total	448.18	447.68	447.82	0.50 (0.11%)	-0.14 (-0.03%)
Mean	29.879	29.845	29.855	---	---
Sigma	0.2380	0.2261	0.2319	---	---
OUTER CORE 34 PINS					
Total	1 246.12	1 240.83	1 244.72	5.43 (0.43%)	-3.89 (-0.31%)
Mean	36.652	35.495	36.609	---	---
Sigma	0.3253	0.2853	0.2640	---	---

From 1286 observations made during 2 yr, the precision was 0.84% and the bias was 0.1% or better.

A neutron coincidence counter has also been constructed to measure these FFTF rods.[55] The reliability is about 1.8%, with half the error owing to counting statistics and half owing to uncertainties in standards, fitting procedures, etc. Little data concerning the performance of this instrument has been published.

For plutonium recycle rods, no instrument is in routine use; indeed, there are few plutonium recycle rods at present. A ^{252}Cf system like that used for uranium LWR rods should work for plutonium rods also. The accuracy of such a system should be better than 0.25%. The neutron coincidence detector mentioned above could also be used. Passive gamma-ray scans of plutonium-recycle rods have been conducted with NaI and GeLi detectors. Some measurements conducted during the plant instrumentation program (PIP) indicated biases of less than 0.5% and precisions of 0.6-0.8%.[56] For one group of 19 rods, production data showed a total of 1169 g of plutonium, while GeLi measurements found 1173 g — a difference of 0.3%.

Several ^{252}Cf-based systems have been constructed for the measurement of uranium LWR fuel rods. One such system uses biased ^{4}He proportional counters to measure the high-energy prompt fission neutrons from thermal neutron irradiation. The system determines total fissile content and has a throughput capacity of about 500 rods/h. The precision is approximately 1% and the accuracy is better than 0.25%.[57] The bias could be made as low as 0.1% if better standards were available and if the fitting model were correct. Probably the major problem is the standard used for calibration. The report[57] describing this instrument contains one of the most complete error analyses for a NDA instrument. This system has been used extensively at two large LWR fuel fabrication plants. Pellet-to-pellet measurements have been added to other ^{252}Cf systems to check fuel rod enrichment uniformity.[58]

In summary, fuel rods can be measured with precisions of 0.5-1% and with biases as low as 0.1%. FBR fuel is measured routinely with a bias of 0.1% and a precision of 0.8%. LWR fuel rods are routinely scanned for total fissile content and enrichment uniformity.[59] These measurements exhibit an accuracy of 0.25% and a precision of about 1%.

CHAPTER 7

SCRAP MEASUREMENT

Scrap consists of process residues that have SNM amounts worth recovering. The SNM content in scrap ranges from that contained in reject product material to that of very dirty residues (less than 10% SNM by weight). Scrap is usually in smaller containers than waste and is usually denser and more homogeneous. This chapter will not describe all the different scrap categories, but will discuss several examples to indicate the range of expected assay performance. Scrap materials are often difficult to sample, causing the results of analytical chemistry measurements to be suspect. Consequently, it is difficult to define the actual SNM content of scrap to be used as a standard for testing a new technique. In some cases, the best procedure is to use results from synthetically prepared standards.

ANALYTICAL CHEMISTRY ASSAY

Since destructive analysis on product and feed materials is quite reliable, these techniques have commonly been applied to scrap, but truly representative samples are often difficult to obtain. Furthermore, the high concentrations of other matrix materials can interfere with titration procedures. These problems make evaluations of new techniques difficult. Two examples will be discussed to illustrate this problem.

A large amount of scrap from the nuclear rocket program (Rover) was measured by a delayed-neutron, active-assay technique. Discrepancies were found between the nondestructive measurement and the original analytical chemistry determination. This material consisted of graphite, zirconium, highly enriched uranium, and a variety of other matrix materials. Samples ranged from 0 to 70% uranium by weight. Several samples of organic ash were first assayed, then remixed, sampled, and assayed a second time. The results of these two determinations (for nine samples in cans) are presented in Table XXXII.[60] The second chemical analysis agreed well with the nondestructive measurement. A can for which the two determinations agreed well still measured only about 20% of the NDA value. The contents of this can were split into five nearly equal parts and placed in bottles. Samples were taken from each bottle. The contents of each bottle were blended in a "V" blender and resampled. All samples were analyzed and the bottles nondestructively assayed. Samples taken before and after blending differed by as much as 30%. The combined assay after blending yielded a value of 477 g, which agreed well with the value (475 g) obtained by passive gamma assay of the five bottles. The individual bottles held between 42 and 152 g of uranium. Even after blending, duplicate samples from the five bottles differed in uranium assay by an average of 2.5%.[61]

The same inconsistencies are found in studies of uranium-contaminated incinerator ash. The ash contained less than 30% uranium by weight and had a ^{235}U enrichment of 1-10%. Sixteen containers were individually blended and sampled, then blended a second time, after which duplicate samples were taken for chemical analysis. The results of these uranium measurements are presented in Table XXXIII. The average RSD for the three determinations was 3.6%. The ^{235}U enrichment of each sample was also determined by mass spectrometry. The average deviation of those determinations was 2.7%. Further, the average standard deviation of the ^{235}U mass determination for each can was about 5% based on errors from the uranium and ^{235}U enrichment analyses. The second and third columns of Table XXXIII provide information on the precision of chemical analysis on duplicate samples from the same blend. The precision for this example is 2.2%, which is similar to that found in the previous case (Rover ash).[62] In another study of duplicate inventory verification samples, biases of 30% were found in calcined ash and other residues.[63]

TABLE XXXII

SAMPLING/ANALYTICAL CHEMISTRY MEASUREMENTS OF HIGHLY ENRICHED URANIUM ASH

Uranium Mass (g)	
First Determination	Second Determination
34	1 576
275	432
834	150
104	105
758	1 193
317	413
628	660
418	282
812	877

TABLE XXXIII

INCINERATOR ASH PRECISION OF SAMPLING/CHEMICAL ANALYSIS[a]

Uranium Mass (g)				
	Second Blend			
First Blend	Sample 1	Sample 2	Average[b]	RSD (%)
597	569	565	577	3.0
1613	1586	1543	1581	2.2
1051	1062	1035	1049	1.3
651	674	689	671	2.9
1146	959	1011	1029	9.3
914	964	949	942	2.7
676	631	659	655	3.5
2448	2387	2358	2398	1.9
1296[c]	518	491	505	3.8
1014	997	1007	1006	0.8
1423	1446	1460	1443	1.3
400	383	402	395	2.6
200	260	273	244	15.9
175	159	168	161	3.6
375	378	386	380	1.5
655	666	644	655	1.7

Average deviation = 3.6%

---

[a] See Ref. 62, p. 1.

[b] Computed as the mean of the first blend and samples 1 and 2 of the second blend.

[c] Omitted from the calculations.

These examples show that without blending (or with insufficient blending), gross errors (factors of 2 or even greater) may occur. With careful blending, sampling errors of 2-3% persist. These errors may become random with sufficient blending, but this is difficult to establish. Because of scrap sampling errors, the accuracy of NDA is often as good as, or better than, that of analytical chemistry.

GAMMA-RAY ASSAY: PLUTONIUM

Plutonium scrap assay by gamma-ray spectroscopy usually involves counting the 414-keV activity from ^{239}Pu with a GeLi detector (or the 333-414 keV complex with NaI). Attenuation corrections are best determined from external-source transmission measurements, and knowledge of the isotopic distribution is used to compute total plutonium from the measured ^{239}Pu mass.

The precision of plutonium gamma assay is illustrated by the following example. Cans of plutonium incinerator ash were measured at two different facilities using the same type of measurement system, a Segmented Gamma Scanner.[64] Table XXXIV compares the results of the two systems for ten ash cans.[65] The bias between the systems owes primarily to biases in the calibration standards. The standard deviation between the two measurements is slightly larger than that predicted by counting statistics (about 3%). Comparisons between other groups of cans show an RSD of 3-4.5%. The precision of individual assays (with System B) is 2-3%, only slightly poorer than that expected from counting statistics alone. These measurements were made by plant personnel under plant, not laboratory, conditions.

Another experiment involved the measurement of synthetic incinerator ash standards using a NaI system with a plutonium transmission source. The standards consisted of a matrix of various oxide materials mixed with a known amount of plutonium oxide. The system was calibrated against a single can containing 50 g of plutonium mixed with diatomaceous earth. Results from

TABLE XXXIV

ASH MEASUREMENT COMPARISON[a]

Plutonium Mass (g)		Relative
System A	System B	Difference[b] (%)
159	164 ± 3	-3.0
124	128 ± 2	-3.1
87	91 ± 2	-4.4
146	151 ± 2	-3.3
176	182 ± 3	-3.3
25	23 ± 1	8.7
55	52 ± 1	5.8
59	58 ± 1	1.7
66	66 ± 2	0
36	36 ± 1	0
		Mean = -0.1%
		Sigma = 4.4%

---

[a] See Ref. 65.

[b] Relative differences are calculated with respect to the measurements of System B.

five measurements of each of these samples are given in Table XXXV.[66] Over this range of plutonium mass the bias is small (less than 1%) and the precision is 1%.

A sample exchange program was conducted in 1972 for several categories of plutonium scrap (incinerator ash, dirty oxide, dirty fluoride, and green cake). Various laboratories conducted calorimetric, gamma spectrometric, neutron coincidence, and active neutron source interrogation assays on 53 samples. Several cans from each category were chosen for chemical analysis by complete dissolution. Because this material originated from a plant that maintained a nearly constant isotopic composition, the calorimetric assay can be considered accurate to better than 1% and can be used to determine the accuracy of the gamma-ray assay. Table XXXVI[67] shows the results for incinerator ash. A segmented gamma scan employing a GeLi detector with a ^{75}Se transmission source was used in making the measurements. The ash samples were in cans about 15 cm in diameter and 25 cm high. The bias (about 2%) is caused by a calibration standard that was in a smaller can. The precision of these measurements is better than 3%. These data probably represent the best demonstration (to date) of reliability for this type of scrap material.

Table XXXVII presents data for another category of scrap. This material was more highly attenuating than the ash, resulting in a larger standard deviation (about 6%). Samples F-12, F-14, and F-15 were less than one-fourth full, so that end-effects contributed significantly to the inaccuracy of the assay. When these samples are omitted, the precision is about 4.5%. Table XXXVIII shows the chemical analysis data for these categories. Complete recovery of selected scrap samples is often suggested for the determination of the accuracy of these nondestructive measurements. This recovery can be very difficult as indicated by the following description of the ash recovery procedure (which required nearly 10 months for completion).[68]

TABLE XXXV

MEASUREMENT OF PLUTONIUM ASH STANDARDS

Plutonium Mass (g)		Measured Precision[a]	Relative Difference[b] (%)
Known	Measured		
10	10.6	1.6%	6[c]
25	25.4	2.0	1.6
50	49.6	1.4	-0.8
100	100	1.8	0
200	199	1.6	-0.5
350	352	1.1	0.6
			Mean = 0.18%
			Sigma = 0.95%

---

[a] The measured values are averages of five replications (four for the 350-g sample) of each known sample, and the measured precisions are calculated from the sample variances.

[b] Relative differences are calculated with respect to the known values.

[c] This sample is omitted from the computation of the mean and standard deviation (sigma).

TABLE XXXVI

COMPARISON OF CALORIMETER AND GAMMA-RAY ASSAYS OF 15 CANS OF INCINERATOR ASH

Plutonium Mass (g)		Percent Difference with Respect to Calorimetry
Calorimeter	Gamma-Ray Assay	
211	219	3.8
382	390	2.1
384	400	4.2
321	330	2.8
357	370	4.2
322	326	1.2
314	314	0.0
378	390	3.2
304	306	0.7
354	355	0.3
41	42	2.4
92	91	-1.1
109	110	0.9
123	125	1.6
160	168	5.0
		Mean = 2.1%
		Sigma = 1.8%

TABLE XXXVII

COMPARISON OF CALORIMETER AND GAMMA-RAY ASSAYS OF 16 CANS OF DIRTY FLUORIDES AND OXIDES[a]

Can	Plutonium Mass (g)		Percent Difference with Respect to Calorimetry
	Calorimeter	Gamma-Ray Assay	
F-1	201	194	-3.5
F-2	13	11	-15.0[b]
F-3	231	214	-7.4
F-4	424	417	-1.7
F-5	24.7	24	-2.8
F-6	476	470	-1.3
F-7	144	139	-3.5
F-8	545	534	-2.0
F-10	14	13	-7.0[b]
F-11	355	320	-9.9
F-12	191	182	-4.7
F-14	95	85	-10.5
F-15	304	267	-12.2
F-16	502	513	2.2
0-6	109	109	0.0
0-11	82	80	-2.4
			Mean = -4.3%
			Sigma = 4.2%

---

[a] See Ref. 67.

[b] Cans F-2 and F-10 have been omitted in calculation of mean and sigma.

TABLE XXXVIII

CHEMICAL RECOVERY DATA ON ASH AND FLUORIDE MATERIALS[a]

Can	Plutonium Mass (g) Gamma Assay	Calorimetry	Chemical Recovery
A-1	219	211	205.3 ± 0.2
A-8	390	378	357.7 ± 0.3
A-11	42	41	40.8 ± 0.2
F-4	417	424	423.3 ± 0.8
F-5	24	25	23.7 ± 0.1
0-6	109	108	105.4 ± 0.5

---

[a] Unpublished data.

"Each ash sample was divided into portions of about 950 g, weighed and refluxed for 8-12 h with 3ℓ of 9M HNO_3 containing 5 mℓ of 47% HF. The solution was cooled, filtered, and refluxed two more times. The residue from the third leach was dried for 6-8 h at 150°C, divided into 300-g portions, and fused with 750 g of a flux of sodium fluoride and potassium pyrosulfate. The melt was then leached with 7ℓ of hot 15.6M HNO_3 containing 450 g of aluminum nitrate. After filtering, the residue was washed with 7ℓ of water and the solution diluted to 15 or 16ℓ. The residue was then carried through this fusion-leach cycle two more times. The final residue was dried and gamma assayed (these residues contained 1.6, 4.3, and 3.8 g plutonium for A-1, 8, 11; even after all this, nearly 10% of sample A-11 was undissolved.) There were initially 13.5 kg of ash divided into 15 portions. The 45 leach cycles generated ∿ 250ℓ of solution. The 5.5 kg residue from the acid leach required 32 fusion cycles. The fusions generated 480ℓ more of solution. The solutions from the dissolution cycles were laden with various and unknown salts so the usual titration assay methods could not be used reliably. Solutions from the reflux-leach were assayed by x-ray fluorescence using yttrium as an internal standard. They were also radioassayed as a check. The fusion-leach solutions were radiochemically assayed as they were too dilute for XRF. In addition, some of the solutions were assayed by spectrophotometric and mass spectrometric isotopic dilution methods to check plutonium contents. All told, approximately 500 analyses were made on the numerous solutions."

The other categories of scrap (oxide and green cake) are more highly attenuating. Consequently, a ^{137}Cs (662-keV) source was used for the transmission measurement because gamma rays from a ^{75}Se source could not penetrate the samples. For these materials, the gamma-ray measurements yielded values that were about 8% lower than those from the calorimetry measurements. This could presumably be improved if all the cans are full and if better standards are used. The RSD between the gamma assay and calorimeter assay was about 8%, surprisingly good considering the nature of the samples. Such materials are probably best assayed by other methods. Further data from this interchange are given in the sections of this report describing calorimetry and the active assay of scrap.

In another gamma/calorimetry assay comparison, cans of incinerator ash of variable isotopic content that had been assayed by gamma rays at LASL were sent to Mound Laboratory for calorimetry measurements as part of a LASL inventory verification inspection. A comparison of the results for 10 cans is presented in Table XXXIX. The gamma measurement in this example is a far-field count with a single average transmission used for the attenuation correction. The gamma measurements were routine analyses performed by plant personnel. A bias of several per cent occurs with a precision similar to that found in the previous example. For similar cases, precisions as poor as 10% have occurred. The calorimetry uncertainty shown here (about 2%) owes primarily to difficulties in determining the plutonium isotopic composition. Some of the samples had large isotopic inhomogeneities.

In a different scrap category, six cans of sand-slag-and-crucible were gamma assayed (also assayed by neutron coincidence and delayed neutron activation) and chemically recovered.[69] This material is more highly attenuating than most incinerator ash materials. The results of the chemical recovery and the gamma assay (which agreed best with the recovery) are presented in Table XL. The uncertainties given for the individual gamma

TABLE XXXIX

GAMMA RAY/CALORIMETRY MEASUREMENT COMPARISON[a]

Can	Gamma Assay	Calorimetry	Relative Difference[b] (%)
328A	85	84.0 ± 1.8	1.19
328B	70	68.2 ± 1.4	2.64
338A	85	80.7 ± 1.7	5.33
338B	7	6.8 ± 0.1	2.94
401A	39	37.1 ± 0.8	5.12
401B	39	36.8 ± 0.8	5.98
430A	87	87.9 ± 1.8	-1.02
430B	57	57.3 ± 1.2	-0.52
433A	52	50.4 ± 1.1	3.17
433B	46	44.7 ± 0.9	2.91
			Mean = 2.77%
			Sigma = 2.36%

---

[a] The calorimetry values of this table are taken from Ref. 67 (Chap. 5), but the gamma data are unpublished.

[b] Relative differences are calculated with respect to the calorimetry values.

TABLE XL

MEASUREMENT OF MEDIUM DENSITY SCRAP[a]

Can	Plutonium Mass (g) Gamma Assay	 Recovery	Relative Difference[b] (%)
40-1	18.5 ± 2.5	17.2	7.6
40-2	15.0 ± 1.5	14.0	7.1
42	12.6 ± 2.0	14.0	-10.0
43	19.6 ± 2.5	20.4	-3.9
44	14.1 ± 1.5	17.2	-18.0
45	14.7 ± 2.0	14.4	2.1
			Mean = -2.5%
			Sigma = 10%

---

[a] See Ref. 69, p. 4 (LA-4523-MS) and p. 25 (LA-4457-MS).

[b] Relative differences are calculated with respect to the recovery values.

measurements are from counting statistics and an estimate of the error resulting from inhomogeneities in the can contents. All but one pair of measurements agree to within the estimated precision (sigma). Some of the observed differences can be attributed to uncertainties in the recovery values.

The next example further emphasizes the large uncertainties involved in assaying bulk scrap by chemical recovery. Table XLI presents data from several gamma assay/recovery comparisons.[70] The first three items are leached incinerator ash, six cans recovered in three batches of two cans each. The next three items are filter media, recovered as two batches of three cans and one batch of two cans. The nondestructive measurements were performed on the individual cans and summed. The recovery involved a hydrofluorination and several bulk fusions. Residues were gamma assayed. The last batch contained eight cans of incinerator ash originating from a plant different than that of the first three items. As can be seen from Table XLI, the agreement ranges from good to poor. Calorimetric and neutron coincidence measurements supported the gamma values. The leached ash and filter media have very low attenuations, and thus are well suited to gamma-ray assay. It is unlikely, then, that a gamma assay would be 20-40% high, although it might be low by that amount. The assayists believed that the nondestructive measurements were accurate within the estimated errors. Those who performed the chemical recovery had no reason to doubt the accuracy of their measurements. After the recovery is performed, it is difficult to resolve this impasse. Thus, great care must be used when attempting to "recover" scrap materials.

In summary, the measurement of low-attenuation scrap ($T^* > 0.1$), such as most incinerator ash, demonstrates a bias of about 2% in the best cases, and precisions ranging from 2-10%. For high attenuation scrap ($0.1 > T > 0.001$), the bias increases to 3-4% and the precision increases to 15% or more as the attenuation increases. Uniform packaging and good standards become more important with increasing attenuation.

---

*T is the gamma transmission coefficient.

TABLE XLI

GAMMA ASSAY AND CHEMICAL RECOVERY MEASUREMENT OF SEVERAL SCRAP CATEGORIES

Can	Plutonium Mass (g) Chemical Recovery	Plutonium Mass (g) Gamma Assay	Relative Difference[a] (%)
1,2	31.0	31.2 ± 1.2	-0.6
3,4	32.8	32.0 ± 1.3	2.5
5,6	18.7	15.8 ± 0.8	18.4
7-9	9.2	10.2 ± 0.2	-9.8
10-12	6.5	10.0 ± 0.2	-35.0
13,14	6.3	5.9 ± 0.2	6.8
8	154	203	-24.1

---

[a] Relative differences are calculated with respect to the gamma assay values.

Even in cases of good measurement performance, the data show biases of 1-2%. Nothing inherent in the gamma measurement techniques would cause this; better calibration standards are probably the major requirement for improvement. With adequate standards (and possibly improved techniques) these measurements may become bias-free, but this has not yet been demonstrated. Some scrap measurement systems exhibit biases considerably greater than 2%, particularly those that do not employ a transmission-based attenuation correction.

GAMMA-RAY ASSAY: URANIUM

The gamma-ray assay of uranium scrap is similar to that of plutonium scrap. Measurements of ^{235}U are based on counting its 185.7-keV gamma ray. For material aged at least 3 months from the time of processing, the ^{238}U content can be measured directly by counting the 1001-keV gamma ray from the ^{238}U daughter ^{234m}Pa. Again, attenuation corrections are best based on the measured transmission of an external gamma-ray source. As with plutonium, it is often possible to measure the ^{235}U content and use knowledge of the ^{235}U enrichment to infer the total amount of uranium. Since the predominant ^{235}U gamma ray has an energy lower than the predominant ^{239}Pu gamma ray, it suffers considerably higher attenuation, especially in high-Z materials such as uranium. For a typical low-Z ($Z \leq 25$) matrix, the mass absorption coefficient is about 0.09 cm^2/g at 414 keV and about 0.13 cm^2/g at 186 keV. The mass absorption coefficient of uranium is about 0.25 cm^2/g at 414 keV and approximately 1.5 cm^2/g at 186 keV (nearly the same as plutonium). Thus, uranium assay is more affected by sample inhomogeneities, especially by local concentrations (lumping) of the source material. Uranium materials emit too little heat to be assayed by calorimetry, so that it is more difficult to determine scrap content in order to judge measurement reliability.

Multiple determinations of the uranium content and ^{235}U enrichment of incinerator ash were discussed earlier in this chapter. Gamma-ray measurements for both ^{238}U and ^{235}U content were also performed on this material. A comparison of the results for ^{235}U content is presented in Table XLII.[71] The analytical chemistry error (average value about 5%) contains contributions from the uranium determination and the ^{235}U enrichment measurement. The average precision of the ^{235}U gamma measurement (not shown in Table XLII) was about 2%. The total ^{235}U content of the 16 cans as measured by the two methods agrees well. The standard deviation of the relative differences between the two measurements (not shown in the table) is just under 6%, in good agreement with the precisions of the individual measurements (5% and 2%).

Also discussed in the analytical chemistry section of this chapter were some measurements on highly enriched Rover ash. One can that proved particularly troublesome in sampling was split into five portions and loaded into 2-liter polyethylene bottles. The contents of each bottle were blended, sampled, and assayed using analytical chemistry techniques. The bottles were then gamma assayed against a set of standards of graphite and uranium oxide contained in the same type of bottles. Results of these measurements are presented in Table XLIII. Based on duplicate samples of these blended materials, the precision of the analytical chemistry assay is about 2.5% (as reported earlier). The observed deviation between the gamma and analytical chemistry assay (about 2.9%) is consistent with a gamma measurement precision (consistent with counting statistics) of about 1.5% for these materials. These results probably demonstrate the best reliability obtainable for uranium gamma-ray assay. It should be noted that for this material a good set of calibration standards existed (not the case for many of the plutonium measurements cited); hence, a negligible bias was observed between the two measurement methods.

When analytical chemistry or chemical recovery are not considered reliable techniques, it is often useful to compare two or more NDA techniques to examine the reliability of scrap measurements. Two common methods of uranium measurement are

TABLE XLII

^{235}U INCINERATOR ASH MEASUREMENTS[a]

Chemical Assay	Chemical Error (%)	Gamma Assay[b]
19.5	7.9	18.8
64.5	3.0	66.3
44.4	3.8	44.5
17.0	5.4	17.9
42.4	9.4	39.3
22.4	3.3	21.8
17.4	4.7	15.9
67.6	3.6	76.3
20.8	4.0	19.5
57.9	2.1	54.7
75.8	2.8	75.0
22.8	4.9	22.3
16.5	15.9	17.1
12.9	3.9	12.0
35.0	3.3	32.0
32.9	1.9	33.0
569.8	Average = 5%	566.4

---

[a] The gamma assay values are taken from Ref. 71, p. 254. The chemical values and their errors are calculated from the data of Tables I and II of Ref. 62. The errors are calculated in quadrature from the uranium content errors of Table I and from the errors in the ^{235}U enrichment from Table II.

The chemical values are calculated from the values of average uranium content of Table I and the average ^{235}U enrichment of Table II.

[b] ^{235}U mass in grams.

TABLE XLIII

ROVER ASH MEASUREMENTS[a]

Uranium Mass (g)		Relative Difference[b] (%)
Gamma Assay	Chemical Assay	
41	42	-2.4
55	55	0
91	88	3.4
142	140	1.4
146	152	-3.9
		Mean = -0.3%
		Sigma = 2.9%

---

[a] See Ref. 61, p. 2.

[b] Relative differences are computed with respect to the chemical values.

delayed-neutron activation and passive gamma-ray assay. Table XLIV compares measurements made with these two techniques of 1-gallon recovery cans of "Rover Dust."[72] (This is a highly enriched uranium scrap consisting mostly of ground-up uranium and graphite fuel rods.) Because of the large can diameter and low gamma-ray energy, the measurements required attenuation corrections between 4.0 and 9.0%, close to the limit for reliable transmission-corrected gamma-ray assay. In spite of the large corrections, the agreement between passive and active assays is very good. The RSD of 3.8% is consistent with a precision of 2-3% for each measurement. The bias is less than 2%. Both the interrogation and induced neutrons are penetrating, so that the active assay should be reliable. The agreement between the passive and active methods lends further credance to the reliability of these measurements.

The final example involves the measurement of insoluble material from HTGR fuel scrap recovery. Table XLV compares data from a segmented-gamma-scan assay and a chemical assay. Here the agreement is not as good as that shown earlier. This material is very resistant to uranium extraction, so that the error in chemical assay may be large.

In summary, the gamma assay of uranium scrap is similar to that of plutonium; i.e., biases of about 2% can be achieved. For the data presented here, this bias applies even to highly attenuating materials. However, because the attenuation problems can be quite severe for ^{235}U gamma assay, one should be cautious in assuming this bias.

NEUTRON-COINCIDENCE ASSAY

Neutron-coincidence counting is used to discriminate between neutrons produced by spontaneous fission events (2-3 neutrons per fission) and neutrons produced by (α,n) reactions with light nuclei. The small spontaneous fission rate of ^{238}U (about 7 neutrons/kg-s) has been used to measure this isotope, mostly for

TABLE XLIV

COMPARISON OF PASSIVE AND ACTIVE ASSAY MEASUREMENTS OF ENRICHED URANIUM SCRAP

Uranium Mass (g)		Relative
Gamma Assay	Active Assay	Difference[a] (%)
138	140	-1.4
229	224	2.2
332	322	3.1
411	416	-1.2
102	94	8.5
172	166	3.6
221	220	0.5
391	399	-2.0
468	453	3.3
		Mean = 1.8%
		Sigma = 3.3%

---

[a] Relative differences are calculated with respect to the active assay values.

TABLE XLV

MEASUREMENTS OF HTGR SCRAP INSOLUBLES[a]

^{235}U Mass (g) Chemical Assay	^{235}U Mass (g) Gamma Assay	Relative Difference[b] (%)
3.9	3.6	8.3
4.0	3.3	21.2[c]
9.3	11.5	-19.1[c]
18.3	18.4	-0.5
22.0	21.9	0.5
12.9	13.0	-0.8
25.3	25.1	0.8
19.4	21.8	-11.0
36.2	37.8	-4.2
16.5	17.9	-7.8
25.8	19.4	33.0[c]
22.9	22.9	0.0
56.0	59.8	-6.4
59.0	64.1	-8.0
34.8	34.7	0.3
		Mean = -2.4%
		Sigma = 5.3%

---

[a] See Ref. 47, p. 100.

[b] Relative differences are computed with respect to the gamma assay values.

[c] These samples were omitted from the calculations of mean and sigma.

low-enriched uranium in large quantities such as LWR product oxide.[73] This section will discuss only plutonium scrap measurements. Spontaneous fission neutrons in plutonium arise mainly from three fertile isotopes, whose spontaneous fission rates are given in Table XLVI.[74] For low-burnup plutonium, neutrons from ^{240}Pu are dominant. For high-burnup plutonium (40 000 MWD/t*) as many as 50% of the neutrons come from ^{238}Pu and ^{242}Pu. For many applications, batch identification may provide sufficient isotopic information for a neutron-coincidence assay. Where isotopic information is not readily available, coincidence measurements for ^{240}Pu may be used with gamma measurements for ^{239}Pu and ^{241}Pu, but this has not been tried. If the isotopic composition is well known, the major errors in the measurement are caused by the effects of matrix material (moderation) on the efficiency of neutron counting. Using the isotopic compositions and uncertainties given in the calorimetry section, the contribution to the error from isotopic uncertainties is 0.1-0.5%. This contribution represents a lower limit to the precision, which will generally be larger owing to matrix effects.

In one neutron-coincidence assay, cans of ash residue were spiked with known amounts of PuO_2. The cans were measured against a simple plutonium metal-disc standard. Table XLVII shows the results of these measurements.[75] The reliability demonstrated here is similar to that for gamma assay of uranium or plutonium ash, i.e., a precision of about 2% and a small bias. It is interesting that such little bias occurs with a standard so different from the unknowns.

Another measurement involved assays on a larger set of scrap standards.[76] Fifteen heterogeneous standards were measured, three in each of five categories: graphite, insulation (mostly SiO_2), slag (mostly CaF_2), ash, and borated glass. These standards were fabricated by mixing PuO_2 with the matrix material in small containers. The small containers were then distributed to

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*Megawatt days/ton.

TABLE XLVI

PLUTONIUM SPONTANEOUS FISSION RATES

Isotope	Spontaneous Fission Rate (neutrons/g-s)
^{238}Pu	1.1×10^3
^{240}Pu	4.71×10^2
^{242}Pu	8.0×10^2

TABLE XLVII

NEUTRON COINCIDENCE MEASUREMENT OF SPIKED ASH STANDARDS[a]

Plutonium Mass (g)		Relative
Neutron Coincidence	Known Spike	Difference[b] (%)
35.30	35.08	0.63
8.86	8.92	-0.67
36.20	35.86	0.95
0.87	0.91	-4.40
8.77	9.05	-3.09
34.96	35.61	-1.83
		Mean = -1.4%
		Sigma = 2.1%

---

[a] The values for the known spikes are unpublished data. Refer to Ref. 75.

[b] Relative differences are calculated with respect to the known values.

fill a 1-gallon polyethylene bottle. Plutonium loadings varied from 3 to 155 g. A small (about 10^{-9} g) ^{252}Cf source was used for the "source addition" technique to correct for matrix and multiplication effects (this technique is similar to the transmission measurement of gamma assay). Figure 3 (see Ref. 76, p. 32) shows the ratio of the measured plutonium value to the known plutonium value plotted against the known plutonium content. The average bias between the measured and the known value was 1%, and the precision was 8%. There were also 11 homogeneous standards of ash or graphite in which the PuO_2 and matrix material were mixed directly in the 1-gallon bottles. Figure 4 (see Ref. 76, p. 32) shows the results of the measurement of these standards. A bias of 1% and a precision of 3% were observed. These results probably represent the most comprehensive data available for neutron-coincidence counting of plutonium scrap.

As part of PIP, neutron-coincidence counters were evaluated at several nuclear facilities. At one mixed-oxide facility, six cans of ash scrap were coincidence-counted and then recovered. In addition, a larger sample of scrap was measured and recovered. Table XLVIII shows the results of these measurements.[77] At another mixed-oxide facility, a neutron-coincidence counter was used as part of an integrated safeguards experiment (ISE) whose purpose was to examine the material balance around two plutonium recycle fuel rod production campaigns.[78] The coincidence counter was used in conjunction with calorimetry and chemical analysis to measure the incoming plutonium feed. The coincidence counter agreed with the chemistry measurements to better than 1%. It was also used to measure the scrap generated in the process. A comparison of neutron-coincidence measurements with weight and analytical chemistry measurements of the scrap material is given in Table XLIX. The scrap material is typical fuel-fabrication hard scrap, that is, reject feed and product material. In most cases, the measurements agree within the quoted error, and the difference for the total inventory is less than 1%.

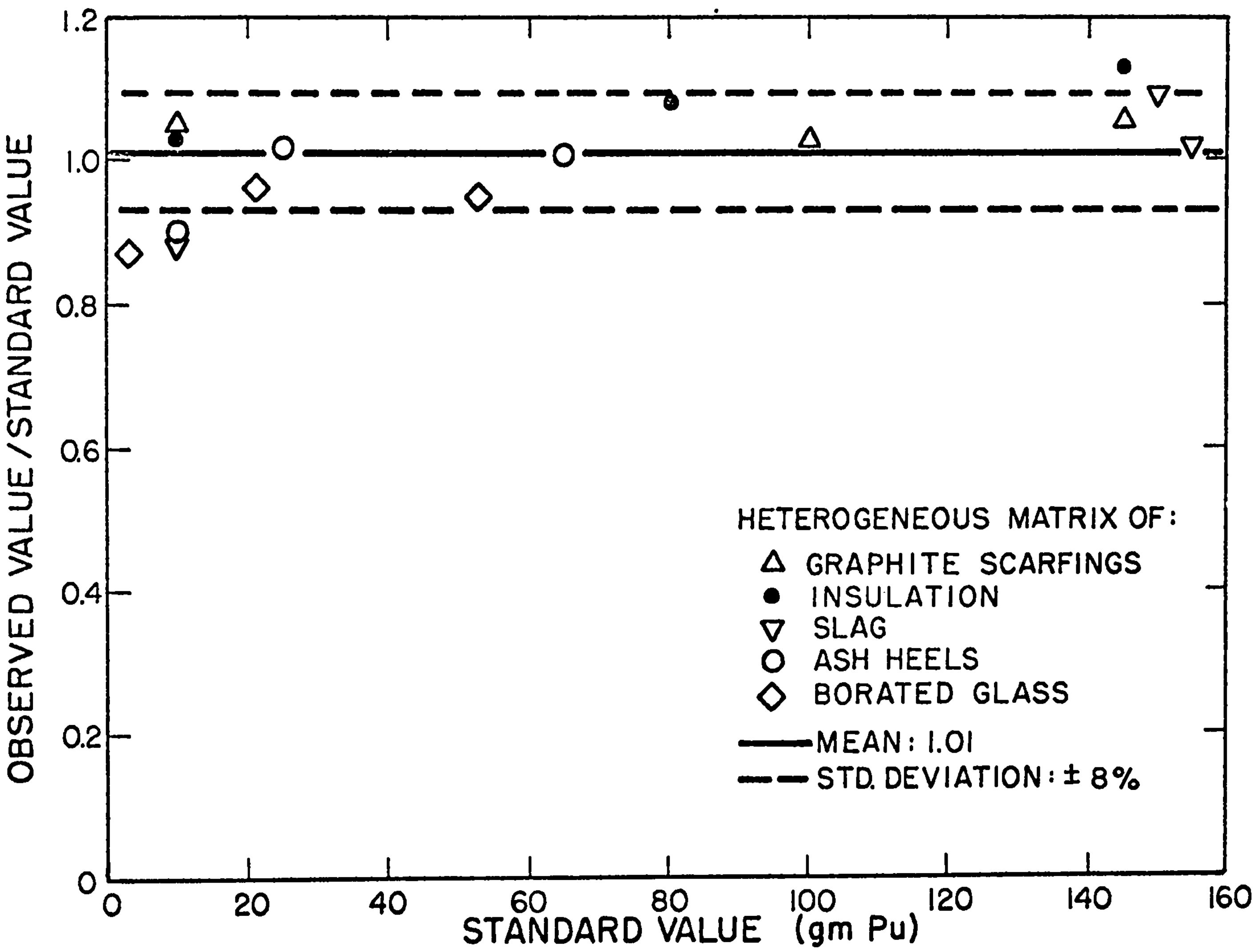

Fig. 3. Neutron coincidence measurement of heterogenous plutonium scrap standards.

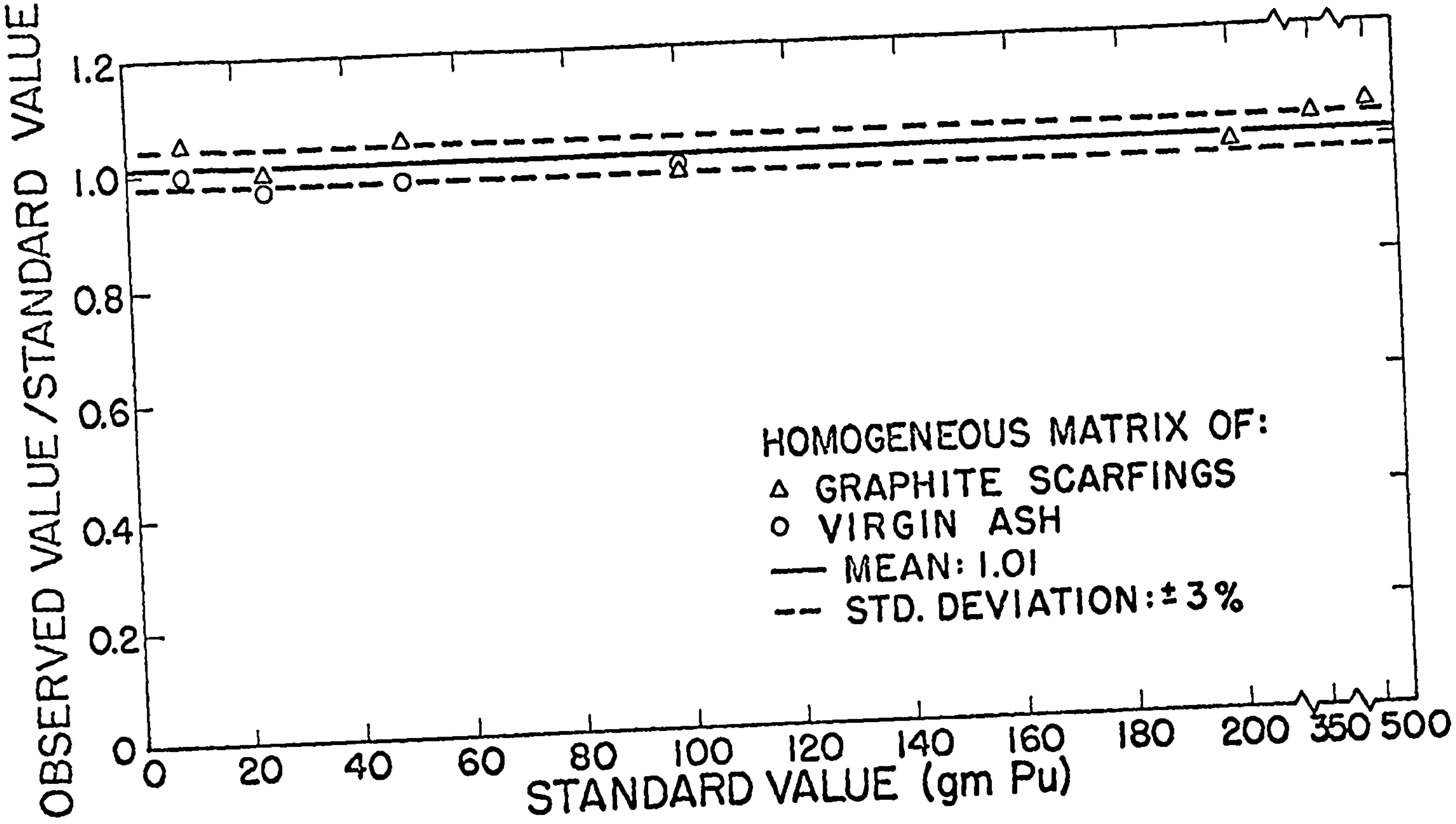

Fig. 4. Neutron coincidence measurement of homogeneous plutonium scrap standards.

TABLE XLVIII

COMPARISON OF NEUTRON COINCIDENCE MEASUREMENTS WITH CHEMICAL RECOVERY

Plutonium Mass (g)		Relative
Neutron Coincidence	Chemical Assay	Difference[a] (%)
183.5	182.3	0.66
62	65.45	-5.3

---

[a] Relative differences are computed with respect to the chemical values.

TABLE XLIX

ISE MATERIAL STREAM COMPARISON[a]

Origin	Material	Plutonium Mass[b] (g)		Relative Difference[c] (%)
		Chemical Assay	Neutron Coincidence	
Campaign 1				
Enrichment 1	Clean sintered scrap	214.2 ± 0.9	213.7 ± 5.6	-0.23
	Green scrap	34.0 ± 0.5	35.0 ± 0.7	2.94
	Dirty green scrap	10.7 ± 0.04	9.8 ± 0.6	-8.41
Enrichment 2	Clean sintered scrap	186.2 ± 0.7	193.8 ± 7.4	4.08
	Green scrap	52.9 ± 0.2	52.3 ± 1.3	-1.13
	Dirty green scrap	7.9 ± 0.02	7.3 ± 0.5	-7.59
	Green recycle	67.2 ± 1.0	65.2 ± 1.8	-2.98
Campaign 2				
Enrichment 1	Green recycle	76.7 ± 2.0	70.7 ± 1.2	-7.82
	Clean sintered scrap	73.9 ± 0.3	69.3 ± 1.8	-6.22
	Green scrap	28.5 ± 0.8	28.9 ± 0.4	1.40
	Dirty sintered scrap	13.3 ± 0.06	12.6 ± 0.2	-5.26
Enrichment 2	Clean sintered scrap	116.6 ± 0.6	117.5 ± 1.4	0.77
	Green scrap	13.6 ± 1.3	14.2 ± 0.2	4.41
	Dirty sintered scrap	15.4 ± 0.08	14.8 ± 0.3	-3.90
		911.1 ± 3.1	905.1 ± 10	

Difference = -6.0 g ~ -0.66%

---

[a] See Ref. 78, p. 5.

[b] Errors are given at the 95% confidence level.

[c] Relative differences are computed with respect to the chemical values.

As a last example, a neutron-coincidence counter has been used by safeguards inspectors to assist in inventory verification at a mixed-oxide fuel facility. Thirty-six samples of plutonium oxide and mixed oxide containing between 500 and 1100 g of plutonium were measured with a neutron-coincidence counter. The standard deviation of the relative differences between the facility tag-values and the neutron-coincidence measurements was found to be 3.8%.[79]

The results described in this section indicate that a bias larger than 2% should be assigned to neutron-coincidence measurements of scrap, particularly in view of possible bias in the plutonium isotopic concentrations. The error arising from bias in isotopic concentrations can be quite large because, as in calorimetry, most of the signal (in this case, neutrons) comes from minor isotopes. Scrap materials are more likely to have heterogeneous isotopic concentrations and so, are more difficult to sample for isotopic determination.

ACTIVE ASSAY

Active-assay systems use neutrons (or high-energy gamma rays) from an accelerator or radioactive source to induce fissions in a sample. The resulting prompt fission gammas and neutrons are then counted using coincidence techniques to discriminate fission particles from interrogation particles. Alternatively, the accelerator may be gated off or the sample and interrogating source may be physically separated to measure delayed emissions. Because of complexity, unreliability, and cost, accelerators have usually been rejected in favor of radioactive source-based systems, several of which are commercially available. These systems have been used primarily for product and feed assay rather than scrap assay. However, their performance for hard-scrap measurements should be quite similar to that for product and feed materials.

The availability of good passive signatures for plutonium assay has resulted in the development of gamma-ray, neutron-coincidence, and calorimetric-assay techniques for plutonium scrap. Two experiments measuring plutonium scrap will be described here. The first involves an Isotopic Source Assay System (ISAS).[80] This system uses a ^{252}Cf source in a moderating assembly to provide neutrons for interrogating the samples. Four slabs of plastic scintillator detect prompt gammas and neutrons following neutron-induced fission. A threefold coincidence is required as the signature of a fission event, a requirement that also improves the signal-to-background ratio. This system was used to measure 1-gallon scrap standards described in the neutron-coincidence section of this chapter. In each of the five categories of heterogeneous scrap, one sample was chosen to provide a calibration reference and three other samples were assayed relative to it. The results of the active assay (see Table L amd Ref. 48, p. 64) are similar to those obtained with a thermal-neutron coincidence counter: a bias of 1-2% and a precision of 5-7%. Each category required a different calibration, and the calibrations differed by more than a factor of two. An ISAS unit can also be used for passive coincidence measurements if the ^{252}Cf source is removed. Measurements of this type also require a separate calibration for each category of material, and the calibrations can differ by a factor of two. Thus, the use of such an instrument requires strict categorization and segregation of material types and standards.

A similar instrument, the Random Driver,[81] was used in the plutonium scrap exchange program described earlier in Chaps. 4 and 5. The Random Driver uses an Am-Li (α,n) neutron source that provides between 10^5 and 10^6 neutrons per second (average energy about 0.5 MeV) to induce fissions in a sample. The source is very closely coupled to the sample. Two plastic scintillators, lead shielded against gamma rays, measure fast coincidences to discriminate between fission neutrons and interrogation neutrons. Both the ISAS and Random Driver systems were used to

TABLE L

ISAS VS STANDARD MAKEUP VALUES FOR 1-GAL PLUTONIUM SCRAP STANDARDS

Scrap Category	Plutonium Mass (g) Known Value	Plutonium Mass (g) Assay Value[a]	Relative Difference[b] (%)
Slag	15	15.6	4.0
	160	162.7	1.7
	45	48.3	7.3
Graphite scarfing	25	25.7	2.8
	175	160.0	-8.6
	140	139.0	-0.7
Insulation	15	13.7	-8.7
	130	105.0	-19.2
	60	61.6	2.7
Glass	1	0.99	-1.0
	38	37.9	-0.3
	20	19.7	-1.5
Ash heel	10	10.6	6.0
	10	10.4	4.0
	55	54.7	-0.5

Mean = -0.8%

Sigma = 6.8%

---

[a] A different standard was used for calibration in each scrap category.

[b] Relative differences are computed with respect to the known values.

assay three fluoride, three oxide, and two green cake samples. Neither system performed as well as the gamma-assay system for the fluoride category, and the gamma system has the additional advantage of using a single independent standard for calibration. The Random Driver had a bias of 7% and a precision of 21%. The ISAS had a bias of 2% and a precision of 11%. The neutron assay techniques were much more effective on the denser oxides and green cakes. Table LI (unpublished) compares the two neutron systems, the segmented gamma scan, and calorimetry for the measurement of oxide and green cake samples. The RSD values (not shown in Table LI) of the relative differences between each measurement and calorimetry are nearly the same, about 8%. The gamma scan shows a larger bias than the two neutron systems, but the gamma scan is the only system calibrated with an independent standard. Relatively little development has been done on active techniques for plutonium assay, but recent work indicates possible applications to special problems not easily amenable to gamma or neutron-coincidence assay. Active techniques may provide higher reliability than shown here, but this has yet to be demonstrated.

Techniques for the passive assay of uranium are not well developed. Neutron-coincidence and calorimetry methods are not applicable, and attenuation problems for gamma assay are severe. Hence, active-assay techniques are more fully developed, especially for hard scrap. Measurements of hard scrap involve essentially the same considerations as for product and feed assay, so that the performance specifications described in Chap. 6 are applicable here.

Rover dust is a scrap material (highly enriched uranium and graphite) obtained by grinding up fuel elements from the nuclear rocket program. Table LII presents measurements of 1-gallon cans of this material by analytical chemistry and delayed-neutron activation using a Cockcroft-Walton neutron generator.[82] The calibration is based on both a chemical assay of the cans and an average delayed-neutron response, so that the low bias

TABLE LI

COMPARISON OF MEASUREMENTS MADE ON OXIDE AND GREEN CAKE SAMPLES[a]

	Plutonium Mass (g)			
Can	Calorimetry	Random Driver	ISAS	Gamma Assay
O-1	454	400	510	470 ± 71
O-2	1 143	1 150	1 110	1 110 ± 110
O-3	1 149	1 155	1 180	1 015 ± 102
O-5	189	175	200	182 ± 36
O-7	450	355	400	385 ± 39
O-9	1 150	1 135	1 120	972 ± 97
O-11	82	80	120	80 ± 5
G-1	744	800	750	705 ± 106
G-3	831	780	840	780 ± 117
Total	6 192	6 030	6 230	5 689 ± 254
Difference in total assay with respect to calorimetry:		-162 g	38 g	-503 g
Relative difference in total assay with respect to calorimetry:		-2.6%	0.6%	-8.1%

---

[a] Unpublished data.

TABLE LII

COMPARISON BETWEEN DELAYED NEUTRON ACTIVATION ASSAY AND CHEMICAL ASSAY FOR HIGHLY ENRICHED URANIUM-GRAPHITE DUST (ROVER DUST)

Uranium Mass (g)		Relative
Neutron	Chemical	Difference[a] (%)
1 153	1 111	3.8
1 133	1 222	-7.3
140	140.7	-0.5
135	133.6	1.0
116	115.4	0.5
121	122.5	-1.2
182	188.1	-3.2
146	145.5	0.3
151	147.3	2.5
118	111.1	6.2
103	102.0	1.0
128	128.1	-0.1
		Mean = 0.3%
		Sigma = 3.4%

---

[a] Relative differences are computed with respect to the chemical values.

between the two measurements is expected. Table LIII summarizes the results of some ISAS measurements for various types of uranium fuel materials (see Ref. 48, pp. 33,34). These are actually product materials, but the results would be similar for such hard scrap as reject oxide and pellets. As this table shows, biases are less than 1% and precisions are 0.25-1%. Such reliability applies only to relatively clean scrap where good standards are available.

As a final example, Fig. 5 compares two active measurements of highly enriched uranium scrap.[83] One measurement was made with a Random Driver and the other with an accelerator-based delayed-neutron technique. The difference between the two assay totals was 1.5%. Instruments of this type have been tested for measuring reject product and feed at an LWR fuel fabrication facility.[84] For 20-liter cans of low-enrichment uranium-oxide powder and pellets, precisions of 3-5% were reported for active measurements of fissile content. These instruments have large density-dependences that must be carefully accounted for in scrap measurements. Still, they should be capable of accurate measurements of uranium hard-scrap materials.

In summary, the active assay of plutonium can be performed with biases of 23% and precisions of 8%. Active-assay techniques are probably effective for uranium but development has been directed primarily toward product and feed materials. For clean scrap (reject product and feed) with good standards, biases of 0.1-0.5% and precisions of 0.5-1.0% are achievable. For dirty scrap, the demonstrated precision is 3-5% and the bias is 2%.

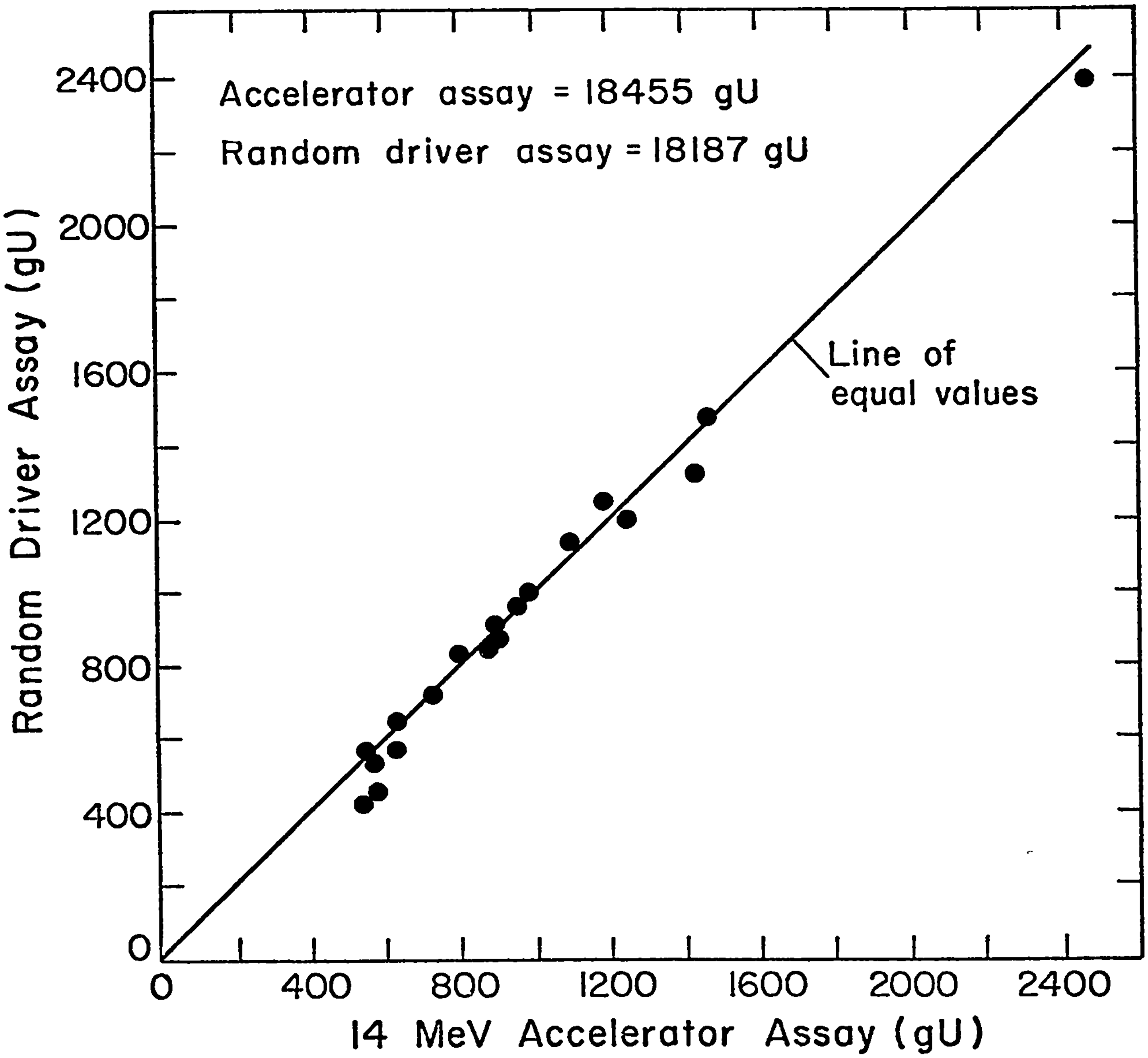

Fig. 5. Comparison of Random Driver and accelerator assay of highly enriched uranium scrap.

TABLE LIII

ISAS VS STANDARD MAKEUP VALUES FOR VARIOUS URANIUM FUEL MATERIALS[a]

Material	Uranium Mass (g) Chemical Assay	ISAS	Relative Difference[b] (%)	Random Error (%)
PBF powder	16 231	16 236	0.03	0.25
PBF pellets	5 373	5 362	-0.2	0.6
Rover fuel	6 328	6 317	-0.17	0.5
ATR plates	3 333	3 336	0.09	0.23
PBF rods	1 260	1 265	0.4	0.48
SPERT rods	1 044	1 053	0.9	0.7

---

[a] The chemical and ISAS values are taken from Ref. 48, p. 33; the random errors in the ISAS values are taken from Ref. 48, p. 34.

[b] Relative differences are calculated with respect to the chemical values.

CHAPTER 8

WASTE MEASUREMENT

Waste is residue that does not contain economically recoverable SNM. It is usually less dense and more heterogeneous, and is stored in larger containers than scrap. The largest category of waste consists of hydrogeneous, combustible, and low-SNM-content materials such as paper, wipes, plastic, glassware, and other disposables. Wastes also include contaminated equipment, tools, and higher density materials that are difficult to measure. Finally, low-level liquid waste streams, usually carrying insignificant amounts of SNM, are relatively easy to measure.

Typically, only 0.25-2% of plant throughput or inventory is waste, so that relatively large waste measurement errors are tolerable because of their minimal impact on LEMUF (limit of error of material unaccounted for). Common practice is to use 120- to 200-liter drums for waste storage and transportation. This large drum size and the fact that the drum contents can vary greatly makes assay difficult. When possible, it is desirable to incinerate large volumes of combustible wastes because the ash occupies a much smaller volume and is more reliably assayed. Bulk waste is often placed into smaller packages and assayed before final loading in the drums. This makes accounting easier and more reliable, as is suggested in NRC guides 5.11 and 5.47. Small-package assay, however, is often impractical, and drum measurement reliability can be adequate for accountability purposes.[85] Waste is usually not amenable to analytical chemistry methods (except for low-level solutions), and, as a result, nondestructive techniques have been widely used (and abused).[86] There is much latitude for error with this type of material, and measurement reliability is difficult to determine.

PLUTONIUM

Plutonium waste is most readily measured by passive assay (gamma and neutron coincidence, and gamma-ray assay). To date, most systems have been built with NaI detectors, but the trend now is toward the use of GeLi systems because of their better resolution. A major concern in waste measurement is the use of proper standards to minimize bias. The passive measurement techniques are essentially the same as those described in Chap. 7. The gamma assay of ^{239}Pu is based on measurement of the 414-keV gamma ray (or 330-420 keV complex with NaI) with attenuation corrections based on the measured transmission of an external source. A number of NaI detector waste measurement systems (both uranium and plutonium) have been used that do not employ transmission corrections. Calibration "standards," erroneously assumed to have attenuation properties representative of the actual waste, are highly susceptible to bias and are not recommended.

An extensive set of plutonium waste drum standards is available at Rocky Flats. The standards apply to seven waste categories: graphite, rashig rings, dry and wet combustibles, resin, washables, and plastics. Matrix material (selected by analysis of typical waste samples) and PuO_2 were mixed in packages about 4 liters in size. These smaller packages were then loaded into drums to provide variable plutonium distribution as well as variable mass distribution.[87] These standards were measured with a gamma-scan system consisting of eight 5- by 5-cm NaI detectors in a vertical array placed along the side of a drum.[88] On the other side of the drum, opposite each detector, was a gamma-ray transmission source. The system was calibrated by measuring a single small can (about 10 cm in diameter by 13 cm tall) containing diatomaceous earth and PuO_2, and performing computer computations to scale the geometry. Results of these measurements are presented in Table LIV. The 6% bias could be improved to better than 1% by using better calibration standards and measurement

TABLE LIV

NaI GAMMA ASSAY VS KNOWN VALUES FOR PLUTONIUM WASTE DRUM STANDARDS[a]

Category	Plutonium Mass (g) Measured	Plutonium Mass (g) Known	Relative Difference[b] (%)
Graphite	59	60	-1.7
	209	195	7.2
	151	145	4.1
Rashig rings	41	40	2.5
	168	185	-9.2
	75	95	-21.1
Washables	9	10	-10.0
	142	160	-11.3
	77	90	-14.4
Combustibles	11	10	10.0
	168	175	-4.0
	155	165	-6.1
Wet combustibles	26	29	-10.3
	123	166	-25.9
Resin	28	25	12.0
	106	110	-3.6
Plexiglas	62	75	-17.3
			Mean = -5.8%
			Sigma = 10.8%

---

[a] Refer to Ref. 88, p. 216.

[b] Relative differences are calculated with respect to the known values.

procedures. The 12% precision is larger than expected from counting statistics alone, and reflects the effects of sample inhomogeneities. The same standards were also measured by high-energy bremsstrahlung (photo fission) interrogation (see Ref. 48, pp. 39-61). Based on an independent calibration, the measurements showed a bias of 2% and a precision of 15%.

The only significant difference between ^{238}Pu and ^{239}Pu waste assay is that the 765-keV gamma ray of ^{238}Pu has a slightly higher penetrability than the 414-keV gamma ray of ^{239}Pu (for low-Z matrices the mass absorption coefficient is about 25% smaller at 765 keV). Two examples of ^{238}Pu waste assay will be discussed here. The first example involves a comparison of measurements of small packages of ^{238}Pu waste using a GeLi assay technique, with NaI drum measurements being performed after the small packages were loaded into 120-liter drums. About 200 small waste packages were first assayed individually (precision 5%). An average of 14 packages was placed into 13 drums that were then assayed with the 8-channel NaI system described above. Table LV compares the two measurements.[89] The bias between the two measurements is much less than 1% (insignificant) and the precision is about 12%. This precision is consistent with the results for the ^{239}Pu drum measurements that were discussed earlier.

Table LVI presents results[90] similar to those of Table LV except that the small packages in the drum were measured calorimetrically. The samples typically contained about 80% ^{238}Pu and could be measured calorimetrically with good accuracy. The drum assay system consisted of a single NaI detector and transmission source. These measurements exhibit a bias of 1% and a precision of 13% (not explicitly shown in Table LVI).

Those results demonstrate that biases of less than 1% (conservative estimate 5%) can be achieved for plutonium waste assay with precisions of 10-13%. Below are several examples of the poorer accuracy of some of the other waste measurement systems currently in use. The eight-channel NaI scan system mentioned above was also used to measure some production waste drums at

TABLE LV

MEASUREMENTS OF ^{238}Pu WASTE IN PACKETS USING GeLi AND NaI ASSAY

^{238}Pu Mass (g)		
NaI Drum Assay	GeLi Package Assay	Relative Difference[a] (%)
33.3	32.7	1.8
0.5	0.3	---[b]
45.3	39.1	15.9
1.0	0.6	---[b]
34.9	39.4	-11.4
37.9	39.6	-4.3
41.1	39.1	5.1
38.3	32.8	16.8
32.9	34.5	-4.6
30.0	34.2	-12.3
30.5	26.6	14.7
34.1	39.6	-13.9
15.8	17.3	-8.7
		Mean = -0.08%
		Sigma = 11.7%

---

[a] Relative differences are computed with respect to the GeLi assay values.

[b] These measurements are not included in the calculation of mean and sigma since the system was not set up to measure low-level wastes accurately. The drums were measured to check for gross errors only.

TABLE LVI

^{238}Pu MEASUREMENT USING CALORIMETRY AND GAMMA ASSAY

^{238}Pu Mass (g)	
Drum Gamma	Calorimetry
0.653	0.627
0.397	0.479
0.347	0.389
0.321	0.389
0.380	0.389
0.421	0.389
10.1	9.33
11.6	9.33
0.186	0.181
0.305	0.241
0.231	0.241
0.241	0.241
0.276	0.273
2.97	2.87
10.6	12.5
12.0	12.5
51.028	50.369

Difference in total assay with respect to calorimetry = 0.659 g

Relative difference in total assay with respect to calorimetry = 1.3%

TABLE LVII

WASTE DRUM PLUTONIUM MEASUREMENT USING TWO DIFFERENT GAMMA ASSAY SYSTEMS

Category	Plutonium Mass (g)	
	Plant Assay	8-Channel Assay
Burnables	35	18
Resin	34	21
Graphite	56	53
Combustibles	93	95
Filters	203	468
Hot metal	71	124
Hot plastic	21	20
	513	799

the same facility that employed the waste drum standards. The plant waste measurements were made with a gamma assay system that used geiger tubes and BF_3 neutron detectors without transmission corrections. Table LVII compares measurements made with these two systems on seven production waste drums.[91] The observed 36% difference in total assay is owing to the lack of a transmission correction and to count-rate problems at high plutonium loadings.

A similar comparison with active bremsstrahlung interrogation exhibited the same problem. For 20 drums in 5 categories, the active assay (confirmed by passive gamma measurement) found 24% more plutonium than the plant assay (see Ref. 48, pp. 39-61).

Gross errors are possible if calibration standards are not properly fabricated. Five drums of mixed-oxide waste were measured at three different facilities to investigate the reliability of waste measurements. All of the plants used gamma-assay techniques (only one used a transmission correction) and two plants "checked" the assay results with passive neutron counting methods. The results of these three measurements are presented in Table LVIII.[92] Large biases exist between each of the first two measurements and the third measurement (the most accurate determination). These errors are probably caused by a calibration standard that contained small vials of mixed-oxide source material distributed throughout a standard drum. Self-absorption within the vials biased the calibration. Such problems are serious because they lead to a bias in all waste measurements based on the erroneous standard.

Most waste assays are performed on large standard drums. However, more reliable measurements are possible by assaying the smaller packages with which the drum is usually loaded. "Bagout" ports at gloveboxes often restrict package sizes to about 4-8 liters. To illustrate the improved reliability of small package assay, Table LIX presents measurements of mixed-oxide waste standards consisting of 4-liter plastic bags filled with Kimwipes mixed with $(U\text{-}Pu)O_2$.[93] A GeLi assay system with a ^{75}Se

TABLE LVIII

WASTE DRUM PLUTONIUM MEASUREMENT AT THREE DIFFERENT FACILITIES[a]

Plutonium Mass (g)		
Plant 1	Plant 2	Plant 3 (best value)[b]
49.7	38.9	19.0 ± 3.8
6.0	5.2	2.8 ± 0.6
4.4	2.6	2.0 ± 0.4
8.4	7.5	3.7 ± 0.9
15.8	12.7	7.0 ± 1.8
84.3	66.9	34.5 ± 4.4[c]

---

[a] The data of plants 1 and 2 are unpublished; the data of plant 3 are from Ref. 92.

[b] Uncertainties are given at the 95% confidence level.

[c] The measurement errors are taken to be statistical only and are added in quadrature.

TABLE LIX

COMPARISON OF GAMMA-RAY ASSAY AND KNOWN VALUE ON SMALL WASTE STANDARDS

^{239}Pu Mass (g)		Relative
Gamma	Known	Difference[a] (%)
0.87	0.830	4.8
2.40	2.440	-1.6
4.15	4.075	1.8
4.01	4.069	-1.4
4.02	4.070	-1.2
4.08	4.070	0.2
0.77	0.749	2.8
2.11	2.205	-4.3
3.46	3.677	-5.9
3.48	3.677	-5.4
3.60	3.676	-2.1
3.59	3.677	-2.4
		Mean = -1.2%
		Sigma = 3.2%

---

[a] Relative differences are computed with respect to the known values.

transmission correction was used to measure the samples. The measurements were made with an independent calibration. Plant personnel where these samples were fabricated measured all the small waste packages with neutron-coincidence counting techniques before loading them into drums.

Neutron-coincidence counting techniques are also reliable for use in drum assay when accurate isotopic information is available. Waste drum measurement systems have been fabricated using thermal-neutron detectors (^{3}He or BF_3)[94] and prompt-coincidence scintillators that detect coincidences between fission neutrons and/or gamma rays.[95] The reliability of neutron-coincidence counting methods for waste assay is similar to that for scrap. Table LX compares neutron-coincidence measurements and a GeLi gamma assay of five drums of mixed-oxide waste. The measurements agree within the uncertainties.

URANIUM

It is more difficult to measure uranium waste than plutonium because of increased gamma-ray absorption and the inapplicability of neutron-coincidence counting techniques. Because of the high self-absorption of uranium ($\mu = 1.5\ cm^2/g$ at 186 keV), potential errors from source material concentrations (lumping) are severe. Still, for low-concentration combustible waste, the measurement of ^{235}U in drums should be as reliable as that of ^{239}Pu; that is, the bias is conservatively estimated as 5% and the precision as 10-15%. Because a set of uranium waste drum standards equivalent to the plutonium standards described in the preceding section does not exist, reliability checks are very difficult. Many uranium-waste measurements have been made, usually with NaI detector systems measuring the 185.7-keV gamma ray from ^{235}U, but many of these systems do not employ a transmission correction. In spite of widespread use, relatively little data describing system reliability is available.

A GeLi segmented gamma scan system has been tested for measurement of HTGR (highly enriched uranium) waste compacted into

20-liter cans. Using a series of standards, the accuracy of these measurements was found to be about 3.5%.[47] Photofission measurements of 220-liter drums of HTGR combustible waste were compared with passive (NaI) gamma measurements of the same materials (see Ref. 48, p. 120). The active and passive measurements differed by 36% for the total contents of 17 drums, and the RSD for an individual measurement was about 130%. This illustrates the large disagreements that have been observed for waste measurements.

TABLE LX

COMPARISON OF GAMMA-RAY AND NEUTRON COINCIDENCE ASSAY ON MIXED-OXIDE WASTE DRUMS[a]

Plutonium Mass[b] (g)	
Gamma-Ray	Neutron Coincidence
19.0 ± 3.8	18.6 ± 4.7
2.8 ± 0.6	3.1 ± 0.8
2.0 ± 0.4	2.0 ± 0.6
7.0 ± 1.8	5.5 ± 1.4
3.7 ± 0.9	4.0 ± 1.0

---

[a] See Ref. 92.

[b] Uncertainties are given at the 95% confidence level.

CHAPTER 9

SUMMARY OF MEASUREMENT RELIABILITY

This chapter summarizes the data in the preceding chapters on the reliability of assays of plutonium and uranium in product, scrap, and waste.

PRODUCT PLUTONIUM

Table LXI summarizes the data for plutonium product material (solutions, oxide powder and pellets, and fuel rods) for both total plutonium content and ^{239}Pu concentration. For titration analyses the optimum precision is much better than the mean from laboratory exchange programs. The analytical chemistry measurements are bias-free in the optimum case, where careful calibration against a standard should exist, but this may not be the case for routine assays. Chemistry measurements should easily give a precision of 0.3% and a bias of 0.2%.

Calorimetry measurements should be very accurate for plutonium assays--the heat determination should have a precision of 0.25%, the uncertainty in the specific power of the sample may introduce a bias of 0.1-0.2%, and there is uncertainty in the isotopic determination. For low-burnup plutonium (94% ^{239}Pu by weight), precisions of 0.08-0.3% have been obtained, while for spent LWR fuel (containing 62% ^{239}Pu) precisions are 0.3-1.0%. In summary, precisions of 0.3-1.0% and biases of 0.1- 0.2% can be expected for calorimetry measurements.

The data shown in Table LXI for fuel rods are routinely obtained for fast-breeder fuel rods with a ^{252}Cf scan system. Plutonium rods and plates have been routinely assayed at Argonne National Laboratory with computer-controlled gamma-scan systems.

TABLE LXI

RELIABILITY OF PLUTONIUM PRODUCT AND FEED ASSAYS

		Precision (RSD, %)			Bias (%)			Interlaboratory Deviation (%)	
Material	Method	Optimum	Mean	Range	Optimum	Mean	Range	Mean	Range
TOTAL PLUTONIUM									
Nitrate solution	Titration	0.04	0.29	0.07-0.6	0	0.16	0.1-0.2	0.35	0.13-0.67
	Gamma spectroscopy	0.5	---	---	0.2	---	---	---	---
Oxide	Titration	0.04	0.15	0.04-0.6	0	0.25	0.0-0.35	0.26	0.07-0.48
	Calorimetry	0.25	---	0.26-0.95	0.1	0.16	---	---	---
Mixed oxide	Coulometry	0.04	0.14	---	---	---	---	0.07	---
Fuel rods	^{252}Cf scan	0.8	---	---	0.1	---	---	---	---
Fuel plates	Gamma spectroscopy	0.5	---	---	0.1	---	---	---	---
^{239}Pu CONCENTRATION									
Nitrate solution	Mass spectroscopy	0.02	0.09	0.01-0.13	0	0.01	0.0-0.08	0.05	0.03-0.1
	Gamma spectroscopy	0.2	---	---	0	0.1	---	---	---
Oxide	Mass spectroscopy	0.02	0.06	0.01-0.16	0	0.08	0.06-0.19	0.09	---

Figure 1 shows the precision of mass spectroscopic determinations of isotopic abundance. Although the figure shows plutonium data, it applies as well to uranium. The upper curve represents a worst case, and the lower curve is optimum.

PRODUCT URANIUM

Table LXII summarizes the data for uranium product assays both for total uranium content and for ^{235}U concentration. Chemical measurements should easily yield a precision of 0.2% and a bias of 0.05%. LWR fuel rods are routinely assayed by ^{252}Cf scan with the reliability shown in the table. Routine uranium solution assays (some in-line) have precisions of 0.25% and biases of 0.1%. Bulk and small-sample uranium active-assay systems are capable of biases of 0.1% or less.

SCRAP

Scrap composition ranges from reject product and feed to residues containing less than 10% SNM by weight. Reject product and feed, the most common form of scrap, is assayed (with similar reliability) by the same methods as are product materials. Calorimetry is a reliable technique for plutonium scrap assay. Reject product calorimetric assays have precisions of 0.3-1% and biases of 0.1-0.2%. For dirty scrap materials the isotopic composition is more difficult to determine, so that the observed precisions are 3% and the biases are 2%.

Analytical chemistry assays of hard-scrap materials are as reliable as are product measurements. For well-blended dirty scrap, sampling errors are 2-3%, and larger errors result for poor blending.

Gamma assays of dirty plutonium scrap have optimum precisions of 2% for low-attenuation materials such as incinerator ash. For more attenuating materials the precision is as poor as 10%. Biases of 2% have been obtained, and smaller biases could probably be achieved.

Neutron-coincidence techniques are useful for the assay of plutonium scrap. For reject materials the accuracy is limited by the determination of the isotopic composition and is predicted to be 0.1-0.5% in the optimum cases. Actual measurements indicate a bias of 1% or worse. For dirty scrap materials, precisions range from 3% for homogeneous to 8% for very heterogeneous materials, with biases of less than 1%.

Uranium scrap can be assayed with gamma techniques. Precisions of 2% are observed for high-transmission materials. Biases are smaller for uranium (0.5-1%) than for plutonium because of the availability of better standards.

Active NDA techniques are used for both plutonium and uranium scrap. Passive techniques are, however, simpler and more reliable for plutonium. For reject uranium product and feed, active techniques have given precisions of 1% and biases of 0.5%.

Table LXIII summarizes the scrap measurement reliability to be expected under plant conditions.

WASTE

Waste typically represents only 0.25-2% of plant throughput, so that large uncertainties, unavoidable because of varying composition, are acceptable. Gamma and neutron-coincidence systems are used for plutonium waste assay. Gamma systems should include transmission measurements to avoid large biases. The precision of waste measurements is 10-13% and the bias is 1-5%. Reliable standards must be used for waste measurements. Measurements on small waste packages are easier and more reliable than are measurements on large waste drums. For individual packages (about 4 liters), precisions of 3% and biases of 1-2% are readily achieved.

Table LXIII summarizes the waste measurement reliability to be expected under plant conditions.

TABLE LXII

RELIABILITY OF URANIUM PRODUCT AND FEED ASSAYS

		Precision (RSD, %)			Bias (%)			Interlaboratory Deviation (%)	
Material	Method	Optimum	Mean	Range	Optimum	Mean	Range	Mean	Range
TOTAL URANIUM									
Nitrate solution	Titration	0.02	0.15	0.03-0.78	0	0.06	0.004-0.29	0.09	0.02-0.2
	Gamma spectroscopy	0.5	---	---	1.0	---	---	---	---
Oxide	Titration	0.02	0.16	0.02-1.4	0	0.03	0.01-0.66	0.05	0.03-0.09
	Gamma (and neutron bulk amounts)	2	---	---	1.0	---	---	---	---
	Active assay	0.5	1.0	0.5-2.0	0	1.0	---	---	---
Fluoride	Titration	0.02	0.08	---	---	---	---	0.18	---
Mixed oxide	Coulometry	---	0.27	---	---	---	---	0.03	---
Fuel rods	^{252}Cf scan	1.0	---	---	0.25	---	---	---	---
^{235}U CONCENTRATION									
Nitrate	Mass spectroscopy	0.014	0.14	0.03-0.48	0	0.01	0.001-0.29	0.07	---
Fluoride	Mass spectroscopy	0.014	0.18	---	---	---	---	0.16	---
Oxide	Mass spectroscopy	0.014	0.25	0.01-2.0	0	0.07	0.02-0.45	0.16	---
Fuel rods	Gamma spectroscopy	0.5	---	---	0.1	---	---	---	---

TABLE LXIII

SCRAP AND WASTE MEASUREMENT RELIABILITY

Material	Method	Precision (RSD, %)	Bias (%)
SCRAP			
Plutonium reject product	Chemical assay	0.3	0.1
	Calorimetry	0.3-1.0	0.1-0.2
	Neutron coincidence	3.0	1.0
Plutonium dirty scrap	Chemical assay	2-3	1.0
	Calorimetry	3	2
	Gamma ($T^a > 0.1$)	2	2
	Gamma ($T > 0.001$)	2-10	2-5
	Neutron coincidence	3-10	1
	Active assay	8	0.5-2.5
Uranium reject product	Chemical assay	0.2	0.05
	Active assay	1.0	0.1-0.5
Uranium dirty scrap	Gamma ($T > 0.1$)	2	1
	Gamma ($T > 0.001$)	2-10	2
WASTE			
Large volume of plutonium waste	Gamma	10-13	5
	Gamma (without transmission correction)	20	10-20
	Neutron coincidence	10	5
Small can of plutonium waste	Gamma	3	1-2
Large volume of low density uranium waste	Gamma	10	5-10
Small can of uranium waste	Gamma	5	2

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[a] T is the gamma transmission coefficient.

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