

*Determination of Plutonium Concentration
and Isotopic Compositions
by Isotope Dilution Gamma-Ray Spectroscopy
on Resin Beads*

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**DETERMINATION OF PLUTONIUM CONCENTRATION
AND ISOTOPIC COMPOSITIONS
BY ISOTOPE DILUTION GAMMA-RAY SPECTROSCOPY
ON RESIN BEADS**

by

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ABSTRACT

We have developed a new technique for simultaneously determining the plutonium concentration and the isotopic composition of highly irradiated fuel dissolver solutions, such as the input to a chemical reprocessing plant. This technique combines the high-resolution, low-energy, gamma-ray spectroscopy technique, the isotope dilution technique, and the resin bead technique in one; it is referred to as isotope dilution gamma-ray spectroscopy (IDGS). The IDGS involves adding a well-characterized plutonium isotope to the unknown solution and then extracting the plutonium from the spiked (mixed) solution on resin beads and subsequently measuring the beads with high-resolution gamma-ray spectroscopy. The spike used in this experiment is a large size dried spike of ^{239}Pu . The plutonium concentration of the dissolver solution obtained from the first IDGS measurement agrees with that obtained by isotope dilution mass spectrometry within 0.042%.

I. INTRODUCTION

The resin bead technique¹ was originally developed to selectively absorb plutonium and uranium from a reprocessing plant input dissolver solution onto anion resin beads, which are then analyzed by isotope dilution mass spectrometry (IDMS).² Each resin bead then serves as a vehicle for loading onto the mass spectrometer filaments. To reduce the complexity of sample preparation, the analysis time, and the cost of IDMS, we have recently demonstrated a rapid method for determining plutonium isotopic composition on resin beads using high-resolution, low-energy, gamma-ray spectroscopy.³ The results obtained from the resin bead gamma-ray technique showed negligible bias when compared with those obtained from mass spectrometry and showed a precision (1σ) of a few percent on samples containing only 9 μg of plutonium. Obviously, the precision obtained from the gamma-ray technique can be improved with better counting statistics that are a function of sample mass, isotopic distribution, assay geometry, count time, etc.

In addition to plutonium isotopic analysis, the resin bead gamma-ray technique can also determine the total plutonium concentration, if the unknown solutions are spiked with an accurately known concentration and isotopic composition of another plutonium isotope. The plutonium is then extracted from the spiked (mixed) solution on resin beads, which are subsequently measured with high-resolution, gamma-ray spectroscopy. This new method of determining plutonium concentration is referred to as isotope dilution gamma-ray spectroscopy (IDGS). The isotopes ^{236}Pu , ^{238}Pu , ^{239}Pu , and ^{240}Pu are all good candidates as a known spike for the IDGS technique. However, for cost and availability concerns, ^{239}Pu is the best choice. A large size dried (LSD) spike⁴ of ^{239}Pu is used as the spike for this experiment. Its certified isotopic composition is listed in Table I.

This report describes the principle of the IDGS, the resin bead sample preparation, and the preliminary results obtained by this new technique.

TABLE I. Plutonium Isotopic Distribution
of Pure LSD-Spike

<u>Isotope</u>	<u>at. %</u>
^{238}Pu	0.002461
^{239}Pu	97.93026
^{240}Pu	2.05199
^{241}Pu	0.013984
^{242}Pu	0.001304

II. ISOTOPE DILUTION GAMMA-RAY SPECTROSCOPY (IDGS) TECHNIQUE

Let W^i , C , and V be the weight fraction of isotope i , concentration (g/ℓ), and volume (ℓ), respectively, and the subscripts u , s , and m stand for unspiked sample (dissolver solution), spike (LSD spike), and spiked sample (mixture of dissolver solution and LSD spike), respectively. Then the relation of unspiked sample, spike, and spiked sample can be expressed as

$$W_m^i = \frac{W_s^i C_s V_s + W_u^i C_u V_u}{C_s V_s + C_u V_u} . \quad (1)$$

The ratio of two isotopes [$i = 0$ for ^{240}Pu and $i = 9$ for ^{239}Pu , in Eq. (1)] in the spiked sample equals

$$\frac{W_m^0}{W_m^9} = \frac{W_s^0 C_s V_s + W_u^0 C_u V_u}{W_s^9 C_s V_s + W_u^9 C_u V_u} . \quad (2)$$

Let

$$R_m = \frac{W_m^0}{W_m^9} ,$$

$$R_u = \frac{W_u^0}{W_u^9} ,$$

$$R_s = \frac{W_s^0}{W_s^9} , \text{ and}$$

$$R_r = \frac{W_u^0}{W_s^9} .$$

Equation (2) can be rewritten as

$$R_m = R_u \cdot \frac{R_s C_s V_s + R_r C_u V_u}{R_u C_s V_s + R_r C_u V_u} \quad (3)$$

After rearranging Eq. (3), the concentration of the unknown dissolver solution, C_u , can be solved for as shown in the following steps:

$$R_u R_m V_s C_s + R_r R_m V_u C_u = R_u R_s V_s C_s + R_u R_r V_u C_u$$

$$C_u V_u R_r (R_m - R_u) = C_s V_s R_u (R_s - R_m)$$

$$\begin{aligned} C_u &= C_s \cdot \frac{V_s}{V_u} \cdot \frac{R_u}{R_r} \cdot \frac{R_s - R_m}{R_m - R_u} \\ &= \frac{M_s}{V_s} \cdot \frac{V_s}{V_u} \cdot \frac{W_u^o/W_u^g}{W_u^o/W_s^g} \cdot \frac{R_m - R_s}{R_u - R_m} \end{aligned}$$

where M_s is the mass of plutonium in the spike. Thus,

$$C_u = \frac{M_s}{V_u} \cdot \frac{W_s^g}{W_u^g} \cdot \frac{R_m - R_s}{R_u - R_m} \quad (4)$$

In this equation, the values of M_s , W_s^g , R_s , and V_u are known. Therefore, only values of R_u and W_u^g in the unspiked dissolver solution sample and R_m in the spiked sample are to be measured by gamma-ray spectroscopy.

In the case of using atom fractions, A^i , one can utilize the relation

$$W^i = \frac{A^i I^i}{\sum A^i I^i} = \frac{A^i I^i}{\bar{A}}$$

(here, I^i = isotopic weight and $\bar{A} = \sum A^i I^i$ = average atomic weight) to convert Eq. (4) from the mass fraction form to the atomic fraction form. Since the $(R_m - R_s)/(R_u - R_m)$ ratio has the same value whether we plug in mass or atomic ratios, the only terms in Eq. (4) we need to convert are

$$\begin{aligned} \frac{W_s^o}{W_u^o} &= \frac{A_s^o I^o / \sum A_s^i I^i}{A_u^o I^o / \sum A_u^i I^i} \\ &= \frac{A_s^o / \bar{A}_s}{A_u^o / \bar{A}_u} \end{aligned}$$

Thus, Eq. (4) can be converted to

$$C_u = \frac{M_s}{V_u} \cdot \frac{\bar{A}_u}{\bar{A}_s} \cdot \frac{A_s^o}{A_u^o} \cdot \frac{R_m - R_s}{R_u - R_m} \quad (5)$$

for the atom fraction calculation.

The measurement method is based on high-resolution, low-energy, gamma-ray spectroscopy techniques. In general, the isotopic ratio $N(m)/N(n)$ of two isotopes m and n can be determined by measuring their respective gamma rays a and b .

$$R = \frac{N(m)}{N(n)} = \frac{CR(a)}{CR(b)} \cdot \frac{I(b)}{I(a)} \cdot \frac{T_{1/2}(m)}{T_{1/2}(n)} \cdot \frac{\epsilon(b)}{\epsilon(a)}, \quad (6)$$

where CR = measured count rate of gamma rays,
 I = absolute branching intensity of gamma rays,
 $T_{1/2}$ = half-life of isotope, and
 ϵ = relative efficiency of selected gamma rays, including detector intrinsic efficiency,
counting geometry, and attenuation.

In this work, the isotopic ratios of $^{238}\text{Pu}/^{239}\text{Pu}$, $^{240}\text{Pu}/^{239}\text{Pu}$, and $^{241}\text{Pu}/^{239}\text{Pu}$ are determined by analyzing the gamma-ray ratios 43.48 keV/51.63 keV, 45.23 keV/51.63 keV, and 148.6 keV/129.3 keV, respectively. The ^{238}Pu , ^{239}Pu , ^{240}Pu , and ^{241}Pu compositions in the sample can then be determined by combining isotopic ratios and correcting for the ^{242}Pu content, which is predicted by isotope correlation techniques. All gamma-ray peak areas are calculated by using a channel-by-channel summation method with a linear, straight-line background subtraction. Minor interferences in the full-energy peaks are taken into account in the assay equations.

For each spectrum, the gamma-ray relative efficiencies are determined from the quotients of the measured peak areas and the known specific activities of the selected ^{239}Pu gamma rays in the sample. A simple linear $\ln \epsilon$ vs $\ln E$ (gamma-ray energy) interpolation between measured efficiency points at 38.66 and 51.63 keV is used to calculate the relative efficiencies at 43.48 and 45.23 keV. The measured efficiency points at 129.3, 144.2, 171.3, 195.7, and 203.5 keV are fit to a quadratic to determine the relative efficiency at 148.6 keV.

The gamma-ray spectroscopy system (Fig. 1) uses a high-resolution hyperpure germanium (HPGe) planar detector, a Canberra Series 90 multichannel analyzer (MCA) with a 16-k-channel analog-to-digital converter, and a Digital Equipment (DEC) Micro-11 computer and peripherals. The MCA is controlled by the computer, which has 128-k, 16-bit words of memory and is a processor for data acquisition and analysis. The detector is 1000 mm² by 13 mm with a resolution (full width at half maximum) of 560 eV at 122 keV. A two-point stabilizer locked to the 51.63- and 129.3-keV gamma rays from ^{239}Pu is used to maintain the energy calibration. An existing plutonium isotopic analysis code, written in FORTRAN under DEC's RT-11 V5.02 operating system, is used for data acquisition and analysis.

III. RESIN BEAD SAMPLE PREPARATION

The resin bead sample preparation procedure is shown in Fig. 2. Four aliquots were prepared after the LSD spike was well mixed with the precise aliquot of the input dissolver solution and then completely dissolved at 90°C with 5M HNO₃ and 0.001M HF. A portion of each sample was prepared for the IDGS measurement and the remaining solution was used to prepare IDMS samples. After evaporation, each aliquot was redissolved with 8M HNO₃. Those solutions were passed

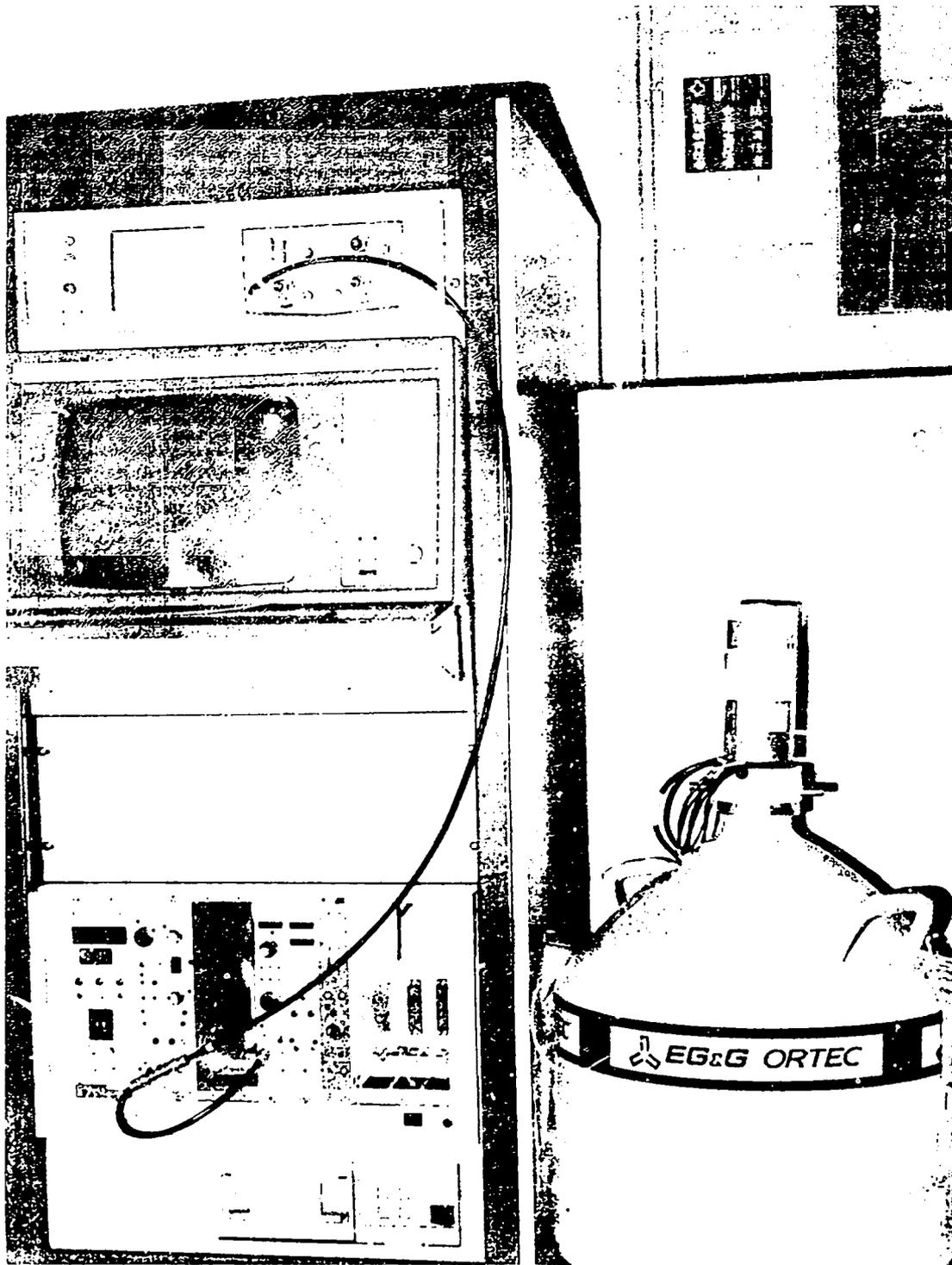


Fig. 1. The high-resolution gamma-ray spectroscopy system for IDGS measurements.

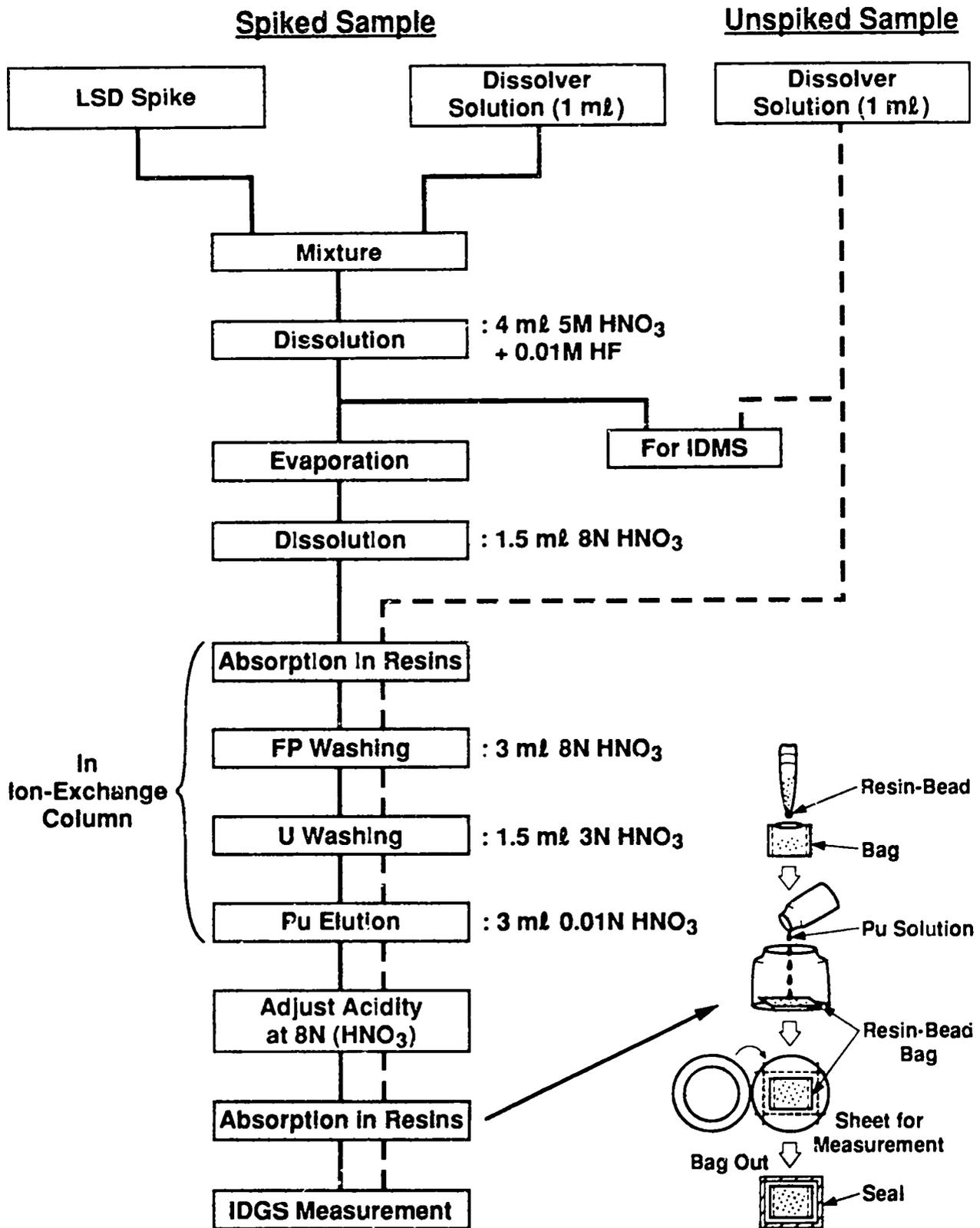


Fig. 2. The resin bead sample preparation procedure for the spiked (solid line) and unspiked (dashed line) samples.

through the anion exchanger column (BIO-RAD AG-MP1 NO₃ form, 0.5 ml, 5 mm ϕ). After washing to remove fission products, uranium, and americium with 8M HNO₃, plutonium was eluted, its acidity adjusted with 8M HNO₃. The plutonium was absorbed in a small gauze bag that was prefilled with resin beads. The resin bead samples then were bagged out from the glove box and placed directly in front of the HPGe detector for the IDGS measurements. The sample preparation flow originally proposed had been such that a certain amount of resins containing plutonium were taken from the ion exchange column for the measurement. It was, however, found that ruthenium, one of the major fission products, was hardly rinsed from the first stage of the ion exchange separation. Therefore, the idea of plutonium elution-reabsorption mentioned above was adopted. Because the dissolver solution used in this experiment has been stocked over 1 month, no valency adjustment has been made. However, for routine operation, it is necessary to adjust the valence before the ion exchange.

Each LSD-spiked aliquot originally contained approximately 4.5 mg of plutonium from the LSD spike and 1 mg of plutonium from the dissolver solution; approximately 60% of the plutonium is lost during sample preparation because fission products were necessarily well rinsed out. Because the LSD spike is expensive and difficult to obtain, measurements were made at several diluted spike concentrations to determine the minimum amount of spike required. Each LSD-spiked aliquot was diluted to X2 (half of original concentration, LSD1), X4 (LSD2), X8 (LSD3), and X16 (LSD4) to select an optimized dilution. The plutonium masses contained in the LSD1, LSD2, LSD3, and LSD4 diluted samples were approximately 1.1 mg, 0.55 mg, 0.28 mg, and 0.14 mg, respectively.

IV. RESULTS AND DISCUSSION

Figure 3 shows low-energy gamma-ray spectra of the (a) LSD spike, (b) unknown dissolver solution, and (c) LSD-spiked (mixed) resin bead samples. The ²⁴⁰Pu/²³⁹Pu atomic ratios obtained from both IDGS and IDMS for LSD-spiked samples (part A) and for the dissolver solution sample (part B) are summarized in Table II. Columns 2 to 5 show the IDGS results for various dilution factors (X2, X4, X8, X16) of four LSD-spiked samples. Most data (ratios) shown are averages from two or three independent measurements. A few samples were contaminated by fission products during preparation in a hot glove box; data from these are not included in the averages. The direct interferences of the K x rays from fission products with the plutonium low-energy gamma rays will affect the accuracy of the measurement. Furthermore, the dramatically increased continuum background produced by higher energy gamma rays from fission products will reduce the precision of measurement. Figure 4 shows a comparison of the gamma-ray spectrum from a fission-product-contaminated resin bead sample (dotted spectrum) and the spectrum from the same sample after it was

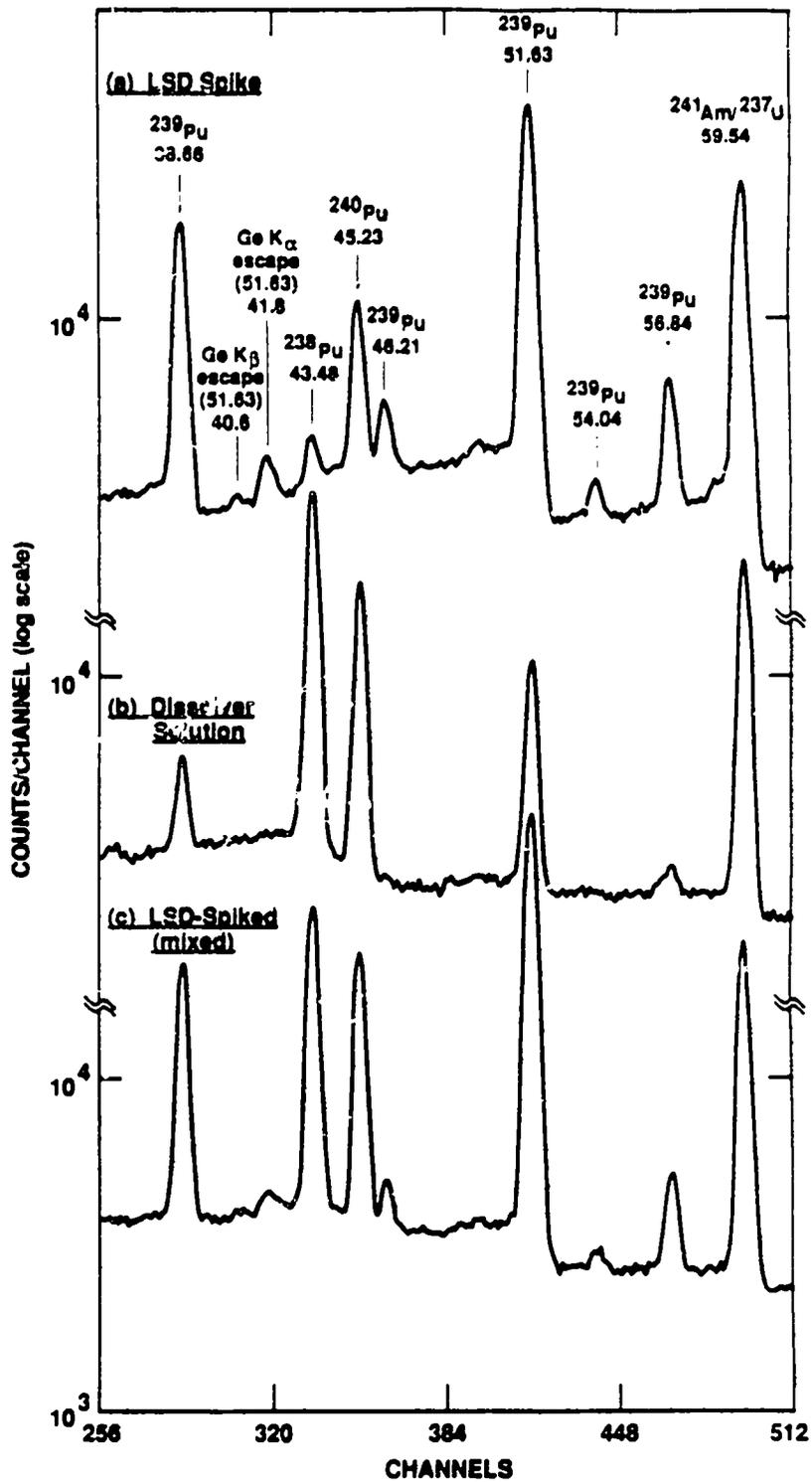


Fig. 3. Low-energy gamma-ray spectra of (a) LSD spike, (b) unknown dissolver solution, and (c) LSD-spiked (mixed) resin bead samples.

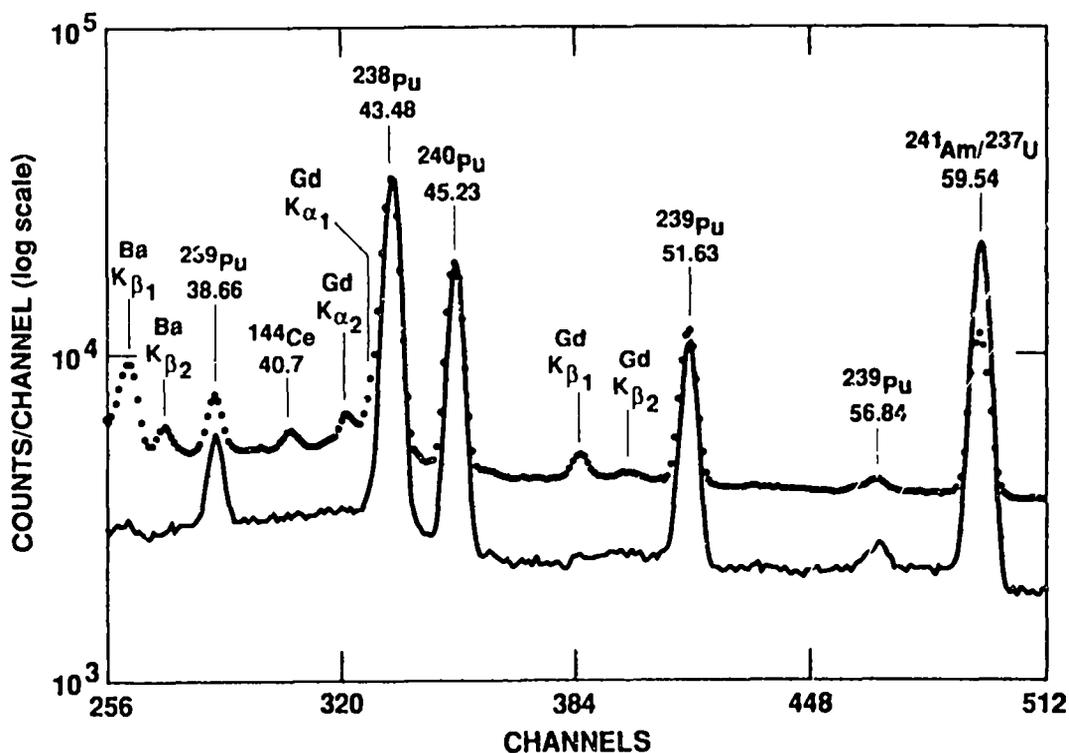


Fig. 4. Comparison of the low-energy gamma-ray spectrum from a fission-product-contaminated resin bead sample (dotted spectrum) and from the same sample after rewashing fission products.

rewashed to remove fission products. In Table II, the last column shows the ratio of the averaged $^{240}\text{Pu}/^{239}\text{Pu}$ ratio (column 6) obtained from IDGS for each LSD-spiked sample and the $^{240}\text{Pu}/^{239}\text{Pu}$ ratio obtained from IDMS (column 7). The average of the IDGS/IDMS ratio of $^{240}\text{Pu}/^{239}\text{Pu}$ is 0.9840 with a relative standard deviation (RSD) of 0.22%. The bias of 1.6% between the IDGS and IDMS results arises because the gamma-ray system has not been calibrated with this type of sample. It can probably be used as a calibration factor, which is affected by the relative efficiency determination, peak integration, background subtraction, branching ratios, and half-life selections. More measurements are needed to confirm this.

From Eq. (4), the total plutonium concentration of the unknown dissolver solution can be calculated by using measured $^{240}\text{Pu}/^{239}\text{Pu}$ values for the LSD-spiked solution (R_m) and for the dissolver solution (R_u) in Table II and certified values for W_s^g and $^{240}\text{Pu}/^{239}\text{Pu}$ (R_s) for the LSD spike from Table I. The volume of the dissolver solution is 0.9958 mL for each spiked sample. The mass of the LSD spike (M_s) taken is 4.5021 mg for LSD 1, 4.49898 mg for LSD 2, 4.48541 mg for LSD 3, and 4.49349 mg for LSD 4. The measured weight fraction of ^{239}Pu (W_u^g) in the dissolver solution is 0.66876 for IDMS and 0.657419 for IDGS. The results of the total plutonium concentrations

TABLE II. Comparison of the $^{240}\text{Pu}/^{239}\text{Pu}$ Ratio (wt%) by IDGS and IDMS

	$^{240}\text{Pu}/^{239}\text{Pu} (x10^{-3})$					IDMS	$\frac{\text{IDGS}}{\text{IDMS}}$
	IDGS				Average		
	x2	x4	x8	x16			
A. LSD							
LSD 1		60.320	60.591		60.456	61.613	0.9812
LSD 2	60.532	60.589	60.834		60.651	51.672	0.9834
LSD 3	60.033	61.137	61.036		61.069	61.937	0.9860
LSD 4		60.943	60.472	61.315	60.910	61.817	0.9853
Average							0.9840
RSD(%)							0.22
B. Dissolver Solution					333.4	336.552	0.9906

from IDGS and IDMS are compared in Table III. The average plutonium concentration obtained by IDGS agrees with that obtained by IDMS within 0.042% with an RSD of 0.384% (the last column in Table III). While the $^{240}\text{Pu}/^{239}\text{Pu}$ ratios show a slight bias between IDGS and IDMS, this excellent agreement for plutonium concentration may be because the systematic errors in the calibration factor were cancelled out in Eq. (4) when we calculated the concentration. Further examination is underway.

TABLE III. Comparison of Total Plutonium Concentration of Dissolver Solution by IDGS and IDMS

TOTAL PLUTONIUM CONCENTRATION (g/l)			
	<u>IDMS</u>	<u>IDGS</u>	<u>IDGS/IDMS</u>
LSD 1	0.97686	0.97242	0.99545
LSD 2	0.97782	0.97725	0.99942
LSD 3	0.98217	0.98610	1.00400
LSD 4	0.98062	0.98337	1.00281
Average			1.00042
RSD(%)			0.384

The estimated precision (1σ) for the $^{240}\text{Pu}/^{239}\text{Pu}$ ratio of the spiked sample, as a function of dilution factor and count time, is tabulated in Table IV. The count time, to give a better than 1% precision when measuring the $^{240}\text{Pu}/^{239}\text{Pu}$ ratio in the spiked sample, is about 1 h for the X2 dilution, 2 h for the X4 dilution, and 4 h for the X8 dilution. For rapid routine measurements, both X2 dilution and X4 dilution are recommended.

TABLE IV. Estimated Precision (%) for LSD-Spiked (Mixed) Samples

Dilution	$^{240}\text{Pu}/^{239}\text{Pu}$				
	1/2H	1H	2H	4H	10H
X2	1.3	0.9	0.6		
X4	1.8	1.2	0.8	0.6	
X8			1.4	1.0	
X16			4.1	3.0	2.1

V. CONCLUSIONS AND FUTURE WORK

The rapid and accurate IDGS technique may provide a prompt and useful verification of input and intermediate process plutonium samples, which is very important for near-real-time accounting at reprocessing plants. It is also a potential on-site verification method for International Atomic Energy Agency (IAEA) inspections. By implementing this new technique, the IAEA could significantly reduce the number of samples sent to Vienna for IDMS analysis. Although the results of the first IDGS measurement are very promising, further development work is underway to improve the gamma-ray analysis and resin bead preparation procedure. The improvements to gamma-ray analysis would include peak fitting, interpolation of background using a smoothed step function, and using an efficiency calibration for a defined sample-to-detector geometry. The improvements for the sample preparation would include reducing preparation time with a simplified procedure and reducing fission product contamination possibilities by using an automatic sample preparation system. Future experiments are planned using different plutonium concentrations in dissolver solutions and different spike-to-dissolver-solution ratios.

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