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AUTHOR(S) T. K. Li
Y. Kuno
S. Sato
J. L. Parker
A. Kurosawa
T. Akiyama

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Los Alamos National Laboratory
Los Alamos, New Mexico 87545

DEVELOPMENT OF ISOTOPE DILUTION GAMMA-RAY SPECTROMETRY FOR PLUTONIUM ANALYSIS*

T. K. Li,[a] Y. Kuno,[b] S. Sato[b] J. L. Parker,[a] A. Kuroswa,[b] and T. Ass...[b]
[a]Los Alamos National Laboratory
Los Alamos, NM 87545 USA

[b]Power Reactor and Nuclear Fuel Development Corporation
Tokai-mura, Ibaraki-Ken, Japan

Abstract

We are studying the feasibility of determining the plutonium concentration and isotopic distribution of highly radioactive, spent-fuel dissolver solutions by employing high-resolution gamma-ray spectrometry. The study involves gamma-ray plutonium isotopic analysis for both dissolver and spiked dissolver solution samples, after plutonium is eluted through an ion-exchange column and absorbed in a small resin bead bag. The spike is well characterized, dry plutonium containing ~98% of ^{239}Pu. By using measured isotopic information, the concentration of elemental plutonium in the dissolver solution can be determined. Both the plutonium concentration and the isotopic composition of the dissolver solution obtained from this study agree well with values obtained by traditional isotope dilution mass spectrometry (IDMS). Because it is rapid, easy to operate and maintain, and costs less, this new technique could be an alternative method to IDMS for input accountability and verification measurements in reprocessing plants.

1. Introduction

Isotope dilution mass spectrometry (IDMS) has long been the most accepted technique for determining the plutonium content of input spent-fuel dissolver solutions in reprocessing plants./1/ However IDMS is time consuming, sample preparation is lengthy, and the equipment and operation are costly. Recently, a hybrid K-edge and K x-ray fluorescence (XRF) densitometer for determining the uranium and plutonium element concentrations of dissolver solutions was developed at Kernforschungszentrum Karlsruhe./2/ However, the hybrid instrument does not measure isotopic compositions. To avoid IDMS's disadvantages but yet deliver acceptable measurement accuracy and precision, and to complement the hybrid K-edge/K-XRF measurement of plutonium concentration, we are developing a new technique—isotope dilution gamma-ray spectrometry (IDGS)—for simultaneously measuring the plutonium concentration and isotopic composition of highly radioactive fuel-dissolver solutions. IDGS is similar to IDMS except that the isotopic distributions of both unspiked (unknown dissolver solution) and spiked (by adding to the dissolver solution a spike of well-characterized plutonium) samples are measured by high-resolution gamma-ray spectrometry rather than mass spectrometry, and that sample preparation is simpler for IDGS. Gamma-ray measurements of highly radioactive dissolver solutions from reprocessing plants require rapid and efficient separation of plutonium from fission products and other actinides. A two step ion-exchange separation was developed to obtain satisfactory purification and recovery of plutonium for the IDGS measurement. Spectral analysis for the required full-energy peak areas and isotope ratios is accomplished by well-established methods. 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 reasons of cost and availability, ^{239}Pu is the best choice. Two proof-of-principle experiments have been carried out at the Tokai Reprocessing Plant. We used large-size dry (LSD) spikes of ^{239}Pu (97.9%), prepared by the International Atomic Energy Agency's (IAEA) Safeguards Analytical Laboratory (SAL), for our experiments./3/ Their certified isotopic compositions (in weight percent) are listed in Table I.

This paper describes IDGS measurement principles and the preparation of the resin bead sample, and discusses plutonium element concentrations and isotopic compositions of dissolver solutions obtained by IDGS.

2. Measurement Principles

Plutonium Isotopic Composition

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

$$R = \frac{N(m)}{N(n)} = \frac{A(a)}{A(b)} \cdot \frac{I(b)}{I(a)} \cdot \frac{T_{1/2}(m)}{T_{1/2}(n)} \cdot \frac{\varepsilon(b)}{\varepsilon(a)} \qquad (1)$$

where A = full-energy peak areas,
I = absolute emission probability 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.

TABLE I. Plutonium Isotopic Abundances (wt %) of LSD Spikes

Isotope	1st Experiment	2nd Experiment
^{238}Pu	0.0(a)24[a]	0.00...7
^{239}Pu	97.921	97.914
^{240}Pu	2.0604	2.0628
^{241}Pu	0.0141	0.0138
^{242}Pu	0.0032	0.0054

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Because of the small sample volumes containing less than 1 mg of plutonium, in these experiments, the isotopic ratios $^{238}Pu/^{239}Pu$, $^{239}Pu/^{239}Pu$, $^{240}Pu/^{239}Pu$, and $^{241}Pu/^{239}Pu$ are determined by measuring the high-intensity, low-energy gamma-ray ratios 43.48 keV/51.63 keV, 45.23 keV/51.63 keV, and 148.6 keV/129.3 keV, respectively [4,5]. The absolute ^{238}Pu, ^{239}Pu, ^{240}Pu, and ^{241}Pu fractions 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 [6], that work well for material from known reactor types. 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. The $\varepsilon(b)/\varepsilon(a)$ ratios are also determined from internal spectral information; the factors $[I(b)/I(a)]$ and $[T_{1/2}(m)/T_{1/2}(n)]$ are known and thus the R may be computed.

Total Concentration of Plutonium

By measuring the isotopic compositions of both unspiked and spiked dissolver solution samples, the concentration of plutonium in the unknown dissolver solution, C_u, can be determined. 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 the unspiked sample (dissolver solution), spike (LSD spike), and spiked sample (mixture of dissolver solution and LSD spike), respectively. Assuming first a mixture of spike solution and unknown solution, the weight fraction of isotope i in the spiked (mixed) samples is

$$W_m^i = \frac{W_s^i C_s V_s + W_u^i C_u V_u}{C_s V_s + C_u V_u} \qquad (2)$$

This is the basic isotope dilution relation. However, in applying the IDGS method to the plutonium concentration of dissolver solutions it is advantageous to work primarily in terms of *isotopic ratios*. The reason for this is that ^{242}Pu does not emit a usable gamma ray and its normally small fraction must be estimated by a correlation technique in order to convert the directly and accurately measured isotopic ratios to absolute fractions. Furthermore, when using ^{239}Pu as the spike we get optimal results when using the $^{240}Pu/^{239}Pu$ ratio. Thus, using $i = 0$ for ^{240}Pu and $i = 9$ for ^{239}Pu, we use Eq. (2) to write

$$\frac{W_m^i}{W_m^9} = \frac{W_s^i C_s V_s + W_u^i C_u V_u}{W_s^9 C_s V_s + W_u^9 C_u V_u} \qquad (3)$$

Solving for the plutonium concentration of the unknown dissolver solution, C_u, we obtain [7]

$$C_u = \frac{W_s^i}{W_u^i} \cdot \frac{W_s^9}{W_u^9} \cdot \frac{R_m - R_s}{R_u - R_m}$$

where W_s = Mass of plutonium in the spike,

$R_m = W_m^0/W_m^9$, the $^{240}Pu/^{239}Pu$ ratio in the spiked sample,

$R_s = W_s^0/W_s^9$, the $^{240}Pu/^{239}Pu$ ratio in the spike, and

$R_u = W_u^0/W_u^9$, the $^{240}Pu/^{239}Pu$ ratio in the dissolver solution sample.

In this equation, the values of W_s, W_s^9, R_s, and R_u are known. Therefore, only the values of R_u and W_u^9 in the unspiked dissolver-solution sample and R_m in the spiked sample need to be measured by gamma-ray spectrometry.

The precision and accuracy to be expected from IDGS measurements of C_u are obviously important. There is confidence that the random and systematic errors of W_s, R_u, W_s^9, and R_s are all <0.1%. Preliminary results indicate that the systematic error in C_u introduced by the gamma-ray spectrometric measurements of R_m, R_u, and W_s^9 is a small fraction of a percent. The random errors arising in the measurements of R_m, R_u, and W_s^9 will dominate the precision. An approximate expression, of reasonable accuracy, giving the relative standard deviation (RSD) of C_u in terms of the RSDs of R_m, R_u, and W_s^9 can be easily derived. R_u and W_s^9 are not fully independent statistically because of the way their values are extracted from the gamma-ray spectra, but they are "near independent." If we assume independence and propagate by usual methods we obtain

$$RSD^2(C_u) \cong \frac{R_m^2(R_u - R_s)^2}{(R_m - R_s)^2(R_u - R_m)^2} RSD^2(R_m) + \frac{R_u^2}{(R_u - R_m)^2} RSD^2(R_u) + RSD^2(W_s^9)$$

This expression is slightly conservative and quite accurate when compared to results of RSDs computed from replicate assays. The analysis routines that produce R_m, R_u, and W_s^9 also give good estimates of their RSDs for use in Eq. (5).

3. Resin Bead Sample Preparation

Two proof-of-principle experiments have been carried out at the Tokai Reprocessing Plant. Because IDGS measurements of highly radioactive dissolver solutions require rapid and efficient separation of plutonium from fission products and other actinides, we have developed a two-step ion-exchange method to purify and recover plutonium on resin beads. The procedure for preparing the resin bead sample is shown in Fig. 1 for the spiked sample (solid line) and the unspiked sample (dashed line). Spiked samples were prepared by mixing dissolver solutions (1 mℓ) with LSD spikes and then completely dissolving them at 90°C with 3 M HNO_3 (5 M HNO_3 and 0.01 M HF were used in the first experiment). After evaporation and redissolution with 8 M HNO_3, plutonium in spiked solutions was completely adjusted to tetra-valency with Fe(II) and $NaNO_2$. Because the dissolver solution used in the first experiment was over one month old, the valency was not adjusted. For each batch of dissolver solution, a 1 mℓ aliquot was also taken as an unspiked sample to be used for the plutonium isotopic composition measurement. Each spiked and unspiked sample was split into two or more subsamples. Each subsample was individually passed through the anion exchanger column (BIO-RAD AG-MP1 NO_3 form, 0.5 mℓ/5 mm ϕ), followed by washing with 8 M HNO_3 to remove fission products and americium and 3 M HNO_3 to remove

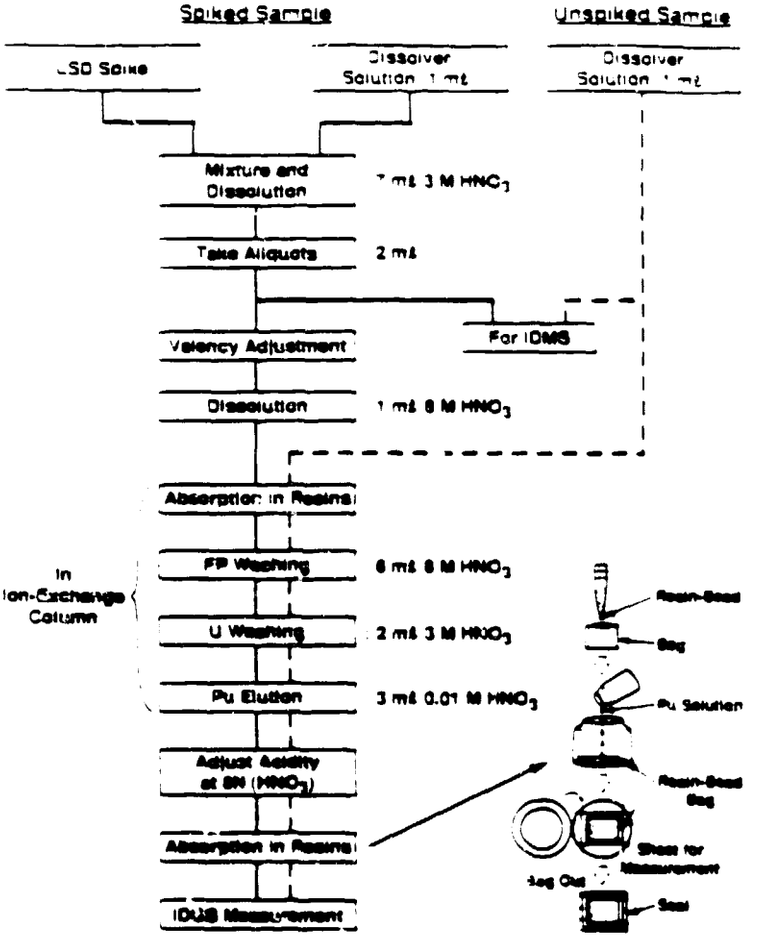

Fig. 1 The resin bead sample preparation procedure used in the second experiment for the spiked (solid line) and unspiked (dashed line) samples. This procedure is slightly different from the first experiment described in the text.

doubled the amount of 8 M HNO_3 solution used in the second experiment. Plutonium was eluted with 0.01 M HNO_3, the acidity was adjusted with 8 M HNO_3, and the plutonium was then absorbed on resin beads contained in small gauze bags. Each resin bead sample was placed in a plastic bag, removed from the glove box, and placed directly against the end cap of the high-purity germanium detector for gamma-ray 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 gamma measurement. It was, however, found that ruthenium, one of the major fission products, was hardly rinsed from the first stage of the ion separation. Therefore, the idea of plutonium elution-reabsorption mentioned above was adopted.

In the first experiment, we spiked four 1 mℓ samples of input dissolver solution from one batch with four LSD spikes. Each LSD spike contained ~4.5 mg of plutonium. In the second experiment, six spiked samples were made from three different batches of dissolver solution. Two 1 mℓ dissolver-solution samples from each batch were individually spiked to make six spiked samples. The mass of plutonium in each spike was ~2 mg. The spike-to-dissolver solution plutonium ratio changed from ~4:1 in the first experiment to ~2:1 in the second experiment to decrease the amount of spike used. In addition to plutonium masses, isotopic compositions of the spikes were also slightly different in the two experiments as shown in Table I.

4. Results and Discussion

Plutonium Isotopic Compositions

Figure 2 shows the low-energy gamma-ray spectra of (a) the pure LSD spike, (b) the unspiked (unknown) dissolver solution, and (c) the spiked dissolver solution from the first experiment. Notice the dramatic differences in gamma-ray intensities among the three samples. In the second experiment, gamma-ray peaks of ^{239}Pu (at 38.66 and 51.63 keV) are relatively smaller compared to gamma-ray peaks of ^{238}Pu (43.48 keV) and ^{240}Pu (45.23 keV) because of the smaller spike-to-dissolver solution ratio. Table II shows the gamma-ray plutonium isotopic compositions (in weight percent) for the dissolver solutions. All IDGS data shown are averages from two or three independent measurements of subsamples. A few subsamples of sample 1 in the first experiment were contaminated by fission products; data from these are not included in the averages. The K

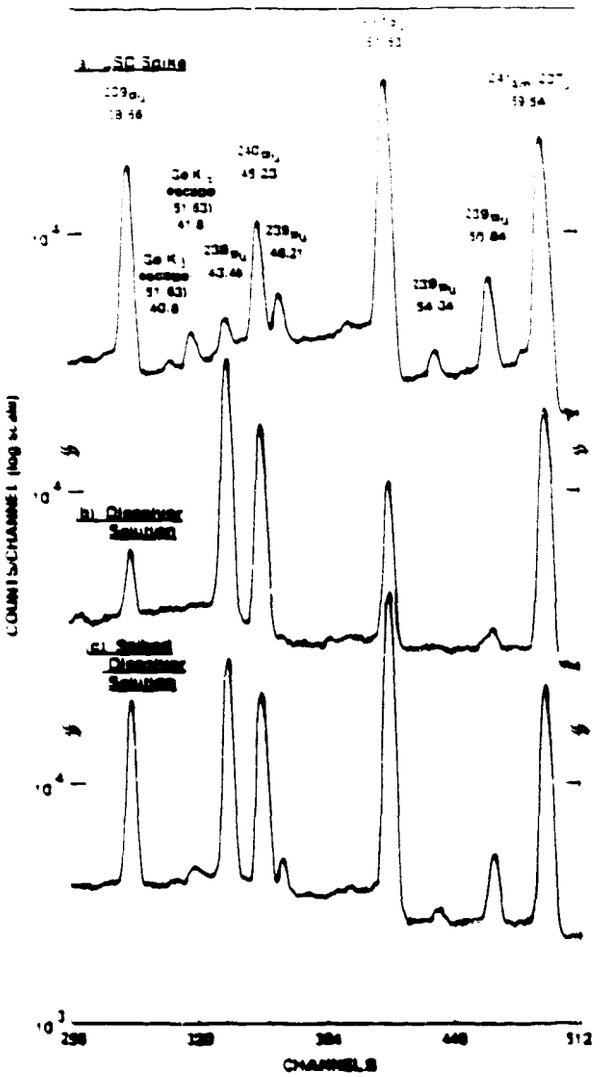

Fig. 2. Low-energy gamma-ray spectra of (a) pure LSD spike, (b) unspiked dissolver solution, and (c) spiked resin bead samples in the first experiment.

Table II. Plutonium Isotopic Abundances (wt %) of Dissolver Solutions as Determined by IDGS

Batch No.	^{238}Pu	^{239}Pu	^{240}Pu	^{241}Pu	^{242}Pu
1	1.30	56.68	27.02	9.62	5.18
2	1.50	56.63	27.14	9.56	5.18
3	1.53	58.22	25.13	10.25	4.87
4	1.55	56.63	26.75	9.83	5.25

x-rays from fission products directly interfere with the plutonium low-energy gamma rays to affect the accuracy of the measurement. Furthermore, the dramatically increased continuum background produced by higher energy gamma rays from fission products reduces the precision of measurement for a given counting time and geometry for the same mass of plutonium. Figure 3 shows a comparison of the low-energy gamma-ray spectrum from a fission-product-contaminated resin bead sample (dotted spectrum) with the spectrum from the same sample after it was rewashed to remove fission products. No low-energy gamma rays from fission products interfered in the second experiment (samples 2–4). This may be due to the double amount of 8 M HNO_3 solution used in the fission-product washings. However, some weak high-energy gamma rays from ruthenium that produce a higher continuum background were observed in spectra in both experiments. Figure 4 compares a dissolver solution spectrum with the higher continuum background with a pure LSD spike spectrum.

Table III(A) shows the comparison of the plutonium isotopic compositions of dissolver solution as determined by IDGS and IDMS. The agreement between IDGS and IDMS is generally good, especially so for the $^{240}Pu/^{239}Pu$ ratio (average IDGS/IDMS ratio is 0.993) and the weight percent of ^{239}Pu (average IDGS/IDMS ratio is 0.999), which are important for calculating the total plutonium concentration. Using Table III(B) we can compare the IDGS and IDMS plutonium isotopic measurements of the pure LSD spike used in the second experiment. The agreement between the IDGS method and the IDMS method is excellent except for ^{241}Pu, which has a very low fraction in the spike. Of course, gamma-ray measurements of the isotopic fractions in the spike need not be made, but were made in this case to increase confidence in the gamma-ray plutonium isotopic measurements.

Total Plutonium Concentration

From Eq. (4), the total plutonium element concentration of the unknown dissolver solution can be calculated by using measured $^{240}Pu/^{239}Pu$ values for the spiked solution (R_m) and for the unspiked dissolver solution (R_u), the measured weight percent of ^{239}Pu in the unspiked dissolver solution (W_u^9), and certified values for W_s^9 and $^{240}Pu/^{239}Pu$ in the LSD spike (R_s). The results of the plutonium element concentrations from IDGS and IDMS are compared in Table IV. The average IDGS/IDMS ratio is 1.0005 and the sample RSD of the average ratio is 0.12%, indicating that any bias between IDMS and IDGS methods is ≤0.2%. Because each of the 10 IDGS plutonium concentration values in Table IV was computed from the average isotope ratios from an unequal number of counts of varying times, the sample RSD of the 10 ratios just mentioned says little about the precision of single measurements. The precision will be a function of sample plutonium masses, detector efficiencies, count times, and isotopic distributions. For the 1000-mm^2 detector used, with ~0.5 mg of plutonium in the spiked samples and ~0.2 mg of plutonium in the unspiked samples (although less than 60% was trapped on the resin beads), and 100-min counts on both spiked and unspiked resin bead samples, Eq. (5) estimates the RSD of the random error to be ~1.2%. By optimizing the sample preparation and perhaps using somewhat larger samples of dissolver solution, the precision could be 1.0% for 1-h count times on both samples.

5. Conclusions

In summary, we have demonstrated for the first time the simultaneous determination of plutonium concentration and isotopic composition of spent nuclear-fuel dissolver solutions from a reprocessing plant by the IDGS technique

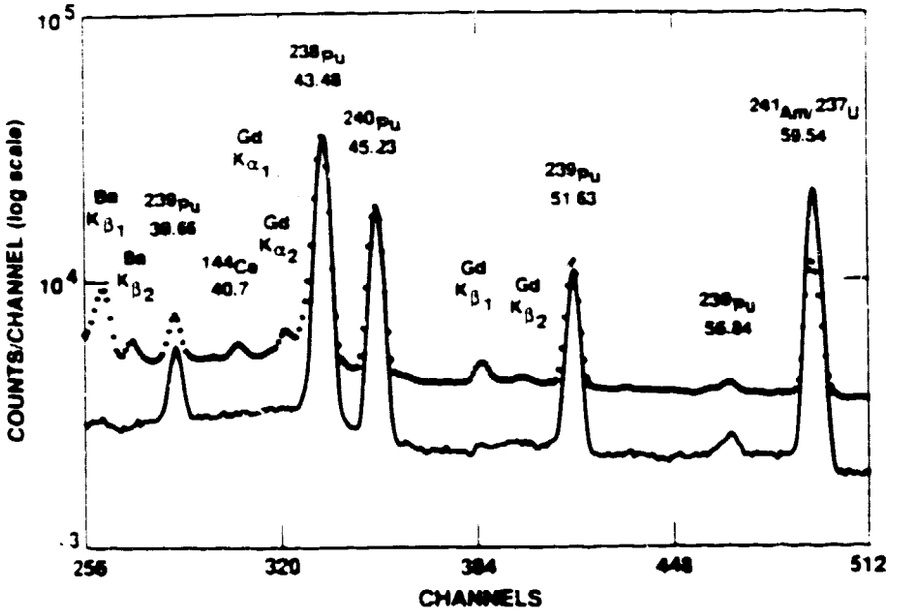

Fig 3 Comparison of the low-energy gamma-ray spectrum from a fission-product-contaminated, unspiked resin bead sample (dotted spectrum) and from the same sample after the fission products were washed again (solid spectrum)

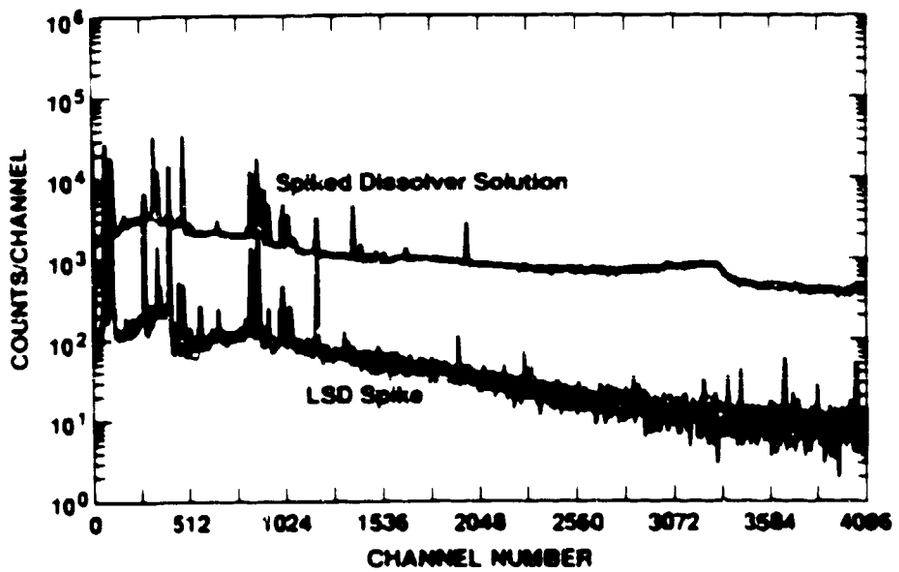

Fig 4 Comparison of continuum background in gamma-ray spectra of (a) LSD spike and (b) spiked dissolver solution resin bead samples

TABLE III Comparison of Plutonium Isotopic Abundances as Determined by IDGS and IDMS

Batch No	$^{238}Pu_2$	$^{239}Pu_2$	$^{241}Pu_2$	^{241}Pu	$^{242}Pu_2$	$^{240}Pu_2/^{239}Pu_2$
IDGS						
A Dissolver Solution						
1	1.149	0.997	0.993	1.003	1.029	0.995
2	1.152	0.996	0.997	0.996	1.028	1.000
3	1.123	1.005	0.989	1.013	0.950	0.984
4	1.125	0.997	0.991	1.007	1.034	0.994
Av	**1.137**	**0.999**	**0.993**	**1.005**	**1.010**	**0.993**
B LSD Spike						
	0.994	1.000	1.001	1.275	—	1.001

TABLE IV Comparison of Total Plutonium Concentrations of Dissolver Solutions as Determined by IDGS and IDMS

Sample	IDGS (g Pu/L)	IDMS (g Pu/L)	IDGS/IDMS
A First Experiment			
1	0.9702	0.9769	0.9931
2	0.9750	0.9778	0.9971
3	0.9838	0.9822	1.0016
4	0.9811	0.9806	1.0005
Average			0.9981
B Second Experiment			
5	1.2968	1.298	0.9991
6	1.2933	1.298	0.9964
7	1.3852	1.375	1.0074
8	1.3776	1.375	1.0019
9	1.2713	1.266	1.0042
10	1.2708	1.266	1.0038
Average			1.0021

Because IDGS is adequately accurate and precise, easy to operate and maintain, and costs less than IDMS, this new technique could be implemented as an alternative method for input accountability and verification measurements in reprocessing plants. It could also complement K-edge/K-XRF measurement of plutonium concentration by providing the isotopic distributions of dissolver solutions. In this case, because only dissolver solution is to be measured and analyzed, no spiked sample is involved. The IDGS technique may also provide useful accountability and verification information on intermediate process and hot-waste streams, which are important for near-real-time accounting at reprocessing plants.

IDGS could also be a potential on-site verification method for IAEA inspections. At present, spiked and unspiked aliquots from each dissolver batch are prepared by the plant operators and given to the inspectors for shipping to the SAL for IDMS analysis. The turnaround time in getting the results of these analyses is usually more than one month because of difficulties in shipping plutonium-bearing samples. A simple, prompt, verification analysis for each dissolver batch that could be done at reprocessing plants would be important. By implementing the IDGS technique for on-site verification, the IAEA and domestic inspectors could promptly detect anomalies and significantly reduce the number of samples sent to the SAL for IDMS analysis.

6. Acknowledgment

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