LA-UR-83-3386

CONF-831106--4

Los Alamos National Laboratory is operated by the University of California for the United States Department of Energy under contract W-7405-ENG-36

LA-UR--83-3386

DE84 003734

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SUBMITTED TO ANS/INMM Conference on Safeguards Technology: The Process-Safeguards Interface, Hilton Head Island, SC, November 28 - December 2, 1983.

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DETERMINATION OF PLUTONIUM ISOTOPIC RATIOS BY USING LOW-ENERGY GAMMA-RAY SPECTROSCOPY[a]

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ABSTRACT

A nondestructive gamma-ray technique has been developed to determine plutonium isotopic ratios. The technique is based on the high-intensity, low-energy gamma rays at 43.48, 45.23, 51.63, 59.54, and 64.83 keV for ^{238}Pu, ^{240}Pu, ^{239}Pu, ^{241}Am, and ^{241}Pu, respectively. The results demonstrate that this technique can accurately measure plutonium samples in a timely manner and in a wide range of masses, isotopic contents, chemical forms, and ages from chemical processing.

I. INTRODUCTION

Plutonium isotopic ratios can be determined by measuring selected close-lying gamma-ray pairs in different energy regions.[1-4] With this technique, small, high-purity germanium (HPGe) planar detectors (1 or 2 cm^2) have been utilized to analyze gamma-ray spectra in the 94- to 420-keV region and/or large coaxial germanium detectors (~70 cm^3) have been used to analyze gamma-ray spectra in the 300- to 670-keV region. In general, the technique can successfully determine the isotopic compositions of ^{238}Pu, ^{239}Pu, and ^{241}Pu within a few hours. However, the precision for ^{240}Pu measurements is 2 to 4% within ~14-h count time[3] for a plutonium sample mass >0.25 g, except in the complex 94- to 104-keV region[4] for solution samples.

It is important to both special nuclear material control and process control to improve the accuracy and precision of plutonium isotopic measurements, especially for ^{240}Pu. A study of these improvements was initiated by the Los Alamos Safeguards Assay Group. Our approach is to analyze the high-intensity, low-energy gamma rays at 43.48, 45.23, 51.63, 59.54, and 64.83 keV for ^{238}Pu, ^{240}Pu, ^{239}Pu, ^{241}Am, and ^{241}Pu, respectively. The 43.48-, 45.23-, and 51.63-keV gamma rays become difficult to analyze in aged samples because of strong interference from the Compton continuum of the very intense 59.54-keV gamma rays from ^{241}Am and/or ^{237}U. Therefore, these low-energy regions have not been used previously for nondestructive assay plutonium isotopic composition, except for freshly separated solutions.[5-6] However, this difficulty can be diminished by careful selection of a detector with the proper combination of resolution, efficiency, and peak-to-Compton ratio at energies below 60 keV. Details of the selection of such a detector are described in Sec. III. We also discuss the measurement method and the results obtained by using low-energy gamma rays for nondestructive assay of plutonium samples in a wide range of masses, isotopic contents, and chemical forms.

II. MEASUREMENT METHOD

The measurement method has been briefly discussed in Ref. 7. In general, the plutonium isotopic ratio N(m)/N(n) of two isotopes m and n can be determined by measuring their selected gamma rays a and b, respectively.

$$\frac{N(m)}{N(n)} = \frac{R(a)}{R(b)} \cdot \frac{I(b)}{I(a)} \cdot \frac{t(m)}{t(n)} \cdot \frac{\epsilon(b)}{\epsilon(a)} , \qquad (1)$$

where

R = measured count rate of gamma rays,
I = absolute branching intensity of gamma rays,
t = half-life of isotope, and
ϵ = relative efficiency of selected gamma rays, including detector intrinsic efficiency, counting geometry, attenuation, and sample self-attenuation.

The isotopic ratios of ^{238}Pu, ^{239}Pu, ^{240}Pu, and ^{241}Am are determined by using gamma rays at 43.48, 51.63, 45.23, and 59.54 keV, respectively. The $^{241}Pu/^{239}Pu$ ratios are measured by

[a]Work supported by the US Department of Energy, Office of Safeguards and Security.

64.83 keV/51.63 keV for ^{241}Pu-^{237}U equilibrium samples (>45 days from uranium separation) and by 148.6 keV/129.3 keV for nonequilibrium samples.

Relative efficiency (ϵ) variations arising from sample self-absorption, detector efficiency, and external absorbers are calculated by using known efficiency points from ^{239}Pu gamma rays at energies (E) 38.66, 51.63, 68.72, 129.3, 144.2, 171.3, 195.7, and 203.5 keV. A simple linear $\ln \epsilon$ vs $\ln E$ interpolation between two relative efficiency points at 38.66 and 51.63 keV is used to calculate the relative efficiencies at 43.48 and 45.23 keV; interpolation between two relative efficiency points at 51.63 and 68.72 keV is used to calculate the relative efficiencies at 59.54 and 64.83 keV. The relative 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.

All gamma-ray net peak areas are calculated by using a channel-by-channel summation with straight-line background-subtraction method. The background is determined from carefully selected regions on both sides of the full energy peak. No peak-fitting routine is employed. Minor interferences in the full energy peaks are taken into account. The isotopic half-lives and the gamma-ray branching intensities are taken from Refs. 1 and 8, respectively.

The $^{233}Pu/^{239}Pu$ ratio is determined by analyzing the 43.48 keV/51.63 keV gamma-ray ratio. In addition to small interferences from ^{237}U (at 43.43 keV) and ^{241}Pu (at 44.20 keV), a strong interference from ^{241}Am at 43.37 keV[9] must be subtracted from the 43.48-keV peak for determining ^{238}Pu content. The ratio is given by

$$\frac{^{238}Pu}{^{239}Pu} = \frac{A(43)}{A(51)} \times 2.494 \times 10^{-3} - \frac{A(59)}{A(51)} \times 4.94 \times 10^{-6} - \frac{A(64)}{A(51)} \times 2.41 \times 10^{-4} , \quad (2)$$

where

$A(a) = R(a)/\epsilon(a)$ (efficiency-corrected count rate of gamma ray).

The $^{240}Pu/^{239}Pu$ ratio is determined by analyzing 45.23 keV (^{240}Pu) and 51.61 keV (^{239}Pu) gamma rays. If the weak interference of ^{241}Pu (44.86 keV) to 45.23 keV is ignored, the ratio can be expressed by

$$\frac{^{240}Pu}{^{239}Pu} = \frac{A(45)}{A(51)} \times 0.1625 \quad (3)$$

The $^{241}Pu/^{239}Pu$ ratio is determined by 64.83 keV/51.63 keV for ^{241}Pu-^{237}U equilibrium samples (>45 days from uranium separation) and by 148.6 keV/129.3 keV for nonequilibrium samples. It is given by

$$\frac{^{241}Pu}{^{239}Pu}\ (\text{equilibrium sample}) = \frac{A(64)}{A(51)} \times 0.507 \quad (4)$$

$$\frac{^{241}Pu}{^{239}Pu}\ (\text{nonequilibrium sample}) = \frac{A(148)}{A(129)} \times 0.0201 . \quad (5)$$

We also measured the $^{241}Am/^{239}Pu$ ratio by the 59.54 keV/51.65 keV ratio. After the contribution from ^{237}U has been taken into account, the ratio is expressed by

$$\frac{^{241}Am}{^{239}Pu} = \frac{A(59)}{A(51)} \times 1.367 \times 10^{-5} - \frac{A(64)}{A(51)} \times 3.62 \times 10^{-4} . \quad (6)$$

III. THE DETECTOR AND THE SYSTEM

To select a germanium detector with the proper combination of resolution, efficiency, and peak-to-Compton ratio at energies below 60 keV, we tested five types of detectors with active volumes varying from 1 to 70 cm^3. Figure 1 shows the low-energy (38- to 60-keV) gamma-ray spectra of a 600-μg Pu sample from various types of detectors with a 20-ks count time. Although the small HPGe planar (SGP) detector (1 cm^3 in volume) shows the best resolution and peak-to-Compton ratio, its efficiency is too low. On the other hand, the N-type coaxial (NTC) detector (49 cm^3 in volume) has the highest efficiency but the lowest resolution. The large HPGe coaxial (LGC, 75 cm^3 in volume) and medium HPGe coaxial (MGC, 41 cm^3 in volume) have poor resolutions, efficiencies, and peak-to-Compton ratios. The large HPGe planar (LGP) detector (10 cm^3 in volume) has the best combination of the resolution, efficiency, and peak-to-Compton ratio. Table I summarizes the

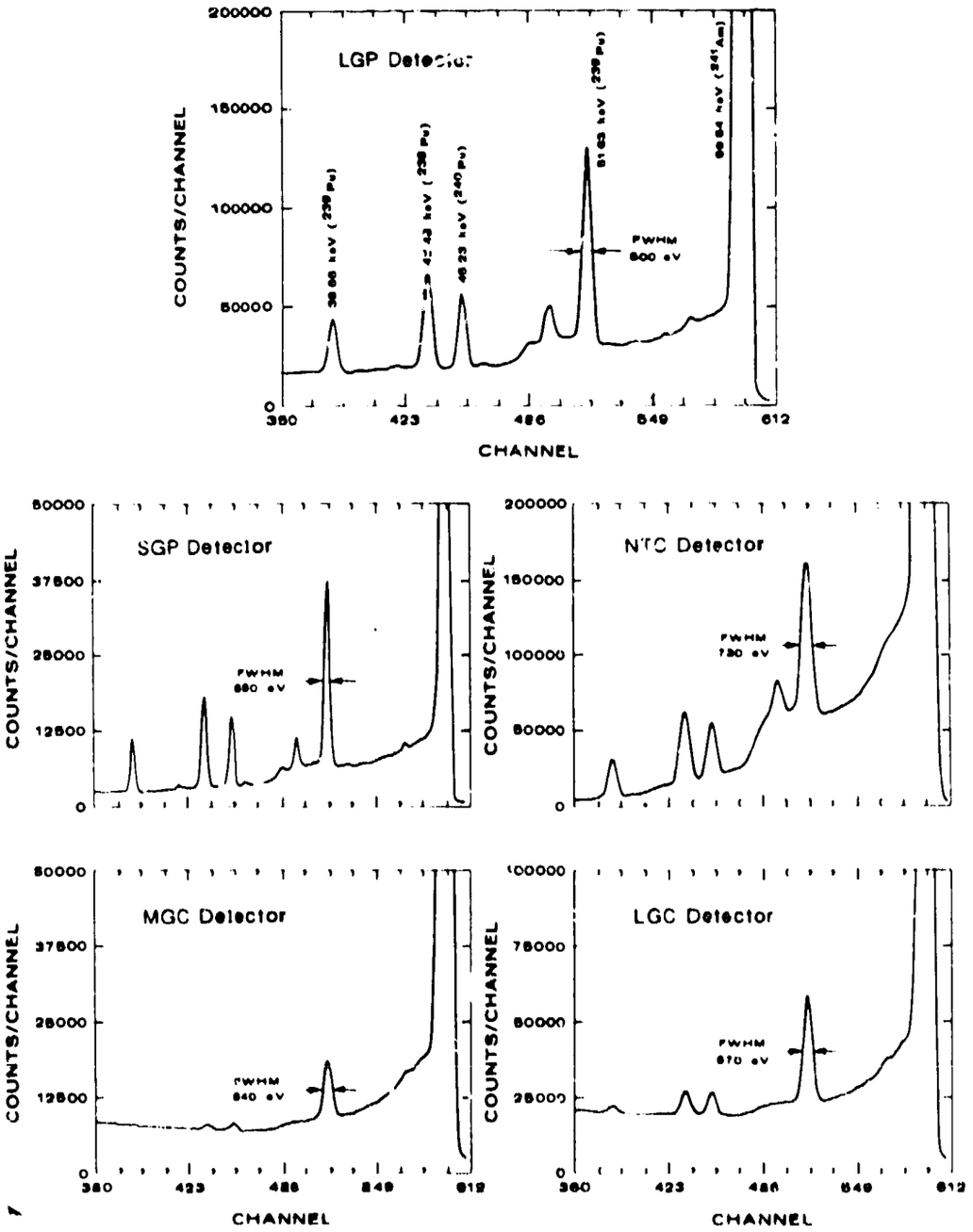

Fig. 1. Low-energy (38- to 60-keV) gamma-ray spectra from various types of detectors for a 70-ks count time.

TABLE I

COMPARISON OF DETECTOR RESOLUTIONS AND PRECISIONS FOR ISOTOPIC RATIOS FROM VARIOUS TYPES OF DETECTORS

DETECTOR	TYPE	SIZE	VOLUME (CM^3)	RESOLUTION (FWHM) AT 51.63 KEV (EV)	ESTIMATED PRECISION (1σ)[A] $^{238}Pu/^{239}Pu$	$^{240}Pu/^{239}Pu$
SGP	PLANAR	100 MM^2 X 10 MM	1	390	0.80	1.02
LGP	PLANAR	1000 MM^2 X 10 MM	10	510	0.40	0.56
MGC	COAXIAL	37.5-MM DIAM X 29 MM	43	640	21.	18.
NTC	N-TYPE COAXIAL	42.3-MM DIAM X 35 MM	49	730	0.48	0.58
LGC	COAXIAL	49-MM DIAM X 39 MM	75	670	4.0%	4.22

[A]PRECISION (1σ) ARE ESTIMATED FROM COUNTING STATISTICS WITHOUT INCLUDING UNCERTAINTIES FROM RELATIVE EFFICIENCIES.

detector types, sizes, and resolutions, and the precision of the isotopic ratios from these detectors. With a 20-ks count time, the best estimated precisions (1σ) of 0.4% and 0.56% for $^{238}Pu/^{239}Pu$ and $^{240}Pu/^{239}Pu$ ratios, respectively, were also obtained by the LGP detector. Based on these results, we chose the LGP detector to measure plutonium isotopic ratios by using low-energy gamma-ray spectra. A 2.2-mm-thick aluminum filter was installed in the front of the detector to minimize sum peak interferences that result from pileups of L x-rays and 26.34-keV gamma rays (^{241}Am and ^{237}U).

The system also consists of a Canberra Series 80 multichannel analyzer (MCA), including an 8-k channel analog-to-digital converter (ADC), and an LSI-11/23 microcomputer and peripherals. A pair of Canberra 8200 stabilizers maintains the energy calibration. The zero and gain stabilization peaks are the 51.63- and 129.3-keV gamma rays from ^{239}Pu. The MCA is controlled by the LSI-11/23 microcomputer, which has 32-k 16-bit words of memory and is a processor for data acquisition, reduction, and analysis. A Winchester/floppy disk system (DSD-880) provides for storage and transfer of the program and data. The control of sample input and output is accomplished through an LA-120 Decwriter. An automatic data-acquisition and -analysis program is written in FORTRAN under Digital Equipment Corporation's RT-11 V-4.0 operating system.

IV. RESULTS AND DISCUSSION

Using the LGP type detector, we analyzed aged samples (see Table II) in several chemical forms with variable isotopic contents (82 to 98% ^{239}Pu) ranging in mass from 10 μg to 4 g Pu with americium contents up to 3390 μg Am/g Pu. Table III compares the preliminary low-energy gamma-ray spectroscopy results for 20-ks count times with mass spectrometry (^{238}Pu and ^{241}Am determined by radioanalysis) results. The average of isotopic ratios of 10 samples measured by gamma-ray spectroscopy shows negligible bias as compared with mass spectrometry and radioanalysis. The 1.4% standard deviation of $^{240}Pu/^{239}Pu$ indicates the overall precision of low-energy gamma-ray measurements in these wide ranges of plutonium mass, isotopic distribution, and Am/Pu ratio. The larger standard deviation of 6.3% in $^{241}Pu/^{239}Pu$ is due to the lower intensity of 64.8-keV gamma rays and the low ^{241}Pu isotopic abundances in some samples (Table II). The 4.6% and 5.6% standard deviations of $^{238}Pu/^{239}Pu$ and $^{241}Am/^{239}Pu$, respectively, may reflect the uncertainties of radioanalysis.

The estimated precisions (1σ) of gamma-ray spectroscopy in Table IV are calculated from counting statistics, including uncertainties from relative efficiencies. Obviously, the precision obtained from the gamma-ray technique is affected by counting statistics of the full energy peaks, which is in turn a function of sample mass, isotopic distribution, and Am/Pu ratio. For example, the uncertainties in sample MS 10 are expected to be large because of the very small sample mass (~10 μg) and high Am/Pu ratio of 3390 ppm; and the precision in the $^{241}Pu/^{239}Pu$ ratio of sample ST 151 is expected to be poor because of the very low ^{241}Pu abundance of 0.0199 in wt%. In Table IV, the estimated precision from low-energy gamma-ray spectroscopy (first column of each isotopic ratio) is compared with those from higher energy gamma-ray spectroscopy (120-160

TABLE II

ISOTOPIC DISTRIBUTION IN WEIGHT PERCENT

SAMPLE	CHEMICAL FORM	^{238}Pu	^{239}Pu	^{240}Pu	^{241}Pu	^{241}Am (ug/g Pu)
MS 10	FLUORIDE	0.118	83.81	6.64	0.519	3390
MS 30	FLUORIDE	0.0467	87.32	11.40	0.943	96
MS 600	FLUORIDE	0.1219	83.42	6.01	0.457	372
ST 121	OXIDE	0.0626	81.73	16.45	1.406	1864
ST 119	OXIDE	0.0388	87.08	11.76	0.952	2220
ST 151	OXIDE	0.00236	97.97	2.01	0.019	40
SOL 01	NITRATE SOLUTION	0.0166	93.38	6.19	0.348	165
SOL 05	NITRATE SOLUTION	0.0692	84.35	14.04	1.253	1514
SOL 06	NITRATE SOLUTION	0.0627	81.73	16.45	1.408	1800
JT 002	METAL	0.020	93.77	5.94	0.240	838

TABLE III

COMPARISON OF ISOTOPIC RATIOS
BY G[illegible]-RAY SPECTROSCOPY WITH MASS SPECTROMETRY

SAMPLE	PU MASS	AM/PU (PPM)	^{240}Pu (WT%)	RATIO: GAMMA SPECTROSCOPY / MASS SPECTROMETRY[A] $^{238}Pu/^{239}Pu$	$^{240}Pu/^{239}Pu$	$^{241}Pu/^{239}Pu$	$^{241}Am/^{239}Pu$
SOLID							
MS 10	10 mg	3390	6.64	0.941	1.038	1.0[illegible]	--
MS 30	30 mg	96	11.40	1.002	0.997	0.967	--
MS 600	600 mg	372	6.01	0.952	1.001	0.999	--
ST 121	4 g	1864	16.45	0.984	1.005	0.991	0.993
ST 119	1.72 g	2220	11.76	1.082	1.008	0.930	0.927
ST 151	2.65 g	40	2.01	1.041	0.933	1.082	0.936
SOLUTION							
SOL 01	0.2 g	166	6.19	1.067	0.997	1.107	1.051
SOL 05	0.2 g	1514	14.04	0.990	0.989	0.929	1.017
SOL 06	0.2 g	1800	16.45	0.997	1.009	1.043	1.065
METAL							
JT 02	2.58 g	838	5.94	0.983	0.991	0.947	1.048
AVERAGE				1.004	1.003	1.003	1.005
STANDARD DEVIATION				0.046	0.014	0.063	0.056

[A] PLUTONIUM 238 AND ^{241}Am DETERMINATION BY RADIOANALYSIS.

TABLE IV

ESTIMATED PRECISION (1σ, IN %)
OF GAMMA-RAY SPECTROSCOPY

SAMPLE	Pu MASS	$^{238}Pu/^{239}Pu$ 43.5/ 51.6	152.7/ 129.3	$^{240}Pu/^{239}Pu$ 45.2/ 51.6	160.3/ 129.3	$^{241}Pu/^{239}Pu$ 64.8/ 51.6	148.6/ 129.3	$^{241}Am/^{239}Pu$ 59.5/ 51.6	125.3/ 129.3
MS 30	30 µg	3.3	37.8	1.6	36.8	13.0	21.5	6.3	39.0
MS 600	600 µg	0.6	10.0	0.7	13.0	5.2	7.3	1.3	8.4
SOL 05	0.2 g	1.5	14.1	1.1	18.9	4.5	9.7	1.9	3.6
ST 121	4 g	3.6	9.6	2.5	10.0	6.1	6.4	2.6	9.1

keV) with a 20-ks counting time. The estimated precisions obtained from the low-energy region are much better than those from higher energy region for all isotopic ratios within the plutonium mass range from 30 µg to 4 g. However, the $^{241}Pu/^{239}Pu$ precision of the higher energy region is improved as the plutonium mass increases. Therefore, a weighted average of low- and high-energy gamma-ray measurement should give a better result for $^{241}Pu/^{239}Pu$ ratio.

In summary, the ratios determined by the low-energy gamma-ray spectroscopy agree very well with those determined by mass spectrometry and radiosnalysis. The precisions of the isotopic ratios, especially $^{240}Pu/^{239}Pu$ and $^{238}Pu/^{239}Pu$, obtained by this technique are better than those obtained from traditional high-energy regions[3] (120 to 670 keV) for aged samples and are comparable with those obtained from the 94- to 104-keV region[4] for solution samples. These results demonstrate that the present plutonium isotopic analysis technique can measure moderately aged plutonium samples in a wide range of masses, isotopic contents, and chemical forms. Furthermore, because of its sensitivity in measuring samples in the microgram mass range, this technique may be ideal for measurement of resin beads of the kind used by the IAEA before shipment to Vienna. A study of this possible application is under way.

ACKNOWLEDGMENTS

I thank S. Johnson for computer programming, and J. L. Parker and T. Sampson for discussions.

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