LEGIBILITY NOTICE

A major purpose of the Technical Information Center is to provide the broadest dissemination possible of information contained in DOE's Research and Development Reports to business, industry, the academic community, and federal, state and local governments.

Although portions of this report are not reproducible, it is being made available in microfiche to facilitate the availability of those parts of the document which are legible.

3

LA-UR -87-2293

CONF-8707113--34

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

TITLE: A STUDY OF IN-LINE PLUTONIUM ISOTOPIC ANALYSIS FOR GASEOUS PLUTONIUM HEXAFLUORIDE

LA-UR--87-2293

DE87 013145

AUTHOR(S): T. K. Li

SUBMITTED TO Institute of Nuclear Materials Management
Los Angeles, California
July 12-15, 1987
(Full Paper)

MASTER

Los Alamos Los Alamos National Laboratory
Los Alamos, New Mexico 87545

FORM NO. 836 R4
ST. NO. 2629 5/81

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

A STUDY OF IN-LINE PLUTONIUM ISOTOPIC ANALYSIS FOR GASEOUS PLUTONIUM HEXAFLUORIDE

T. K. Li
Los Alamos National Laboratory
Los Alamos, NM 87545 USA

ABSTRACT

In-line plutonium isotopic analysis of gaseous plutonium hexafluoride (PuF_6) is very important for process control and special nuclear material accountability in any plutonium-isotope-separation process that requires a gaseous phase. Although much effort had been devoted to analyze arbitrary plutonium samples, no isotopic analysis had been done on gaseous PuF_6 samples. We have initiated a study on the use of a high-resolution, gamma-ray spectroscopy technique to analyze gaseous plutonium hexafluoride. For the first time, PuF_6 gas samples with pressures varying from 0.15 to 31 torr, which were directly fed into a gas cell from a process flow loop, were measured. The isotopic results of these measurements agree very well with those of mass spectrometry measurements of solid PuF_4. The precision of a 10-min measurement of a 10-torr reactor-grade PuF_6 is 1.5% for ^{238}Pu, 0.22% for ^{239}Pu, 0.87% for ^{240}Pu, and 17.5% for ^{241}Pu.

INTRODUCTION

The Los Alamos Special Isotope Separation (SIS) Facility is designed to demonstrate the first large-scale separation of plutonium isotopes by using the molecular laser isotope-separation (MLIS) process to produce special isotopes and to convert plutonium scrap and waste. The MLIS process[1] separates specific plutonium isotopes from gaseous plutonium hexafluoride (PuF_6) using two types of lasers. The PuF_6 gas, prepared from reacting plutonium tetrafluoride (PuF_4) with fluorine, is mixed with an inert carrier gas. The mixture is cooled through a supersonic nozzle to lower its energy. The first laser irradiates the gas and is tuned to excite a specific isotope in the PuF_6 molecules. Another laser then dissociates the excited PuF_6 to form PuF_4 in a solid form, which is collected on a series of filters.

In-line isotopic analysis for gaseous PuF_6 is very important for process development, process control, and special nuclear material accountability in any isotope-separation process that requires plutonium in a gaseous phase. Although much effort has been devoted to analyse arbitrary (solid and solution) samples, no isotopic analysis has been done previously on gaseous PuF_6 samples. We have initiated a study of an in-line nondestructive technique to measure PuF_6 gas from the MLIS process flow loop. In this paper we report on the first analysis of plutonium isotopic compositions in gaseous PuF_6.

MEASUREMENT METHOD

The measurement method is based on high-resolution, low-energy gamma-ray spectroscopy techniques similar to those described in Refs. 2-4. In general, the 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.

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

where

- R = 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 $^{238}Pu/^{239}Pu$, $^{240}Pu/^{239}Pu$, and $^{241}Pu/^{239}Pu$ are determined by analysing 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.[5] 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 by using the quotient of the measured peak areas and their known specific activities of the selected ^{239}Pu gamma rays in the sample. A simple linear $\ln \varepsilon$ 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. A similar interpolation between 51.63 and 68.72 keV is used to calculate the relative efficiency at 59.54 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 measurement system consists of a high-resolution hyperpure germanium planar detector and associated electronics, 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. A two-point digital stabilizer locked to the 51.63- and 129.3-keV gamma rays from ^{239}Pu is used to maintain the energy calibration. 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. The data acquisition and analysis program is written in FORTRAN under DEC's RT-11 V-5.02 operating system in the extended memory environment.

The detector has dimensions of 1000 mm^2 by 13 mm and a resolution (full width at half maximum) of 560 eV at 122 keV. It is located outside the glove box directly under the gas sample cell, which is separated from the detector by a 3.2-mm thick by 17.3-cm-diam polycarbonate window. The cell is a right circular aluminum cylinder (~76 cm^2 by 6.4 cm) with a 1.6-mm-thick window facing the detector. It is installed in a sample chamber that provides a minimum of 5 cm of lead shielding to prevent the detection of gamma rays from extraneous plutonium in the vicinity. Two valves control the flow of PuF_6 gas through the cell.

RESULTS AND DISCUSSION

To study the sensitivity in measuring a gaseous sample using this low energy gamma-ray technique, we measured PuF_6 feed gaseous samples with plutonium pressures varying from 0.15 to 31 torr that were directly fed into the gas cell from the process flow loop. Plutonium isotopic distributions of a typical reactor-grade PuF_6 feed gaseous samples are listed in Table I. In Fig. 1, the estimated precision (1σ) of plutonium isotopes for 10-min measurements are plotted as a function of PuF_6 partial pressure in torr (bottom horizontal scale) and as a function of plutonium mass in milligrams (top horizontal scale). The estimated precisions (solid circles for ^{238}Pu, open triangles for ^{239}Pu, solid squares for ^{240}Pu, and open circles for ^{241}Pu) are calculated from counting statistics, including uncertainties from

TABLE I

ISOTOPIC DISTRIBUTIONS (in wt%) OF PuF_6 FEED GASEOUS SAMPLE

Isotope	Weight Percent
^{238}Pu	0.059
^{239}Pu	87.32
^{240}Pu	11.50
^{241}Pu	0.916
^{242}Pu	0.202

relative efficiencies and background run. Typically, within a 10-min count time, the precisions for a 10-torr PuF_6 sample are 1.5% for ^{238}Pu, 0.22% for ^{239}Pu, 0.87% for ^{240}Pu, and 17.5% for ^{241}Pu. The larger uncertainty of ^{241}Pu is due to the low quantity in the samples and the larger uncertainty of relative efficiency at 148.6 keV, which is determined by the efficiency points at lower gamma-ray intensities from 129.3 keV to 203.5 keV.

A typical relative efficiency curve for a 135-mg PuF_6 gaseous sample is compared to that from a 25-mg PuF_4 solid sample in Fig. 2. For gamma-ray energy above 100 keV, the relative efficiency curves are similar. However, the relative efficiency of the PuF_4 solid sample decreases steeply as energy decreases at lower gamma-ray energies. This shows that the effect of sample self-attenuation on the PuF_6 gas is very small as compared to that of the solid PuF_4.

In addition to sample mass, PuF_6 partial pressure, isotopic distribution, and Am/Pu ratio, the precision obtained from gamma-ray techniques is also affected by count time. Figure 3 shows that the precision (1σ) obtained for a 85-mg (~11 torr) PuF_6 sample for count time from 1 min to 240 min. The curves indicate estimated precision and data points indicate measured precision. The measured precisions are obtained from 15 repeated runs. The measured precisions appear to be better than the estimated precisions. This is because the same background data have been used for 15 repeated runs. In this case, every run of the 15 subtracts a constant background. By using different background runs for every measurement, especially when background is high, one may expect that the measured precision agrees well with estimated precision. Background is slowly increased from decomposed PuF_4 deposited on the inner surface of the aluminum gas sample cell. For a 85-mg PuF_6 sample in the gas cell, we demonstrate that one can expect better than 1% precision within 20 s for ^{239}Pu, 7 min for ^{240}Pu, and 25 min for ^{238}Pu. The rapid plutonium isotopic analysis for a PuF_6 gas development sample is very valuable for process development and process control.

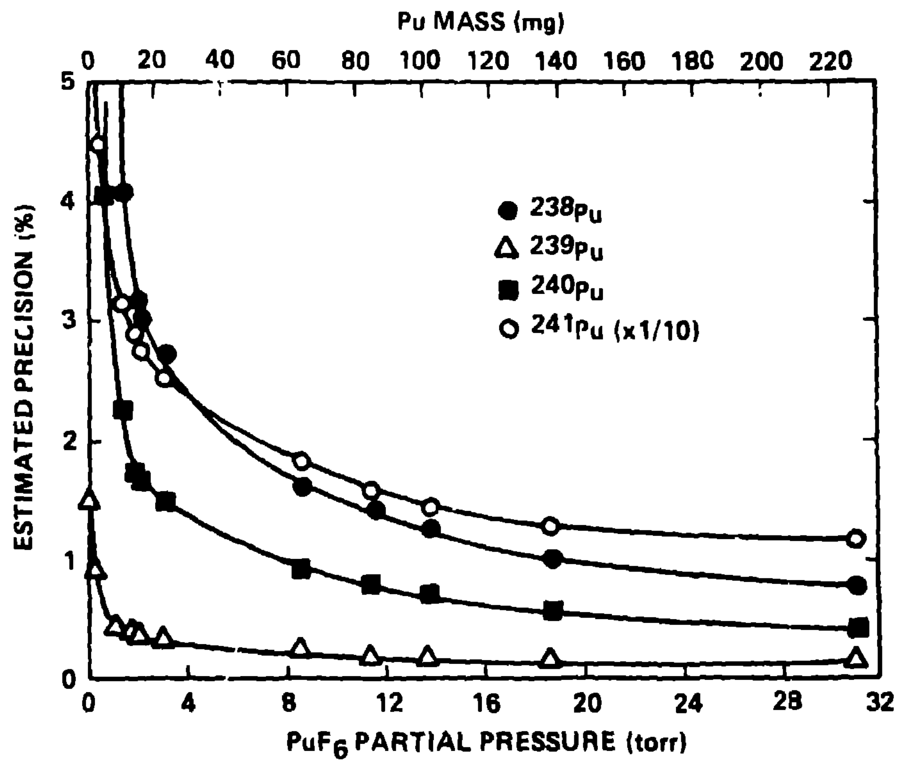

Fig. 1. Estimated precisions (1σ) of plutonium isotopes for 10-min measurements are plotted as a function of PuF_6 partial pressure in torr (bottom horizontal scale) and as a function of plutonium mass in milligrams (top horizontal scale). The solid circles are for ^{238}Pu, the open triangles are for ^{239}Pu, the solid squares are for ^{240}Pu, and the open circles are for ^{241}Pu.

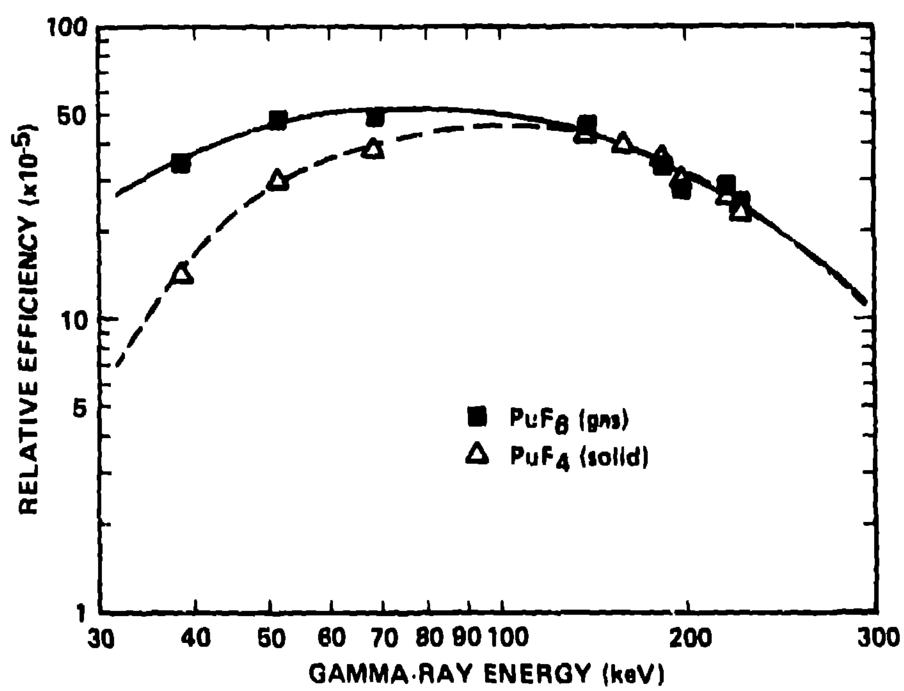

Fig. 2. Typical relative efficiency curves for PuF_6 gaseous and PuF_4 solid samples.

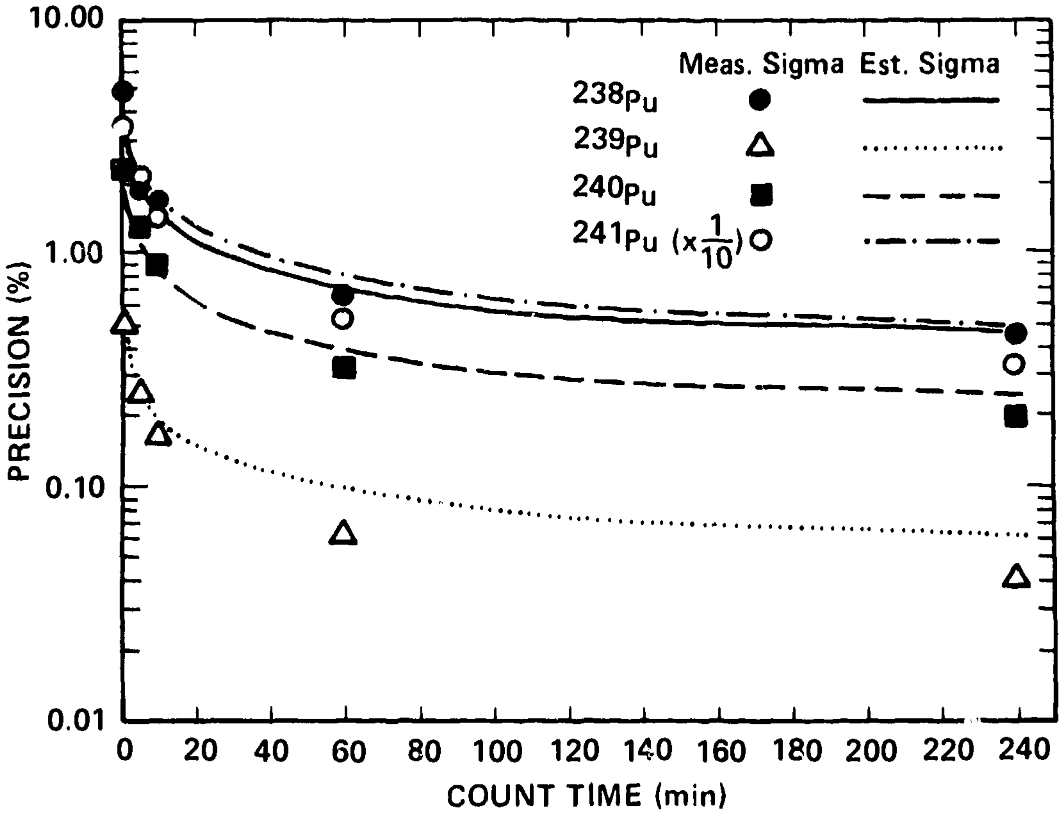

Fig. 3. The precision (1σ) of plutonium isotopes on a 85-mg (~11 torr) PuF_6 sample as a function of count time (min). The curves indicate estimated precisions and data points indicate measured precisions. The measured precisions are obtained from 15 repeated runs. The solid curve and solid circles are for ^{238}Pu, the dotted curve and open triangles are for ^{239}Pu, the dashed curve and solid squares are for ^{240}Pu, and the dashed- dotted curves and open circles are for ^{241}Pu.

To evaluate accuracy, three samples with different isotopic compositions and PuF_6 gas pressures were decomposed from PuF_6 gas to PuF_4 solid form and then sent to the Analytical Chemistry Group for mass spectrometry analysis. The uncertainties represent the estimated precision of gamma-ray spectroscopy. The average ratios of gamma spectroscopy to mass spectrometry are 0.999 for $^{238}Pu/^{239}Pu$, 0.9945 for $^{240}Pu/^{239}Pu$, and 1.0143 for $^{241}Pu/^{239}Pu$, as shown in Table II.A. The average ratios of gamma spectroscopy to mass spectrometry are 1.0041 for ^{238}Pu, 1.0012 for ^{239}Pu, 0.9913 for ^{240}Pu, and 1.0071 for ^{241}Pu, as shown in Table II.B. These results show negligible bias when compared with mass spectrometry results.

CONCLUSION

In summary, we have demonstrated the first isotopic analysis of gaseous PuF_6 by using a nondestructive gamma-ray spectroscopy technique. The rapid and accurate in-line isotopic analysis of PuF_6 in a process flow loop provides important information on process development, process control, and nuclear safeguards for any plutonium-isotope-separation process that requires plutonium in a gaseous phase.

ACKNOWLEDGMENTS

The author gratefully acknowledges the support of the operations staff of the Los Alamos SIS Facility and in particular Dick Briesmeister, Harry Dewey, Lorenzo Trujillo, Don Zickert, and Bobby Dye. Much of this work would be impossible without their excellent support, assistance, and cooperation.

TABLE II

COMPARISON OF PLUTONIUM ISOTOPIC ANALYSIS BY GAMMA-RAY SPECTROSCOPY WITH MASS SPECTROMETRY

A. Plutonium Isotopic Ratios

Sample	Pu Partial Pressure (torr)	Ratio: Gamma Spectroscopy/Mass Spectrometry		
		$^{238}Pu/^{239}Pu$	$^{240}Pu/^{239}Pu$	$^{241}Pu/^{239}Pu$
1	13.8	1.0046 ± 0.19%	0.9975 ± 0.10%	1.0265 ± 2.1%
2	3.1	1.0037 ± 0.68%	0.9895 ± 0.35%	1.0040 ± 6.1%
3	5.9	0.9887 ± 0.37%	0.9965 ± 0.2%	1.0123 ± 3.4%
Average		0.9990	0.9945	1.0143
Std Dev		±0.0089	±0.0044	±0.0114

B. Plutonium Isotopes

Sample	Pu Partial Pressure (torr)	Ratio: Gamma Spectroscopy/Mass Spectrometry			
		^{238}Pu	^{239}Pu	^{240}Pu	^{241}Pu
1	13.8	1.0102 ± 0.19%	1.0008 ± 0.03%	0.9939 ± 0.11%	1.0188 ± 2.1%
2	3.1	1.0102 ± 0.2%	1.0018 ± 0.08%	0.9875 ± 0.37%	0.9974 ± 6.1%
3	5.9	0.9918 ± 0.37%	1.0011 ± 0.04%	0.9924 ± 0.2%	1.0051 ± 3.4%
Average		1.0041	1.0012	0.9913	1.0071
Std Dev		±0.0106	±0.0005	±0 0033	±0.0108

REFERENCES

1. D. B. Fradkin, "Los Alamos Special Isotope Separation (SIS) Program, Laser Plutonium Isotope Separation," LA-10594-MS (June 1986).

2. T. K. Li, T. E. Sampson, and S. S. Johnson, "Plutonium Isotopic Measurement for Small Product Samples," in Proc. 5th Annual ESARDA Symp. on Safeguards and Nuclear Material Management, Versailles, France, April 19-21, 1983 (ESARDA 1983), ESARDA 16, pp. 289-291.

3. T. K. Li, "Determination of Plutonium Isotopic Ratios by Using Low-Energy Gamma-Ray Spectroscopy," Transactions of the American Nuclear Society 45 (Supplement 1), 17-20 (1983), and in Safeguards Technology: The Process-Safeguards Interface (Proc. of ANS/INMM Topical Conference on Safeguards Technology, Hilton Head Island, South Carolina, November 28-December 2, 1983), eds. E. A. Hakkila et al., CONF-831106 (US DOE, 1984), pp. 170-176.

4. T. K. Li, "Feasibility Study of Plutonium Isotopic Analysis of Resin Beads by Nondestructive Gamma-Ray Spectroscopy," Proc. 7th Annual ESARDA Symp. on Safeguards and Nuclear Material Management, Liege, Belgium, May 21-23, 1985 (ESARDA 1985), ESARDA 19, pp. 245-248.

5. R. Gunnink, "Use of Isotope Correlation Techniques to Determine ^{242}Pu Abundance," J. Inst. Nucl. Mater. Manage. 9 (2), 83-93 (1980).