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

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

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ABSTRACT

In-line plutonium isotopic analysis of gaseous plutonium hexafluoride (PuF₆) 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 analyse arbitrary plutonium samples, no isotopic analysis had been done on gaseous PuF₆ samples. We have initiated a study on the use of a high-resolution, gamma-ray spectroscopy technique to analyse gaseous plutonium hexafluoride. For the first time, PuF₆ gas samples with pressures varying from 0.1 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 on solid PuF₄. The precision of a 10-min measurement of a 10-torr reactor-grade PuF₆ is 1.5% for ²³³Pu, 0.22% for ²³⁹Pu, 0.87% for ²⁴⁰Pu, and 17.5% for ²⁴¹Pu.

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 separately separates specific plutonium isotopes from gaseous plutonium hexafluoride (PuF₆) using two types of lasers. The PuF₆ gas, prepared from reacting plutonium tetrafluoride (PuF₄) 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 PuF₆ molecules. Another laser then dissociates the excited PuF₆ to form PuF₄ in a solid form, which is collected on a series of filters.

In-line isotopic analysis for gaseous PuF₆ 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 PuF₆ samples. We have initiated a study of an in-line nondestructive technique to measure PuF₆ gas from the MLIS process flow loop. In this paper we report on the first analysis of plutonium isotopic compositions in gaseous PuF₆.

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.

\[
\frac{N(m)}{N(n)} = \frac{R(a)}{R(b)} \times \frac{T_H(m)}{T_H(n)} \times \frac{\epsilon(a)}{\epsilon(b)} \tag{1}
\]

where

- \( R \) = measured count rate of gamma rays,
- \( I \) = absolute branching intensity of gamma rays,
- \( T_H \) = half-life of isotopes, and
- \( \epsilon \) = relative efficiency of selected gamma rays, including detector intrinsic efficiency, counting geometry, and attenuation.

In this work, the isotopic ratios of ²³³Pu/²³⁹Pu, ²⁴⁰Pu/²³⁹Pu, and ²⁴¹Pu/²³⁹Pu 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 ²³³Pu, ²³⁹Pu, ²⁴⁰Pu, and ²⁴¹Pu compositions in the sample can then be determined by combining isotopic ratios and correcting for the ²⁴²Pu 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 by using the quotient of the measured peak areas and their known specific activities of the select 239Pu gamma rays in the sample. A simple linear ln E 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 analyser (MCA) with a 15-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 239Pu is used to maintain the energy calibration. A two-point stabilizer locked to the 51.63- and 129.3-keV gamma rays from 239Pu 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 mm² 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 17.1-cm-diam polycarbonate window. The cell is a right circular aluminum cylinder (~76 cm² by 6.4 cm) with a 1.6-mm-thick window facing the detector. It is installed in a sample chamber that provides 5 cm of shielding to prevent the detection of gamma rays from extraneous plutonium in the vicinity. Two valves control the flow of PuF₆ 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 PuF₆ 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 PuF₆ 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 PuF₆ 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 239Pu, open triangles for 238Pu, solid squares for 240Pu, and open circles for 241Pu) are calculated from counting statistics, including uncertainties from relative efficiencies and background run. Typically, within a 10-min count time, the precisions for a 10-torr PuF₆ sample are 1.5% for 239Pu, 0.22% for 238Pu, 0.87% for 240Pu, and 1.75% for 241Pu. The larger uncertainty of 241Pu 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 115-mg PuF₆ gaseous sample is compared to that from a 25-mg PuF₄ solid sample in Fig. 2. For gamma-ray energy above 100 keV, the relative efficiency curves are similar. However, the relative efficiency of the PuF₄ solid sample decreases steeply as energy decreases at lower gamma-ray energies. This shows that the effect of sample self-attenuation on the PuF₆ gas is very small as compared to that of the solid PuF₄.

In addition to sample mass, PuF₆ 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) PuF₆ 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 PuF₄ deposited on the inner surface of the aluminum gas sample cell. For a 85-mg PuF₆ sample in the gas cell, we demonstrate that one can expect better than 1% precision within 20 s for 239Pu, 7 min for 240Pu, and 25 min for 241Pu. The rapid plutonium isotopic analysis for a PuF₆ gas development sample is very valuable for process development and process control.

**TABLE I**

<table>
<thead>
<tr>
<th>Isotope</th>
<th>Weight Percent</th>
</tr>
</thead>
<tbody>
<tr>
<td>238Pu</td>
<td>0.059</td>
</tr>
<tr>
<td>239Pu</td>
<td>87.32</td>
</tr>
<tr>
<td>240Pu</td>
<td>11.50</td>
</tr>
<tr>
<td>241Pu</td>
<td>0.916</td>
</tr>
<tr>
<td>242Pu</td>
<td>0.202</td>
</tr>
</tbody>
</table>

**ISOTOPIC DISTRIBUTIONS (in wt%) OF PuF₆ FEED GASEOUS SAMPLE**
Fig. 1. Estimated precisions (1σ) of plutonium isotopes for 10-min measurements are plotted as a function of PuF₆ partial pressure in torr (bottom horizontal scale) and as a function of plutonium mass in milligrams (top horizontal scale). The solid circles are for ²³⁸Pu, the open triangles are for ²³⁹Pu, the solid squares are for ²⁴⁰Pu, and the open circles are for ²⁴¹Pu.

Fig. 2. Typical relative efficiency curves for PuF₆ gaseous and PuF₄ solid samples.
Fig. 3. The precision (1σ) of plutonium isotopes on a 85-mg (-11 torr) PuF₆ 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 ²³⁸Pu, the dotted curve and open triangles are for ²³⁹Pu, the dashed curve and solid squares are for ²⁴⁰Pu, and the dashed-dotted curves and open circles are for ²⁴¹Pu.

To evaluate accuracy, three samples with different isotopic compositions and PuF₆ gas pressures were decomposed from PuF₆ gas to PuF₄ 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 ²³⁸Pu/²³⁹Pu, 0.9945 for ²⁴⁰Pu/²³⁹Pu, and 1.0143 for ²⁴¹Pu/²³⁹Pu, as shown in Table II.A. The average ratios of gamma spectroscopy to mass spectrometry are 1.0041 for ²³⁸Pu, 1.0012 for ²³⁹Pu, 0.9911 for ²⁴⁰Pu, and 1.0071 for ²⁴¹Pu, 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 PuF₆ by using a non-destructive gamma-ray spectroscopy technique. The rapid and accurate in-line isotopic analysis of PuF₆ 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 Zlickert, and Hobby 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

<table>
<thead>
<tr>
<th>Sample</th>
<th>Pressure (torr)</th>
<th>238Pu/239Pu</th>
<th>240Pu/239Pu</th>
<th>241Pu/239Pu</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>13.8</td>
<td>1.0046 ± 0.19%</td>
<td>0.9975 ± 0.10%</td>
<td>1.0265 ± 2.1%</td>
</tr>
<tr>
<td>2</td>
<td>3.1</td>
<td>1.0037 ± 0.68%</td>
<td>0.9895 ± 0.35%</td>
<td>1.0040 ± 6.1%</td>
</tr>
<tr>
<td>3</td>
<td>5.9</td>
<td>0.9887 ± 0.37%</td>
<td>0.9965 ± 0.2%</td>
<td>1.0123 ± 3.4%</td>
</tr>
<tr>
<td>Average</td>
<td></td>
<td>0.9990</td>
<td>0.9945</td>
<td>1.0143</td>
</tr>
<tr>
<td>Std Dev</td>
<td></td>
<td>±0.00009</td>
<td>±0.00044</td>
<td>±0.00114</td>
</tr>
</tbody>
</table>

B. Plutonium Isotopes

<table>
<thead>
<tr>
<th>Sample</th>
<th>Pressure (torr)</th>
<th>238Pu</th>
<th>239Pu</th>
<th>240Pu</th>
<th>241Pu</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>13.8</td>
<td>1.0102 ± 0.19%</td>
<td>1.0008 ± 0.03%</td>
<td>0.9939 ± 0.11%</td>
<td>1.0188 ± 2.1%</td>
</tr>
<tr>
<td>2</td>
<td>3.1</td>
<td>1.0102 ± 0.2%</td>
<td>1.0018 ± 0.08%</td>
<td>0.9875 ± 0.37%</td>
<td>0.9974 ± 6.1%</td>
</tr>
<tr>
<td>3</td>
<td>5.9</td>
<td>0.9918 ± 0.37%</td>
<td>1.0011 ± 0.04%</td>
<td>0.9924 ± 0.2%</td>
<td>1.0051 ± 3.4%</td>
</tr>
<tr>
<td>Average</td>
<td></td>
<td>1.0041</td>
<td>1.0012</td>
<td>0.9913</td>
<td>1.0071</td>
</tr>
<tr>
<td>Std Dev</td>
<td></td>
<td>±0.0106</td>
<td>±0.0005</td>
<td>±0.0033</td>
<td>±0.0108</td>
</tr>
</tbody>
</table>

REFERENCES


