A Novel Technique to Overcome Difficult Problems in Simultaneously Measuring Plutonium and Uranium in Spent-Fuel Dissolver Solutions

T. K. Li
Group NIS-5, MS E-540
Los Alamos National Laboratory
Los Alamos, NM 87545 USA

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ABSTRACT

We have developed a novel technique to overcome difficult problems that arise when isotope dilution gamma-ray spectrometry (IDGS) technique is used to simultaneously measure plutonium and uranium in the spent-fuel dissolver solutions of reprocessing plants. IDGS determines the plutonium isotopic abundance by analyzing the high-resolution, low-energy gamma-ray spectra and determining the plutonium concentration by employing the isotope dilution principle. It has proven to be versatile, expeditious and cost-efficient for the plutonium analysis of input dissolver solution. In cases of applying the IDGS technique to measure uranium simultaneously with plutonium, the $^{235}$U concentration can then be deduced from the combination of the $^{235}$U/$^{239}$Pu ratio and the $^{239}$Pu concentration in a same sample. Because of the fact that the U/Pu ratio is altered during the fission product separation phase, it is necessary to develop a method which will accurately correct for this effect. Such a method is developed from the unique decay properties of $^{241}$Pu. In this paper, we describe that with the addition of this new correction method, a simultaneous measurement of plutonium and uranium in the spent fuel dissolver solutions of fuel reprocessing plants can be achieved to an accuracy that meets stringent safeguard standards.

1. INTRODUCTION

Rapid yet accurate assays of the plutonium and uranium in reprocessing input dissolver solutions are very important for input accountability analysis, nuclear material control, and on-site verification. Several years ago we developed, and have since thoroughly tested, an assay method called isotope dilution gamma-ray spectrometry (IDGS) which, in the case of plutonium-only solutions, produces fast and accurate assays. To expedite the overall assay process a combined assay of uranium and plutonium is highly desirable. It is to this problem that the present paper is directed. We show that one of the major obstacles that presents itself in the case of such simultaneous assays can be overcome by applying a novel technique which takes advantage of the unique characteristics of the decay of $^{241}$Pu.

IDGS determines the concentration and isotopic composition of highly radioactive spent-fuel dissolver solutions, and is similar to the traditional approach—isootope dilution mass spectrometry (IDMS)—except that the isotopic distributions are measured by application of high-resolution gamma-ray spectrometry rather than mass spectrometry. The measurement method, equipment, and analysis each are simpler and much less costly for IDGS, thus the technique is far better suited for rapid on-site verification. Previous IDGS experiments have succeeded in measuring the plutonium concentration and isotopic composition of dissolver solutions with spent-fuel burnups ranging up to 28 000 MWD/T. Typically a 1-h counting period produces a precision better than 1% for plutonium concentrations and a bias between IDGS and IDMS of less than 0.2%. Precision of 0.5% and 0.2% is typical for $^{240}$Pu/$^{239}$Pu ratio and the $^{239}$Pu weight percent, respectively. The agreement between IDGS and IDMS is generally excellent, especially for the $^{240}$Pu/$^{239}$Pu ratio (average IDGS/IDMS ratio is 0.997) and the weight percent of $^{239}$Pu (average IDGS/IDMS ratio is 0.999). Success in these isotopic measurements is essential if an accurate determination of the total plutonium concentration is to be made.

Gamma-ray measurements of plutonium in highly radioactive dissolver solutions from reprocessing plants require the rapid and efficient separation of fission products. Ion-exchange separation was used to satisfactorily purify and recover just plutonium for the gamma-ray measurement. It was, however, found that a certain amount of uranium could hardly be recovered after fission products were washed and separated in the nitric acid medium. Therefore, for simultaneous measurements of uranium and plutonium, we are developing a new sample preparation method, extraction chromatography using U/TEVA•Spec resin (for uranium and tetravalent actinides specifically) to purify and recover both uranium and plutonium from dissolver solutions. Detailed separation methods have been reported in previous papers and will not be discussed here.

The objective of the present study is to adapt the IDGS technique to a simultaneous measurement of the concentrations and isotopic compositions of plutonium and uranium in the spent-fuel dissolver solutions of reprocessing plants. The plutonium analysis is based on the IDGS technique and the uranium analysis is based on the U/Pu ratio in the same sample. However, because the U/Pu ratio is altered during the fission product separation phase, it is necessary to develop a method that will accurately correct for this effect. This paper describes the application of the IDGS method to the U/Pu problem and presents a novel approach that corrects for the random change in U/Pu ratio that occurs in the chemical separation phase.
II. ANALYSIS METHODS

A. Plutonium Analysis

Details of the IDGS measurement technique and method are described in Refs. 1 and 2. Briefly, in IDGS the isotopic composition is determined by measuring the respective gamma rays emanating from the isotopes within the dissolver solution. The measurement method of the plutonium isotopic ratios is based on high-resolution, low-energy, gamma-ray spectrometry (LEGS). Because the assay necessitates the use of small sample volumes (containing less than 1 mg of plutonium), the isotopic ratios $^{238}\text{Pu}/^{239}\text{Pu}$, $^{240}\text{Pu}/^{239}\text{Pu}$, and $^{241}\text{Pu}/^{239}\text{Pu}$ are best determined from the very high-intensity, low-energy gamma-ray ratios $43.48\text{ keV}/51.63\text{ keV}$, $45.23\text{ keV}/51.63\text{ keV}$, and $148.6\text{ keV}/129.3\text{ keV}$, respectively.\(^1\)\(^-\)\(^3\) All gamma-ray peak areas are determined by using peak fitting with response function analysis. The absolute $^{238}\text{Pu}$, $^{239}\text{Pu}$, $^{240}\text{Pu}$, and $^{241}\text{Pu}$ fractions in the sample are then determined by combining isotopic ratios and correcting for the $^{242}\text{Pu}$ content, which is predicted by isotope correlation techniques — a method known to work well for conventional power reactor spent fuels.

To measure the total plutonium concentration, the unknown solutions are spiked with plutonium of accurately known plutonium mass and isotopic composition. The isotopic compositions of both unspiked dissolver solution (unknown sample only) and spiked dissolver solution (unknown sample plus the spike) samples\(^1\)\(^-\)\(^2\) are measured by LEGS. The concentration of plutonium, $C(\text{Pu})$, in the unknown dissolver solution is then determined by calculating the difference among the isotopic $^{240}\text{Pu}/^{239}\text{Pu}$ ratios of the spike, the spiked samples, and the unspiked samples.

$$C(\text{Pu}) = \frac{M_S}{V_U} \cdot \frac{W_9^{\text{Pu}}}{W_9^{\text{Pu}}} \cdot \frac{R_m - R_s}{R_u - R_m}, \quad (1)$$

where

- $M_S$ = mass of plutonium in the spike,
- $V_U$ = volume of dissolver solution taken,
- $W_9^{\text{Pu}}$ = weight fraction of $^{239}\text{Pu}$ in the spike,
- $W_9^{\text{Pu}}$ = weight fraction of $^{239}\text{Pu}$ in the dissolver solution,
- $R_m$ = the $^{240}\text{Pu}/^{239}\text{Pu}$ ratio in the spiked sample,
- $R_s$ = the $^{240}\text{Pu}/^{239}\text{Pu}$ ratio in the spike, and
- $R_u$ = the $^{240}\text{Pu}/^{239}\text{Pu}$ ratio in the dissolver solution sample.

In this equation, the values of $M_S$, $V_U$, $W_9^{\text{Pu}}$, and $R_S$ are known. Therefore, only the values of $R_U$ and $W_9^{\text{Pu}}$ in the unspiked dissolver-solution sample and $R_m$ in the spiked sample need to be measured by gamma-ray spectrometry.

B. Uranium Analysis

1. Problems Associated with Traditional Approaches

Traditional approaches, which have had a history of success in the accurate analysis of uranium isotopics and uranium solution concentrations, are in general not effective in the particular case we are dealing with here. The problems associated with traditional approaches of uranium analysis are briefly described below.

a. Uranium Isotopic Measurements

i.) $^{238}\text{U}$ Isotope

- The useful gamma rays for $^{238}\text{U}$ actually come from the decay of its granddaughter, $^{234}\text{Pa}$, with ingrowth governed by its parent $^{234}\text{Th}$ (half-life = 24.1 days). Therefore, they are not directly usable for freshly separated samples.
- The only gamma ray directly from the decay of $^{238}\text{U}$, 49.55 keV, is very weak with an emission probability of 0.070%\(^4\) and is immersed in the stronger escape peak (49.66 keV) of 241 Am.

ii.) $^{234}\text{U}$ Isotope

Uranium-234 has reasonably intense gamma rays at 53.2 keV and 120.9 keV. However, the weight percents of $^{234}\text{U}$ in dissolver solutions are typically less than 0.02 wt%.

b. Uranium Concentration Measurements

i.) Absorption-Edge Densitometry and X-Ray Fluorescence - Because of the small mass and low concentrations in the resin samples, the use of induced and self-fluoresced uranium x-rays and absorption-edge densitometry techniques is ruled out.

ii.) IDGS - Because of difficulties in measuring precise uranium isotopic ratios (see discussions below), the recently developed IDGS technique for plutonium analysis achieves precisions of 5%-10% for uranium concentrations, which is unacceptable for accountability purposes.

2. Approaches with a Potential for Success

Although uranium isotopic compositions and uranium concentration are, for the above-mentioned reasons, almost impossible to measure simultaneously with plutonium in the dissolver solutions, the $^{235}\text{U}/^{239}\text{Pu}$ ratio and concentration of $^{235}\text{U}$, which is the critical uranium isotope for safeguards, may be measured by applying the following methods:
a. The $^{235}U/^{239}Pu$ Ratio

Figure 1 shows the gamma-ray spectrum of dissolver solution after chemical separation with extraction chromatography using U/TEVA•Spec resins. Since plutonium and uranium are carried forward in the same sample after fission product removal, the $^{235}U/^{239}Pu$ ratio can be extracted from the measured intensities of a single gamma-ray spectrum of the unspiked dissolver solution.

$$\frac{^{235}U}{^{239}Pu} = \frac{A(\gamma_{186})}{A(\gamma_{129})} \cdot \frac{T_{1/2}(^{235}U)}{T_{1/2}(^{239}Pu)} \cdot \frac{I(\gamma_{129})}{I(\gamma_{186})} \cdot \frac{\epsilon(\gamma_{129})}{\epsilon(\gamma_{186})}$$  \hspace{1cm} (2)

where

- $A$ = full-energy peak area,
- $I$ = absolute emission probability of gamma ray,
- $T_{1/2}$ = half-life of isotope, and
- $\epsilon$ = relative efficiency for specified gamma ray, which includes detector intrinsic efficiency, counting geometry, and sample attenuation.

Eqs. 2 and 3 are correct provided that the U/Pu ratio remains unchanged, or if a change in this ratio does occur during the separation phase, this change is highly predictable. Unfortunately, neither of these two conditions is met. The U/Pu ratios after separations tend to be very different from the original ratios and in a manner that is highly unpredictable. In order to apply the above-described method to the simultaneous analysis of uranium and plutonium, it was necessary to develop a correction method under a situation that was hopeless but for the unique characteristics of the decay of $^{241}Pu$. An intensive study of these unusual decay attributes suggested a novel correction technique whose application has produced remarkably good results in a situation that otherwise has no hope of determining the dissolver concentration of $^{235}U$ before separation. The following section describes this method.

3. A Novel Correction Method to Overcome Difficult Problems

The method takes advantage of the unique decay characteristics of $^{241}Pu-^{237}U$ (see Figure 2) to make corrections for the U/Pu changes after separation, thus permitting accurate determinations of the original $^{235}U$ concentrations before the chemical extraction phase. Plutonium-241 decays to both $^{241}Am$ through $\beta$ decay (99.998%) and $^{237}U$ by $\alpha$ decay (2.46 x $10^{-3}$). Because $^{235}U$ has a half-life of only 6.75 days, it comes into secular equilibrium with its $^{241}Pu$ parent within a period of 30-40 days. In the $^{241}Pu-^{237}U$ equilibrium case, several strong gamma rays emitted from $^{237}U$ $\beta$ decay can be used successfully as a measure of $^{241}Pu$ (Eq. 4). In the present case, one day after separation, the strongest $^{241}Pu-^{237}U$ peak at 208.0 keV has only ~0.007% contributed from $^{241}Am$ $\alpha$ decay. Therefore the $^{241}Pu$ quantity in an aged sample determined from the 208-keV gamma ray peak is:

$$^{241}Pu-^{237}U = A(\gamma_{208}) \cdot \frac{T_{1/2}(^{241}Pu)}{I(\gamma_{208})} \cdot \epsilon(\gamma_{208})$$  \hspace{1cm} (4)

The quantity of $^{241}Pu$ in a sample can also be measured by the intensity of the 148.6-keV gamma ray that is emitted directly from the decay of $^{241}Pu$ (Eq. 5).

$$^{241}Pu = A(\gamma_{148}) \cdot \frac{T_{1/2}(^{241}Pu)}{I(\gamma_{148})} \cdot \epsilon(\gamma_{148})$$  \hspace{1cm} (5)
Decay Modes of $^{241}$Pu

Because the original dissolver solutions were sufficiently aged to bring about equilibrium between $^{241}$Pu and its daughter by $\alpha$ decay, the amount of $^{241}$Pu determined from the 148.6-keV gamma ray should be the same as that determined from the 208-keV gamma ray (or 164.6 keV and other $^{241}$Pu-$^{237}$U gamma rays). Any difference between the measured $^{241}$Pu and $^{241}$Pu-$^{237}$U indicates a change in the ratio of $^{241}$Pu/$^{237}$U (or Pu/U) caused by the fission product separation phase. Thus, the ratio of $^{241}$Pu (as determined from the 148.6-keV gamma ray) and $^{241}$Pu-$^{237}$U (as determined from the 208.0-keV gamma ray) is indeed the actual ratio of recovery of plutonium and uranium after the separation from fission products if measurements of 208-keV and 148.6 keV gamma rays from the separated samples are performed promptly after separation. The ratio can be used as a correction factor for determining the original U/Pu ratio before the separation:

$$\text{Correction Factor (CF)} = \frac{^{241}\text{Pu}}{^{241}\text{Pu}-^{237}\text{U}} \cdot \frac{A\left(\gamma_{148}\right)}{A\left(\gamma_{208}\right)} \cdot \frac{I\left(\gamma_{208}\right)}{I\left(\gamma_{148}\right)} \cdot \frac{E\left(\gamma_{208}\right)}{E\left(\gamma_{148}\right)} \cdot \frac{C\left(\gamma_{148}\right)}{C\left(\gamma_{208}\right)} \cdot W_u^9 \cdot \epsilon. \quad (6)$$

The pre-separation ratio of $^{235}$U to $^{239}$Pu, $(^{235}\text{U}/^{239}\text{Pu})_{\text{orig.}}$, is then defined in terms of the post-separation ratio, $(^{235}\text{U}/^{239}\text{Pu})_{\text{sep.}}$, by the following formula:

$$(^{235}\text{U})_{\text{orig.}} = \left(\frac{^{235}\text{U}}{^{239}\text{Pu}}\right)_{\text{sep.}} \cdot \text{CF}. \quad (7)$$

The concentration of $^{235}$U in Eq. 3 then can be expressed as

$$C\left(^{235}\text{U}\right) = \left(\frac{^{235}\text{U}}{^{239}\text{Pu}}\right)_{\text{orig.}} \cdot C(\text{Pu}) \cdot W_u^9. \quad (8)$$

To validate the correction method, four synthetic mixed solutions (using the same separation methods as is used for real dissolver solutions) were prepared and measurements conducted immediately following sample preparation. Four mixed solutions contained the same uranium and plutonium concentrations and isotopic distributions but varied with solution volumes and U/TEVA Spec resin volumes. The IDGS-predicted $^{235}$U/$^{239}$Pu for the four solutions are compared with the reference values in Table I. The reference values of the uranium isotopic wt% were determined by mass spectrometry, and the uranium concentration was determined by the hybrid X-ray fluorescence (HXRF) technique. The IDGS-predicted $^{235}$U concentrations for the four solutions are compared with the reference values in Table II. The agreements between IDGS and these reference values for both $^{235}$U/$^{239}$Pu and $^{235}$U concentrations are very good.

### Table I. Comparison of $^{235}$U/$^{239}$Pu of pure mixed solutions as determined by IDGS and reference values (Ref) *

<table>
<thead>
<tr>
<th>Pure Mixed Solution</th>
<th>IDGS Correction Factor</th>
<th>Before Correction</th>
<th>After Correction</th>
<th>IDGS/Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.767</td>
<td>1.320</td>
<td>1.720</td>
<td>0.999</td>
</tr>
<tr>
<td>2</td>
<td>1.249</td>
<td>2.168</td>
<td>1.735</td>
<td>1.007</td>
</tr>
<tr>
<td>3</td>
<td>1.254</td>
<td>2.165</td>
<td>1.726</td>
<td>1.002</td>
</tr>
<tr>
<td>4</td>
<td>1.270</td>
<td>2.178</td>
<td>1.715</td>
<td>0.996</td>
</tr>
</tbody>
</table>

*Uranium isotope weight percents were determined by mass spectrometry and uranium concentrations were measured by HKED. Reference value (Ref) was 1.723 in all cases.

### Table II. Comparison of IDGS determined values to reference values (Ref) of $^{235}$U concentrations for the pure mixed solutions.

<table>
<thead>
<tr>
<th>Pure Mixed Solution</th>
<th>$^{235}$U Concentration (g/L)</th>
<th>IDGS</th>
<th>IDGS/Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2.118</td>
<td>2.116</td>
<td>0.999</td>
</tr>
<tr>
<td>2</td>
<td>2.118</td>
<td>2.132</td>
<td>1.007</td>
</tr>
<tr>
<td>3</td>
<td>2.118</td>
<td>2.122</td>
<td>1.002</td>
</tr>
<tr>
<td>4</td>
<td>2.118</td>
<td>2.110</td>
<td>0.996</td>
</tr>
</tbody>
</table>

Average 1.001
Std. Dev. 0.0047
% RSD 0.47
III. CONCLUSIONS

The first result from the simultaneous measurements of $^{235}\text{U}$ concentrations and $^{235}\text{U}$ wt% using the correction method proposed herein are very encouraging. Future proof-of-principle experiments are planned. Decay corrections need not be made if the IDGS measurements follow promptly sample preparation. Any objective comparison of IDGS to IDMS or other methods, requires that identical samples be used and that decay corrections be made if the above criterion is not met. The appropriateness of the correction method to other applications is currently under study.

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REFERENCES


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