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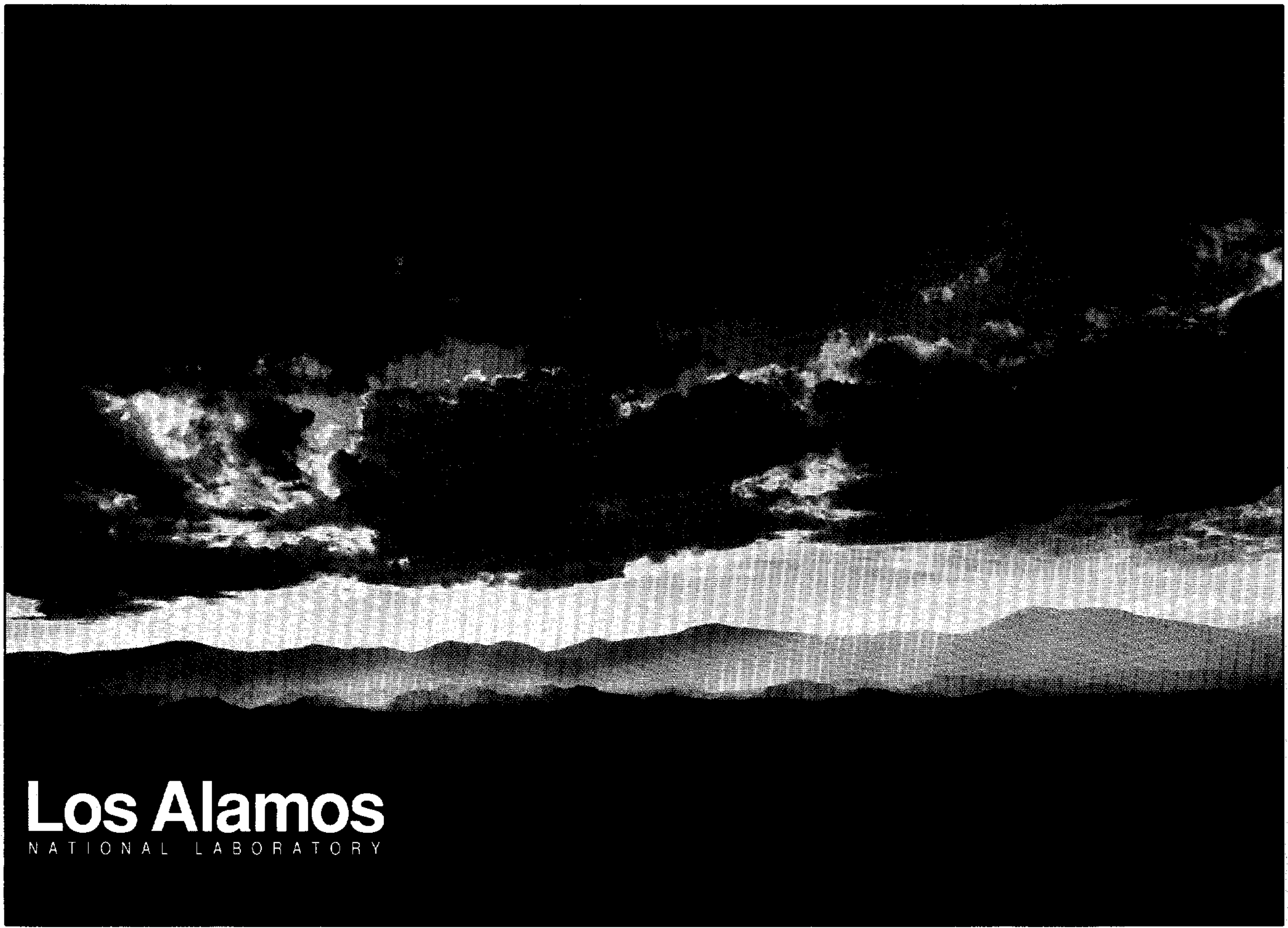

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Simultaneous Measurements of Plutonium and Uranium in Spent-Fuel Dissolver Solutions*

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Abstract

We have studied the isotope dilution gamma-ray spectrometry (IDGS) technique for simultaneous measurements of elemental concentrations and isotopic compositions for both plutonium and uranium in input spent-fuel dissolver solutions at a reprocessing plant. The technique under development includes both sample preparation and analysis methods. For simultaneous measurements of both plutonium and uranium, a critical issue is to develop a new method to keep both plutonium and uranium in the sample after they are separated from fission products. Furthermore, it is equally important to improve the analysis method so that the precision and accuracy of the plutonium analysis remain unaffected while uranium is retained in the sample. To keep both plutonium and uranium in the sample for simultaneous measurements, extraction chromatography is being studied and shows promise to achieve the goal of cosegregation of the plutonium and uranium. The technique uses U/TEVA•Spec resin to separate fission products and recover both uranium and plutonium in the resin from dissolver solutions for subsequent measuring using high-resolution gamma-ray spectrometry. Owing to the fact that the U/Pu ratio is altered during the fission product separation phase, it is necessary to develop a method which could accurately correct for this effect. Such a method was developed using the unique decay properties of ^{241}Pu to ^{237}U and shows considerable promise in allowing for accurate determination of the ^{235}U concentrations before the chemical extraction.

I. Introduction

Spent-fuel dissolver solutions are the input to the main chemical process area where separation and purification occurs. In general, dissolver solutions contain high levels of fission products and uranium (up to 250 g/L). Plutonium concentrations are generally about 1% of uranium concentrations. Accurate, rapid determinations of the plutonium and uranium in reprocessing input dissolver solutions are very important for input accountability analysis, nuclear material control, and for on-site verification, which are essential elements of the near-real-time accounting (NRTA) system at reprocessing plants. Recently, we have developed a novel technique, isotope dilution gamma-ray spectrometry (IDGS),[1-3] to measure the plutonium concentration and isotopic composition of highly radioactive spent-fuel dissolver solutions. IDGS is similar to the isotope dilution mass spectrometry (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. Sample preparation is simpler for IDGS and is better suited to rapid on-site analysis.

From previous experiment,[1-5] IDGS has been successful in measuring plutonium isotopic composition and elemental concentrations of spent-fuel dissolver solutions with burnups up to 28 000 MWD/T. Precision for this measurement is better than 1% with a bias between IDGS and IDMS of less than 0.2%. Using IDGS to analyze dissolver solutions for plutonium isotopic compositions, the precision is approximately 0.5% for the ^{240}Pu/^{239}Pu ratio and 0.2% for the ^{239}Pu weight percent within a 1-h count time. The agreement between IDGS and IDMS for dissolver solutions is very good, especially so for the ^{240}Pu/^{239}Pu ratio (average IDGS/ IDMS ratio is 0.997) and the weight

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percent of ^{239}Pu (average IDGS/IDMS ratio is 0.999), which are important for determining the total plutonium concentration. The chemical separation methods used to recover plutonium exclusively were anion-exchange resin beads (BIO-RAD AG-MP1 NO_3 form)[1-4] and filter paper techniques.[5]

The objective of the present feasibility study is to further develop the IDGS technique for the simultaneous measurements of concentrations and isotopic compositions for both plutonium and uranium in spent-fuel dissolver solutions at a reprocessing plant. The technique under development includes both sample preparation and analysis methods. Previous experiments have demonstrated that the IDGS technique can determine the elemental concentrations and isotopic compositions of plutonium in dissolver solutions. The chemical separation and recovery methods for just plutonium were ion-exchange techniques using anion-exchange resin beads and filter papers. To keep both plutonium and uranium in the sample for simultaneous measurements, new sample preparation methods have been studied and developed. For simultaneous measurements of both plutonium and uranium, the most important issue is to develop a new method to separate uranium and plutonium from fission products and other actinides and then recover both uranium and plutonium with high yields. Furthermore, it is equally important to improve the analysis method so that the precision and accuracy of the plutonium analysis is not degraded in the case where uranium is co-recovered with plutonium in the sample. Of the few separation methods available, we found extraction chromatography[6] to be the best method. The technique uses U/TEVA•Spec resin[7] to separate fission products and recover both uranium and plutonium in the resin from dissolver solutions for measurements by high-resolution gamma-ray spectrometry.

This paper will discuss extraction chromatography for recovering both plutonium and uranium in the sample and will discuss the results of plutonium and uranium analysis by using this new separation method.

II. Analysis Methods

A. Plutonium Analysis

Details of the IDGS measurement technique and method are described in Ref. 1 and 2. In this technique, briefly, the isotopic composition is determined by measuring the respective gamma rays of isotopes from the dissolver solution. The measurement method of plutonium isotopic ratios is based on high-resolution gamma-ray spectrometry. Because of the small sample volumes (containing less than 1 mg of plutonium) in the experiment, the isotopic ratios ^{238}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.[1-3] All gamma-ray peak areas are determined by using peak fitting of response function analysis. 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 that work well for material from known reactor types.

With regard to the total plutonium concentration, the unknown solutions are spiked with a plutonium isotope of accurately known concentration and isotopic composition. The total plutonium concentration is determined by calculating the difference among the isotopic ratios of the spike, the spiked samples (unknown sample plus the spike), and the unspiked samples (unknown sample only). By measuring the isotopic compositions of both unspiked and spiked dissolver solution samples, we can determine the concentration of plutonium in the unknown dissolver solution, $C(\mathrm{Pu})$, as follows:[1-2]

$$C(\mathrm{Pu}) = \frac{M_s}{V_u} \bullet \frac{W_s^9}{W_u^9} \bullet \frac{R_m - R_s}{R_u - R_m} \quad , \tag{1}$$

where M_S = mass of plutonium in the spike,
V_u = volume of dissolver solution taken,

W_s^9 = weight fraction of ^{239}Pu in the spike,
W_u^9 = weight fraction of ^{239}Pu in the dissolver solution,
R_m = the ^{240}Pu/^{239}Pu ratio in the spiked sample,
R_s = the ^{240}Pu/^{239}Pu ratio in the spike, and
R_u = the ^{240}Pu/^{239}Pu ratio in the dissolver solution sample.

In this equation, the values of M_s, V_u, W_s^9, and R_s 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.

B. Uranium Analysis

Compared to plutonium analysis for spent-fuel dissolver solutions, uranium analysis is even more difficult. The gamma rays for ^{238}U actually come from the decay of its granddaughter, ^{234m}Pa, with ingrowth governed by its parent ^{234}Th (half-life = 24.1 days). Therefore, they are not directly usable for freshly separated solutions. Uranium-234 has reasonably intense gamma rays at 53.2 keV and 120.9 keV. However, the weight percents of ^{234}U in dissolver solutions are typically less than 0.02 wt%. The applications of induced and self-fluoresced uranium x-rays are ruled out because of the small mass and low concentrations in the samples. Although uranium isotopic compositions and total elemental concentration are almost impossible to measure simultaneously with plutonium in the dissolver solutions for the above-mentioned reasons, the concentration of ^{235}U, which is an important uranium isotope for safeguards, might be determined as is stated in the following paragraphs.

Because both plutonium and uranium were absorbed in the same sample after being separated from fission products, the ^{235}U/^{239}Pu ratio can be determined by the measured intensities of 185.7 keV of ^{235}U and 129.3 keV of ^{239}Pu in the same gamma-ray spectrum of an unspiked dissolver solution.

$$\frac{^{235}\mathrm{U}}{^{239}\mathrm{Pu}} = \frac{A(\gamma_{186})}{A(\gamma_{129})} \bullet \frac{T_{1/2}(^{235}\mathrm{U})}{T_{1/2}(^{239}\mathrm{Pu})} \bullet \frac{I(\gamma_{129})}{I(\gamma_{186})} \bullet \frac{\varepsilon(\gamma_{129})}{\varepsilon(\gamma_{186})} , \tag{2}$$

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.

By combining the measured concentration of plutonium [C(Pu)] and weight percent of ^{239}Pu (W_u^9) from IDGS as described in Eq. 1, the concentration of ^{235}U then can be calculated as follows:

$$\begin{aligned} C(^{235}\mathrm{U}) &= \frac{^{235}\mathrm{U}}{^{239}\mathrm{Pu}} \bullet C(^{239}\mathrm{Pu}) \\ &= \frac{^{235}\mathrm{U}}{^{239}\mathrm{Pu}} \bullet C(\mathrm{Pu}) \bullet W_u^9 \quad . \end{aligned} \tag{3}$$

However, Eq. 3 can be only applied if one can prove the U/Pu ratio remains unchanged or the U/Pu ratio change is a constant before and after the separation during the sample preparation. Unfortunately, this is not the case. The U/Pu ratios can be randomly different from the original ratios after separations. In order to use the above-mentioned method to analyze uranium simultaneously with plutonium for dissolver solutions, we developed a correction method,[8] under a situation that was nearly hopeless.

Such a method was developed by taking advantage of the unique decay characteristics of ^{241}Pu to ^{237}U to make corrections for the U/Pu changed after separation and in allowing for accurate determination of the ^{235}U concentrations before the chemical extraction. Plutonium-241 decays to both ^{241}Am through β (99.998%) and ^{237}U by α decay (2.46 x 10^{-3}). Because ^{237}U has a short half-life of 6.75 days, its daughter rapidly comes into secular equilibrium with its ^{241}Pu parent. Several strong gamma rays emitted from ^{237}U can be used as a measure of ^{241}Pu for the ^{241}Pu-^{237}U equilibrium samples (Eq. 4). The strongest ^{241}Pu-^{237}U peak at 208.0 keV has only ~0.07% contributed from ^{241}Am one day after separation. ^{241}Pu can also be measured by the intensity of the 148.6 keV gamma ray which is emitted directly from the decay of ^{241}Pu (Eq. 5).

$$^{241}\mathrm{Pu}\text{-}^{237}\mathrm{U} = \frac{A\left(\gamma_{208}\right)\bullet\ T_{1/2}\left(^{241}\mathrm{Pu}\right)}{I\left(\gamma 2_{208}\right)\ \bullet\varepsilon\ \left(\gamma_{208}\right)} \tag{4}$$

$$^{241}\mathrm{Pu} = \frac{A\left(\gamma_{148}\right)\bullet T_{1/2}\left(^{241}\mathrm{Pu}\right)}{\mathrm{I}\left(\gamma_{148}\right)\bullet\ \varepsilon\left(\gamma_{148}\right)} \tag{5}$$

Because the original dissolver solutions were aged, the ^{241}Pu determined by the 148.6-keV gamma ray should be the same as that determined by the 208-keV gamma ray (or 164.6 keV and other ^{241}Pu-^{237}U gamma rays). Any differences between the measured ^{241}Pu and ^{241}Pu-^{237}U would indicate a change in the ratio of ^{241}Pu/^{237}U (or Pu/U) after the separations. 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, ^{241}Pu/^{241}Pu-^{237}U, is indeed the actual ratio of recovery of plutonium and uranium after the separation from fission products and can be used as a correction factor for determining the original U/Pu ratio before the separation. Therefore,

$$\begin{aligned}\text{Correction Factor (CF)} &= \frac{^{241}\mathrm{Pu}}{^{241}\mathrm{Pu}\text{-}^{237}\mathrm{U}} \\ &= \frac{A\left(\gamma_{148}\right)}{A\left(\gamma_{208}\right)}\bullet\frac{I\left(\gamma_{208}\right)}{I\left(\gamma_{148}\right)}\bullet\frac{\varepsilon\left(\gamma_{208}\right)}{\varepsilon\left(\gamma_{148}\right)}\ .\end{aligned} \tag{6}$$

The actual original ^{235}U/^{239}Pu ratio, (^{235}U/^{239}Pu)$_{\mathrm{orig.}}$, before the separations then can be determined from the measured ^{235}U/^{239}Pu, (^{235}U/^{239}Pu)$_{\mathrm{sep.}}$, after the separations:

$$\left(\frac{^{235}\mathrm{U}}{^{239}\mathrm{Pu}}\right)_{\mathrm{orig.}} = \left(\frac{^{235}\mathrm{U}}{^{239}\mathrm{Pu}}\right)_{\mathrm{sep.}}\bullet\mathrm{CF}\ . \tag{7}$$

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

$$C\left(^{235}U\right) = \left(\frac{^{235}U}{^{239}Pu}\right)_{\mathrm{orig.}}\bullet C(\mathrm{Pu})\bullet W_u^9\ . \tag{8}$$

III. Sample Preparation

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 plutonium for the IDGS 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[7] (for uranium and tetravalent actinides specifically) to purify and recover both uranium and plutonium from dissolver solutions. U/TEVA•Spec is a novel extraction chromatographic resin composed of diamyl amylphosphonate absorbed on an inert polymeric support (Amberlite XAD-7 or Amberchrom CG-71). The resin is commercially available from EIChroM Industries, Inc.

Plutonium and uranium in dissolver solutions (1 mL) were first completely adjusted to tetravalency with Fe(II) and $NaNO_2$. After evaporation and redissolution with 8M HNO3, dissolver solutions were passed through the extraction chromatographic column where fission products and americium were removed by 8M HNO_3 followed by 3M HNO_3. The absorbed plutonium and uranium are then eluted using 0.01M HNO_3. The best results were obtained when the elution of purified plutonium and uranium was reabsorbed in an extraction chromatographic column where the fission products were rewashed with 3M HNO_3. The completely purified plutonium and uranium sample is measured by high-resolution gamma-ray spectrometry to determine the plutonium isotopic composition.

For plutonium concentration measurements, 1-mL dissolver solutions were well mixed with spikes. These large-size dry (LSD) spikes, containing ~98% ^{239}Pu, were used in previous experiments.[1-5] The spiked dissolver solutions were then separated, eluted, recovered, and measured as described above for unspiked dissolver solutions.

The new procedure for preparing the sample by using the extraction chromatography is shown in Fig. 1 for the spiked sample (solid line) and the unspiked sample (dashed line). One mL aliquot for the spiked samples and the unspiked samples were taken from dissolver solutions, and the weight of the taken 1 mL aliquot for the spiked samples was measured by a precise electronic balance. The spiked samples were prepared by dissolving the dissolver solutions (1 mL aliquot) with LSD spikes at 90°C (on a heater and then mixing them by a magnetic stirrer). Plutonium in these samples was completely adjusted to tetravalency with Fe(II) and $NaNO_2$, and they were dissolved again with 8M HNO_3 (1 mL) after heating them to near dryness at 90°C. Each sample was individually passed through the extraction chromatographic columns (U/TEVA•Spec resin) adjusted with 8M HNO_3, fission products and americium were separated from uranium and plutonium by washing with 8M HNO_3 and 3M HNO_3. Uranium and plutonium were eluted with 0.01M HNO_3. For adjusting acidity to 8M, concentrated nitric acid was added to the eluted solutions. Plutonium and uranium were then absorbed in the columns again, and fission products like ruthenium were completely separated by washing with 3M HNO_3. Because gamma rays of fission products can degrade the quality of the gamma-ray measurements if significant amounts of fission products were still contained in the samples, each sample was carefully removed from a glove box with a plastic bag to avoid any contaminations and set directly on the end cap of the high-purity germanium detector for the gamma-ray measurement.

IV. Measurement Method

The measurement system is a standard high-resolution gamma-ray spectrometer, consisting of a hyperpure germanium (HPGe) planar detector, an EG&G ORTEC 92X-W3 Spectrum Master, and an IBM/PC compatible computer. The HPGe planar detector had dimensions of 1000 mm^2 by 13 mm and a resolution (full width at half maximum) of 560 eV at 122 keV. The EG&G ORTEC 92X-W3 features a high-voltage bias supply for the detector, spectroscopy amplifier, pile-up rejecter and

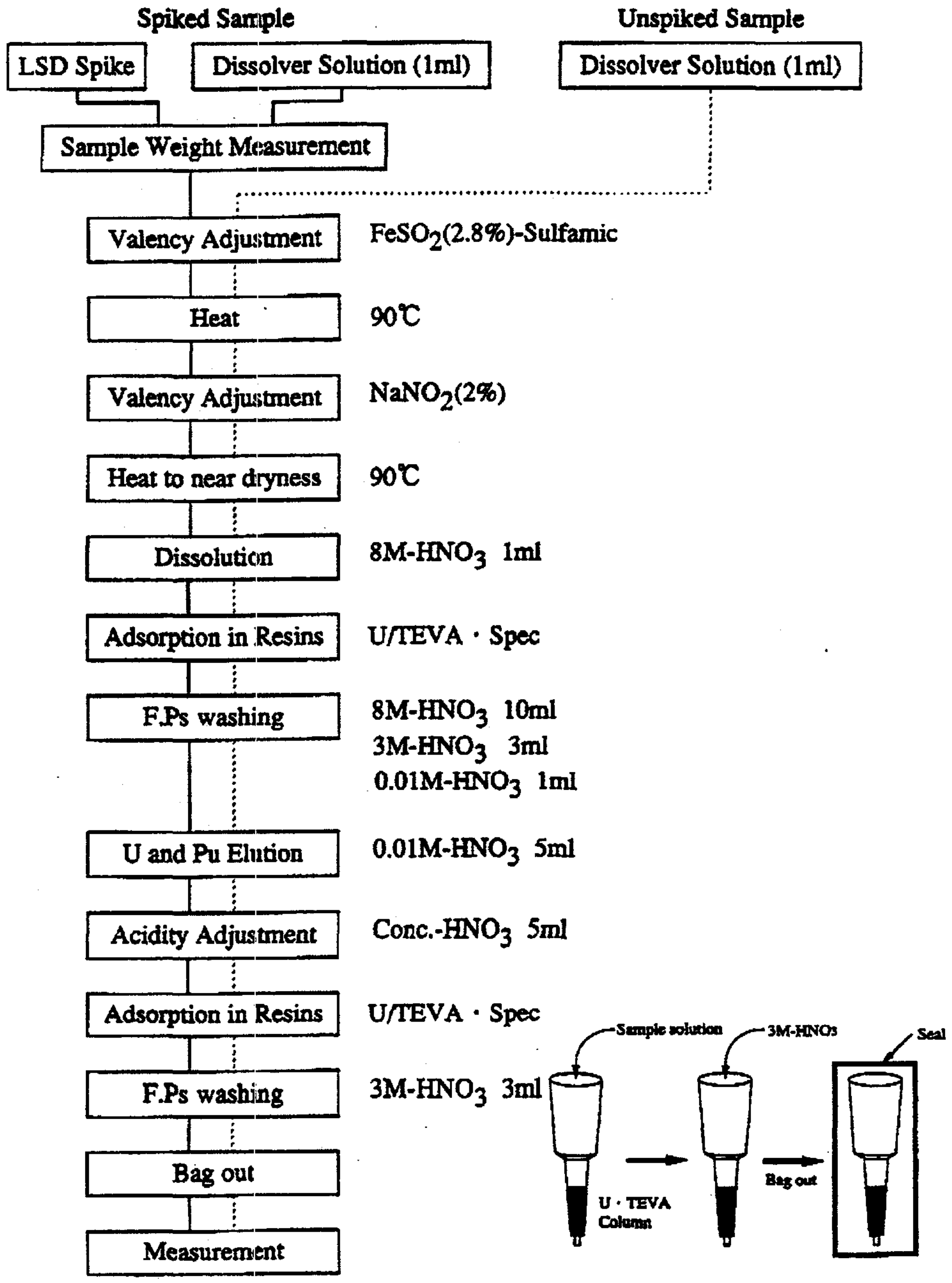

Fig. 1. The new sample preparation procedure using the extraction chromatography for the spiked (solid line) and unspiked (dash line) samples.

live-time corrector, and a 16-k-channel analog-to-digital converter. Figure 2 shows the IDGS system that was used for this study.

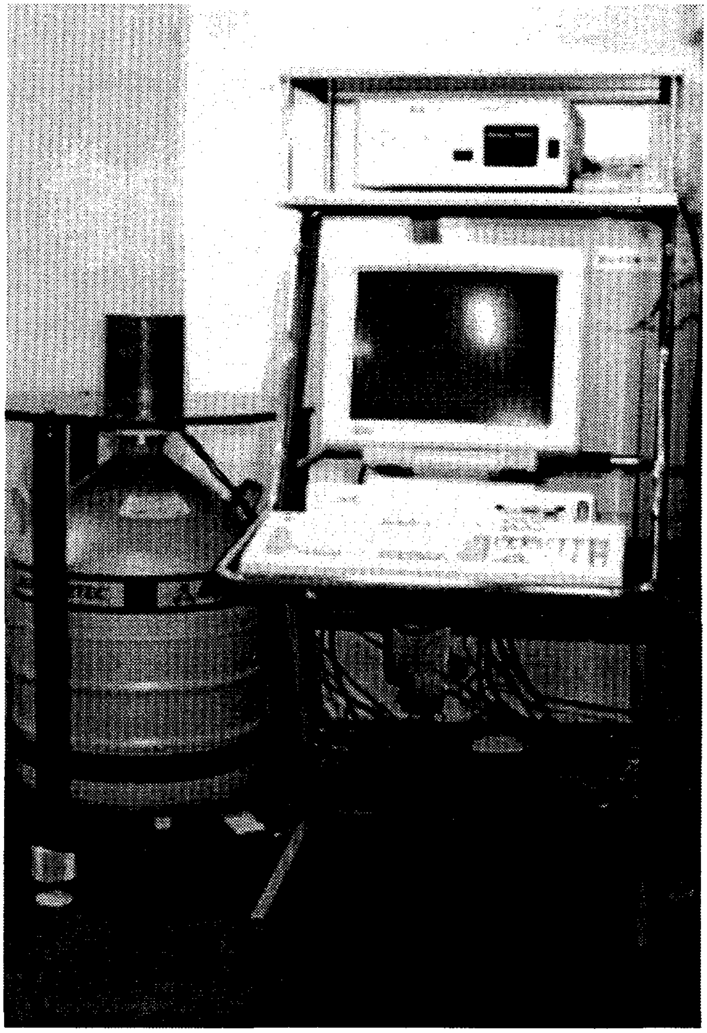

Fig. 2. IDGS system used for this study.

V. Results And Discussion

Six batches of input spent-fuel dissolver solutions with various ranges of plutonium concentrations and isotopic compositions were prepared, measured, and analyzed in this study.

A. Performance of Sample Preparation

Figure 3 shows the gamma-ray spectra of dissolver solutions from two different sample preparation methods for a 1-h count time. For easy comparison, we shifted the plot of the top gamma-ray spectrum slightly to the right. The top (dotted) spectrum is the gamma-ray spectrum from a dissolver solution obtained by using anion-exchange resins, as in the previous experiments. No uranium gamma rays are present in the spectrum. This indicates that no uranium has been recovered by using anion-exchange resins. The bottom (solid) spectrum is the gamma-ray spectrum of another dissolver solution prepared with extraction chromatography using U/TEVA•Spec resins. Clear and intense gamma rays of uranium (e.g., 143.8 keV and 185.7 keV from ^{235}U) can be identified indicating that uranium can be recovered with a high yield. Furthermore, the continuum background from high-energy gamma rays of fission products in the bottom spectrum is lower than that in the top spectrum. This indicates that the fission products are better removed with the extraction chromatographic method than with the former method employing the anion-exchange resins.

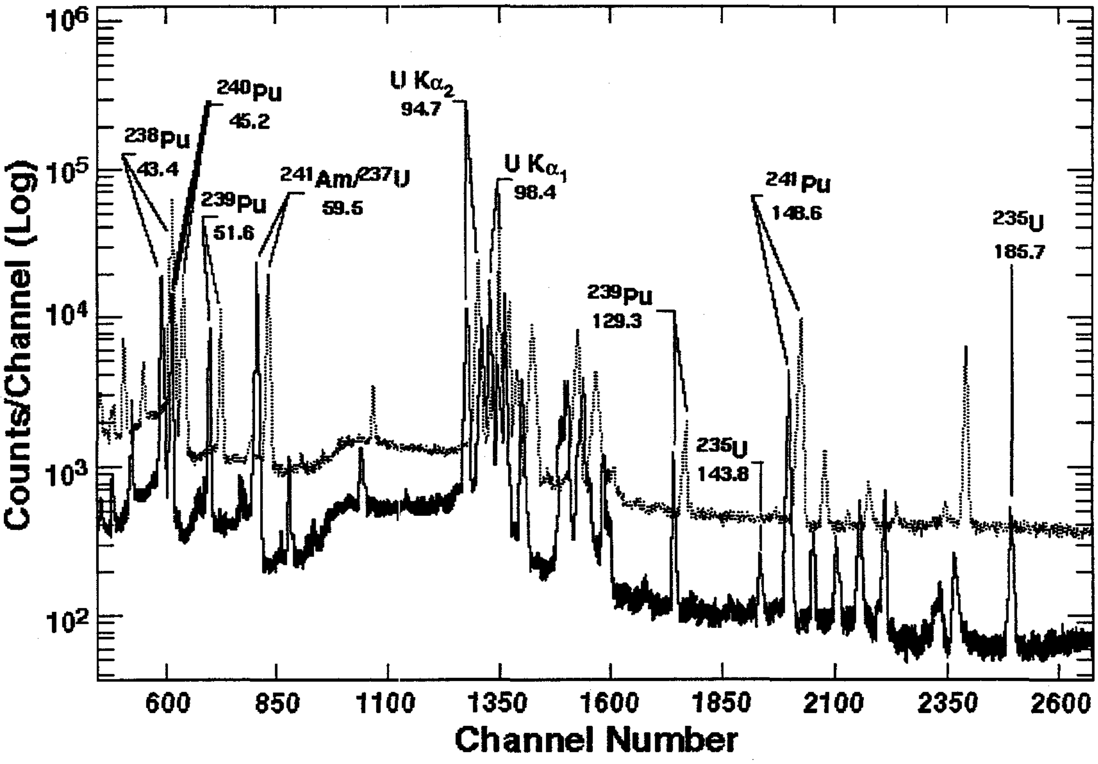

Fig. 3. Gamma-ray spectra of dissolver solutions from two different sample preparation methods for a 1-h count time. For easy comparison, we shifted the plot of the top gamma-ray spectrum slightly. The top (dotted) spectrum is the gamma-ray spectrum from a dissolver solution obtained by using anion-exchange resins, as in the previous experiments. The bottom (solid) spectrum is the gamma-ray spectrum of another dissolver solution prepared with extraction chromatography using U/TEVA•Spec resins.

B. Plutonium Analysis

1. Plutonium Isotopic Compositions

Table I shows the gamma-ray plutonium isotopic compositions (in weight percent) for the dissolver solutions as determined by IDGS. The range of plutonium isotopic abundances (wt%) is 0.34% to 1.24% for ^{238}Pu, 58.24% to 70.84% for ^{239}Pu, 21.21% to 27.94% for ^{240}Pu, 4.00% to 8.9% for ^{241}Pu, and 1.4% to 5.2% for ^{242}Pu. The uncertainties represent the estimated precision (1σ) of gamma-ray spectroscopy for a 1-h count time as calculated from counting statistics including uncertainties from relative efficiencies. The typical precision within a 1-h count time is 0.6% for ^{238}Pu, 0.2% for ^{239}Pu, 0.5% for ^{240}Pu, and 1.3% for ^{241}Pu.

The plutonium isotopic compositions of dissolver solutions as determined by IDGS and IDMS are compared in Table II. The average IDGS/IDMS ratios for six samples are 1.000, 1.003, 0.998, and 1.003 for ^{239}Pu, ^{240}Pu, ^{241}Pu, and ^{240}Pu/^{239}Pu, respectively. The agreements between IDGS and IDMS are extremely good. For ^{238}Pu wt%, IDGS results are compared with alpha counting results. The bias, ~2%, between IDGS and alpha counting might come from the uncertainty of the alpha counting method.

TABLE I. Plutonium Isotopic Compositions (wt%) of Dissolver Solutions as Determined by IDGS

Dissolver Solution	^{238}Pu		^{239}Pu		^{240}Pu		^{241}Pu		^{242}Pu
	wt%	σ (%)	wt%	σ (%)	wt%	σ (%)	wt%	σ (%)	wt%
1	0.729	0.50	66.793	0.14	22.754	0.41	7.034	1.11	2.69
2	0.498	0.59	69.738	0.15	21.995	0.47	5.802	1.22	1.97
3	0.480	0.76	70.576	0.19	21.211	0.62	5.861	1.57	1.87
4	1.242	0.47	58.241	0.16	26.419	0.38	8.899	0.99	5.20
5	0.340	0.82	70.840	0.19	23.418	0.60	4.001	1.67	1.40
6	0.751	0.63	59.601	0.21	27.943	0.47	7.362	1.31	4.34

TABLE II. Comparison of Plutonium Isotopic Compositions as Determined by IDGS and IDMS

Dissolver Solution	IDGS/IDMS				
	^{238}Pu*	^{239}Pu	^{240}Pu	^{241}Pu	^{240}Pu/^{239}Pu
1	1.0549	1.0027	1.0026	0.9905	1.0000
2	0.9482	1.0008	1.0093	1.0008	1.0084
3	0.9413	1.0051	1.0000	0.9909	0.9949
4	0.9971	0.9963	0.9970	0.9999	1.0007
5	0.9638	1.0012	1.0112	1.0051	1.0100
6	0.9937	0.9942	0.9974	0.9983	1.0033
Average	0.9832	1.0000	1.0029	0.9976	1.0029
Std. Dev.	0.0420	0.0041	0.0061	0.0058	0.0056
% RSD	4.26	0.41	0.60	0.58	0.56

*For ^{238}Pu wt%, IDGS results are compared with alpha counting results.

2. Plutonium Element Concentrations

The plutonium element concentrations from IDGS and IDMS are compared in Table III. The plutonium concentrations of six dissolver solutions varied from 0.62 g Pu/L to 1.34 g Pu/ L. The typical uncertainty of IDGS measurements for both unspiked and spiked samples is less than 1% for a 1-h count time. The average plutonium concentration obtained by IDGS in this experiment agrees with that obtained by IDMS within 0.13%. That is consistent with the results from previous experiments of 0.16% by anion-exchange resin and filter techniques.[5] This result indicates that the precision and accuracy of the plutonium analysis are not affected while uranium is retained in the sample with plutonium.

TABLE III. Comparison of Plutonium Concentrations of Dissolver Solutions as Determined by IDGS and IDMS

Dissolver Solution	IDMS (g Pu/L)	IDGS (g Pu/L)	IDGS σ (%)	IDGS/IDMS
1	1.168	1.169	0.93	1.0011
2	0.850	0.847	0.93	0.9961
3	0.615	0.619	1.17	1.0058
4	1.342	1.344	0.87	1.0012
5	0.677	0.676	1.12	0.9984
6	0.941	0.946	0.92	1.0052
Average				1.0013
Std. Dev.				0.0037
% RSD				0.37

C. Uranium Analysis

The results of ^{235}U concentration in dissolver solutions as determined by using Eq. 7 are compared with those measured by IDMS in Table IV. The agreement between the two methods are reasonably good, especially for solutions 3 and 4. On the other hand, solutions 2 and 6 showed larger disagreements. These disparities result from a long indeterminate delay between sample preparation and gamma-ray spectrometry measurements. The lack of accurate information on sample preparation and measurement dates for IDGS did not permit us to make appropriate decay corrections.

To prove the principle, we prepared four synthetic mixed solutions (using the same separation methods as dissolver solutions) and measured them as soon as the samples had been prepared. Four mixed solutions contained the same uranium concentration and isotopic distribution but varied with solution volumes and U/TEVA•Spec resin volumes (Table V).

TABLE IV. Comparison of ^{235}U Concentrations of Dissolver Solutions as Determined by IDGS and IDMS

Dissolver Solution	^{235}U Concentration (g/L) IDMS	^{235}U Concentration (g/L) IDGS	IDGS/IDMS
1	1.880	1.710	0.91
2	1.827	1.531	0.84
3	1.243	1.236	0.99
4	1.267	1.255	0.99
5	1.956	1.793	0.92
6	1.026	0.795	0.78

TABLE V. Volumes of Synthetic Mixed Solutions

Solutions	Volume (mL)	
	U/Pu Mixed Solution	U/TEVA•Spec resin
1	1	1
2	1	2
3	2	2
4	1	4

In addition to ^{235}U concentration measurements, we also investigated the higher recovery rates for different combinations of solution volumes and absorption resin volumes. The uranium recovery rates of the four solutions were varied within 30%. Therefore, the most practical and economical combination would be solution 1 using 1 mL mixed solution and 1 mL absorption resin.

The ^{235}U concentrations of synthetic mixed solutions from IDGS and the known values are compared in Table VI. The known values were determined by mass spectrometry for uranium isotopic wt% and by hybrid K-edge/K XRF (HKED) for uranium concentrations. The agreements between IDGS and the known values are very good.

TABLE VI. Comparison of ^{235}U Concentrations of Pure Mixed Solutions as Determined by IDGS and Known Values

Pure Mixed Solution	^{235}U Concentration (g/L) Known Value (KV)*	^{235}U Concentration (g/L) IDGS	IDGS/ KV
1	2.118	2.116	0.999
2	2.118	2.132	1.007
3	2.118	2.122	1.002
4	2.118	2.110	0.996

*Uranium isotope weight percents were determined by mass spectrometry and uranium concentrations were measured by HKED.

V. Conclusions

The previous IDGS technique[1-5] analyzed plutonium only. By developing a new sample preparation method in this study, we can now recover uranium from dissolver solutions. The new sample preparation method rapidly separates fission products and recovers plutonium and uranium from highly radioactive input spent-fuel dissolver solutions through an extraction chromatographic technique. Precision and accuracy of the plutonium analysis are not affected, and even better, while uranium is retained in the sample with plutonium. For plutonium isotopic compositions in dissolver solutions, the bias between IDGS and IDMS is <0.3% for the ^{240}Pu/^{239}Pu ratio and <0.01% for ^{239}Pu wt%. The precision is ~0.5% for the ^{240}Pu /^{239}Pu ratio and <0.2% for ^{239}Pu wt%, within a 1-h count time. For plutonium concentrations in dissolver solutions, the bias between IDGS and IDMS is less than 0.15% with a precision of better than 1% within a 1-h count time.

The results of the first simultaneous measurements of ^{235}U concentrations with plutonium concentrations and isotopic analyses are very encouraging. Future proof-of-principle experiments for dissolver solutions should be continued. Decay corrections should be carefully made if the IDGS measurements follow sample preparation dates by more than 24 hours. For comparing IDGS to IDMS or other methods, the same samples should be used and the analysis dates for IDMS should be also accurately recorded.

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