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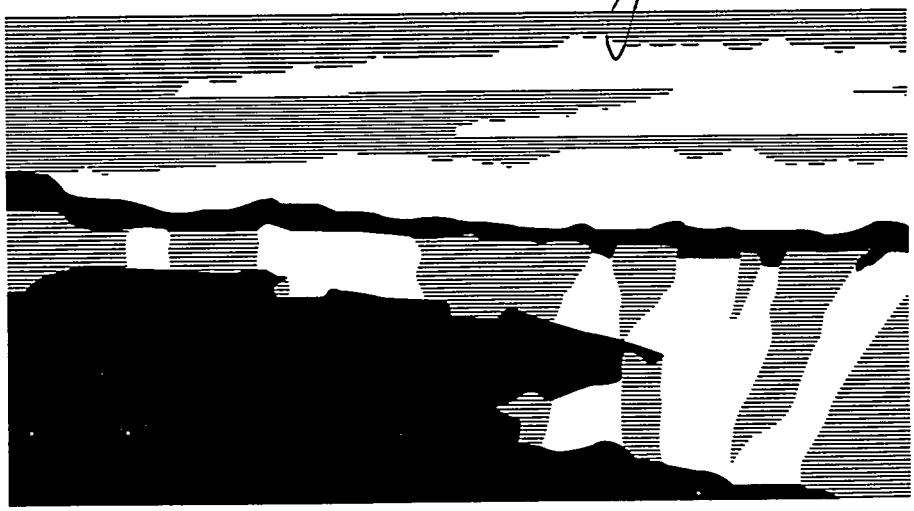

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FEASIBILITY STUDY OF PLUTONIUM AND URANIUM MEASUREMENTS IN INPUT DISSOLVER SOLUTIONS[a]

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ABSTRACT

We are studying the isotope dilution gamma-ray spectrometry (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. 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, a new sample preparation method is being studied and developed: extraction chromatography. The technique uses U/TEVA•Spec resin to separate fission products and recover both uranium and plutonium in the resin from dissolver solutions for measurements by high-resolution gamma-ray spectrometry.

I. INTRODUCTION

Accurate, rapid determinations of the plutonium and uranium in input dissolver solutions at reprocessing plants are very important for input accountability analysis and nuclear material control and for on-site verification: essential elements of the near-real-time accounting system at reprocessing plants. Recently, we have developed a novel technique, isotope dilution gamma-ray spectrometry (IDGS),[1-3] by using the isotope dilution principle and low-energy, high-resolution gamma-ray spectrometry.

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 isotope dilution mass spectrometry (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 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 bead (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. 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. 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

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also recovered from the sample. Of the few separation methods available, we found extraction chromatography[6] to be the best method.

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

II. 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. However, for simultaneous measurements of uranium and plutonium, we are developing a new sample preparation method, extraction chromatography using U/TEVA•Spec resin[6] (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 sorbed 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 HNO_3, 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 re-washed 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 concentration measurements, 1-ml dissolver solutions were well mixed with spikes. These large-size dry (LSD) spikes, containing ~98% ^{239}Pu and ~19% ^{235}U, 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.

III. MEASUREMENT METHOD

Details of the IDGS measurement technique and method are described in Refs. 1-2. 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_u, as follows:[1-2]

$$C_u = \frac{M_s}{V_u} \bullet \frac{W_s^9}{W_u^9} \bullet \frac{R_m - R_s}{R_u - R_m} ,$$

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.

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 live-time corrector, and a 16-k-channel analog-to-digital converter.

IV. 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 1 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 found 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. The 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 removed well with the extraction chromatographic method.

B. 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

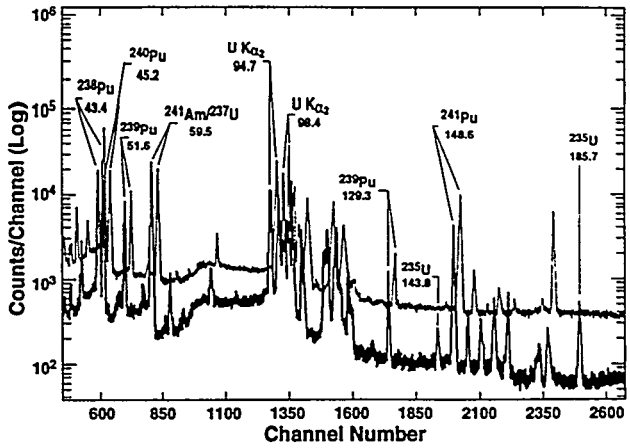

Fig. 1. Gamma-ray spectra of dissolver solutions from two different sample preparation methods, for a 1-h count time. For easy comparison, we shifted the plot of the top gamma-ray spectrum slightly. The top (dotted) spectrum is the gamma-ray spectrum from a dissolver solution obtained by using anion-exchange 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.

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 6 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.

B. 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

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 computed with alpha counting results.

Pu/l to 1.34 g Pu/ℓ. The typical uncertainty of IDGS measurements is less than 1% within a 1-h count time for both unspiked and spiked samples. 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.

V. CONCLUSIONS

The previous IDGS technique analyzed plutonium only. By developing a new sample preparation method, 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

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

Dissolver Solution	IDMS (g Pu/L)	IDGS		IDGS/IDMS
		(g Pu/L)	σ (%)	
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

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.

For future work, we are developing a prototype IDGS system, including analysis physics and algorithms and analysis software, to simultaneously determine uranium concentration and isotopics along with plutonium concentration and isotopics in input spent-fuel dissolver solutions at a reprocessing plant.

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