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Title: **IMPROVEMENT IN MEASUREMENTS OF PLUTONIUM IN SPENT-FUEL DISSOLVER SOLUTIONS**

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IMPROVEMENT IN MEASUREMENTS OF PLUTONIUM IN SPENT-FUEL DISSOLVER SOLUTIONS

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Abstract

We have studied the improvement in simultaneous measurements of concentrations and isotopic compositions for plutonium in input spent-fuel dissolver solutions at a reprocessing plant by isotope dilution gamma-ray spectrometry (IDGS) technique. The IDGS technique uses the high-resolution low-energy gamma-ray spectrometry and isotope dilution method. The dissolver solutions are subsequently measured using high-resolution gamma-ray spectrometry following the fission product separations by extraction chromatography using U/TEVA•Spec resins. The improved method can simplify the separation procedure and save more than 2 hours in sample preparation time. The results of plutonium concentrations and isotopic compositions of dissolver solutions analyzed by IDGS agree very well with those obtained by traditional isotope dilution mass spectrometry. The rapid and accurate IDGS technique with the improved separation method could provide a timely, less expensive, and simpler on-site verification method for the input accountability measurements.

Introduction

The rapid and accurate measurements of samples derived from spent fuel is a requisite 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. Presently, materials are prepared and sent to a centralized location for destructive analysis by isotope dilution mass spectrometry (IDMS); this process is expensive and time consuming and therefore precludes the possibility of timely results. One possible means of reducing the analysis time is to employ on-site nondestructive assay techniques where samples can be analyzed within the processing facility. One such technique that recently has been developed, isotope dilution gamma-ray spectrometry (IDGS),[1-3] employs a standard plutonium spike and passive gamma spectroscopy to determine the plutonium isotopics and concentration in spent-fuel dissolver solutions.

Isotope dilution gamma spectroscopy permits the simultaneous determination of plutonium isotopics and concentration in spent fuel dissolver solutions based on information from two gamma spectra, one each from the spiked and unspiked solutions, and a previously characterized plutonium spike. Resin bead techniques have previously been developed using ion-exchange[1-2] and extraction chromatography[3] to rapidly separate fission fragments and recover plutonium for the spectroscopy measurements. The plutonium isotopic ratios are determined from the high-intensity low-energy gamma lines since typical samples may contain less than 0.5 milligrams of plutonium; in principle; however, any resolved plutonium lines may be used for this purpose.

For concentration measurements, the technique involves the dissolution of a plutonium spike with well characterized mass and isotopics: previously used spikes consisted of 0.00245% ^{238}Pu, 97.921% ^{239}Pu, 2.0604% ^{240}Pu, 0.0141% ^{241}Pu, and 0.001324% ^{242}Pu. Gamma spectra are acquired for the spent-fuel dissolver solution before and after the spike is added and the relative isotopics are determined for each.

Previously, over 20 dissolver solutions[1-3] with plutonium concentrations varied from 0.6 g Pu/L to 1.6 g Pu/L have been analyzed. The range of plutonium isotopic abundances in weight percent is 0.34% to 1.24% for ^{238}Pu, 58.24% to 70.84% for ^{239}Pu, 21.21% to 27.94% ^{240}Pu, 4.00% to 8.9% for ^{241}Pu, and 1.4% to 5.2% for ^{242}Pu. For plutonium isotopic analysis of dissolver solutions, the agreements between the results of IDGS and IDMS are extremely good. The average IDGS/IDMS result ratios are 1.000, 1.003, 0.998, and 1.003 for ^{239}Pu, ^{240}Pu, ^{241}Pu, ^{240}Pu/^{239}Pu respectively.

To reduce sample preparation and measurement time, we have studied several separation scheme options. This paper will discuss the improvement in fission product separation and measurement methods on input spent-fuel dissolver solutions and will also examine the results of plutonium by using this simplified sampling method incorporated into the IDGS technique.

Improvements in Sample Preparation

In addition to ion-exchange, we have developed a new sample preparation method, extraction chromatography using U/TEVA•Spec resin[3] (for uranium and tetravalent actinides specifically) to purify and recover both plutonium and uranium 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.

The new separation scheme for preparing the sample by using the extraction chromatography is showed in Fig. 1. Each 1 mL aliquot for the spiked samples and the unspiked samples were taken from dissolver solutions, and the weight of the taken 1 mL aliquot sample was measured by a precise electronic balance. The spiked samples were prepared by dissolving the dissolver solutions (1 mL aliquot) with large size dry (LSD)[4] spikes at 90°C on a heater and then mixing them by a magnetic stirrer. Plutonium in these samples was completely adjusted to tetra-valence 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. Eluted ones were 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 have possibly influencing the gamma-ray measurements if significant amount of fission products were still contained in the samples. Each sample was carefully removed not to contaminate with a plastic bag from a glove box and measured by a high-resolution gamma-ray spectrometry (HRGS).

A typical gamma-ray spectrum of spent-fuel dissolve solution after chemical separation with extraction chromatography using U/TEVA•Spec resins is shown in Fig. 2.

To improve and simplify the sample preparation procedure, we have considered and examined several optional separation schemes as follows:

1. Scheme A: Same as discussed above and shown in Fig. 1, except heat at 90°C for 30 min. after valency adjustment with $NaNO_2$.

2. Scheme B: Same as discussed above and shown in Fig. 1, except heat at 90°C for 10 min. after valency adjustment with $NaNO_2$.

3. Scheme C: No heat steps after additions of both ferrous sulfamate and $NaNO_2$ for valency adjustment.

4. Scheme D: No elution with 0.01M-HNO_3 and the second fission product's rewashing. Bag out the column for HRGS after the first fission product's removal. Scheme D is shown in Fig. 3.

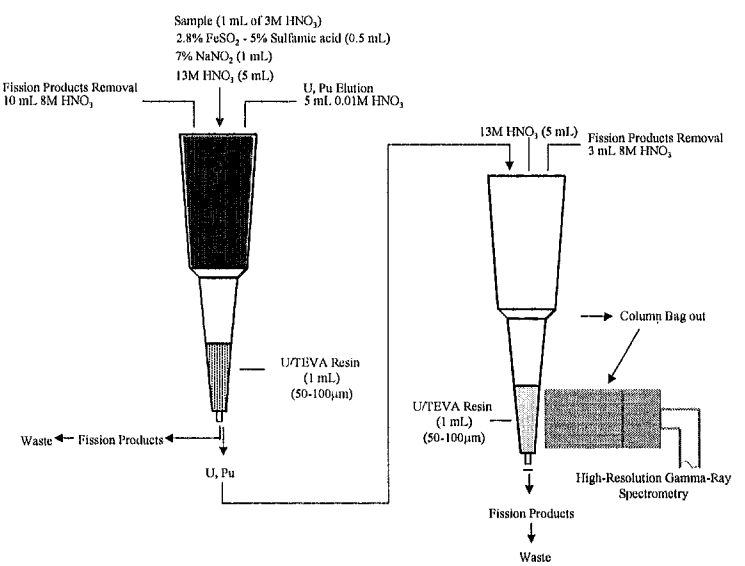

Fig. 1. Plutonium and Uranium separation scheme using U/TEVA•Spec® resin

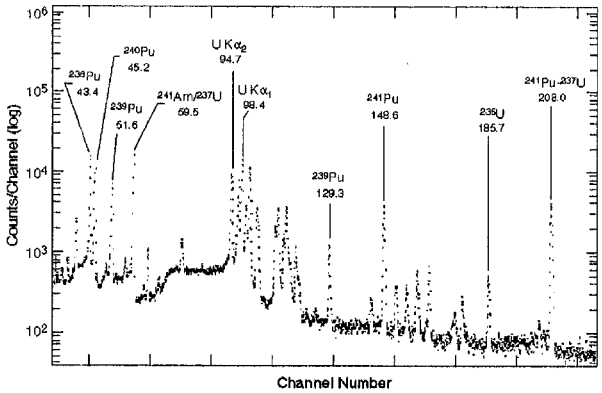

Fig. 2. Gamma-ray spectrum of spent-fuel dissolve solution after chemical separation with extraction chromatography using U/TEVA•Spec resins.

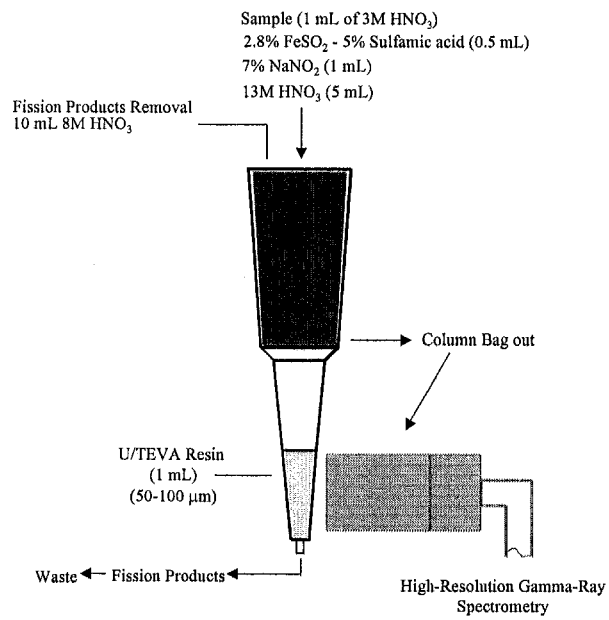

Fig. 3. Simplification of separation scheme using U/TEV•Spec® resin.

Analysis Methods

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 0.5 mg of plutonium), the isotopic ratios $^{238}Pu/^{239}Pu$, $^{240}Pu/^{239}Pu$, and $^{241}Pu/^{239}Pu$ are best determined from the very 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] 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(Pu), in the unknown dissolver solution is then determined by calculating the difference among the isotopic $^{240}Pu/^{239}Pu$ ratios of the spike, the spiked samples, and the unspiked samples.

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

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 spike-related parameters W_s^9 and R_s are known values while M_s are V_u are determined by standard analytical techniques. This leaves the quantities W_u^9 and R_u in the unspiked dissolver-solution sample and R_m in the spiked sample to be determined via gamma-ray spectrometry.

Results and Discussions

Table I shows the gamma-ray plutonium isotopic compositions (in weight percent) for the dissolver solutions as determined by IDGS. The uncertainties represent the estimated precision (1σ) of gamma-ray spectroscopy as calculated from counting statistics, including uncertainties from relative efficiencies. The typical precision within a one-hour count time is 0.6% for ^{238}Pu, 0.2% for ^{239}Pu, 0.5% for ^{240}Pu, and 1.3% for ^{241}Pu. We measured four hours for each sample in this experiment. The IDGS results are also compared with IDMS results in Table I. The IDGS results of four separation schemes are similar and agree with the IDMS reasonably well.

The plutonium element concentrations from IDGS and IDMS are compared in Table II. The plutonium concentrations obtained by IDGS in this experiment agree with those obtained by IDMS within 1% for schemes A and B and within 0.5% for schemes

C and D. The results of schemes C and D are very encouraging. The simplified separation schemes C and D could save more than two hours in sample preparation time. We are planning to measure more samples with schemes C and D to confirm the present results.

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

Sample	Separation Scheme	IDGS						IDGS / IDMS		
		^{239}Pu		^{240}Pu		^{241}Pu		^{239}Pu	^{240}Pu	^{241}Pu
		wt%	σ (%)	wt%	σ (%)	wt%	σ (%)			
1	A	58.77	0.15	26.713	0.38	7.229	0.94	0.9969	0.9695	1.0175
2	B	59.53	0.13	26.849	0.3	7.318	0.83	1.0098	0.9744	1.03
3	B	60.956	0.08	25.919	0.19	6.878	0.51	1.0035	0.9953	0.9967
4	C	59.645	0.1	26.946	0.23	7.107	0.64	1.0117	0.9779	1.0003
5	D	59.453	0.13	27.021	0.29	7.218	0.7	1.0085	0.9807	1.0159

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

Dissolver Solution	Separation Scheme	IDMS (g Pu/L)	IDGS (g Pu/L)	IDGS/ IDMS
1	A	1.3633	1.276	0.9901
2	B	1.2989	1.276	1.0180
3	B	1.2143	1.217	0.9974
4	C	1.2677	1.276	0.9935
5	D	1.2815	1.276	1.0043

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