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IN-LINE MEASUREMENT OF PLUTONIUM AND AMERICIUM IN MIXED SOLUTIONS*

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ABSTRACT

A solution assay instrument (SAI) has been developed at the Los Alamos National Laboratory and installed in the plutonium purification and americium recovery process area in the Los Alamos Plutonium Processing Facility. The instrument is designed for accurate, timely, and simultaneous nondestructive analysis of plutonium and americium in process solutions that have a wide range of concentrations and Am/Pu ratios. For a 25-mL sample, the assay precision is <1%, both for plutonium and for americium having concentrations >5 g/L within a 2000-s count time.

INTRODUCTION

During the past several years, the Plutonium Processing Facility at the Los Alamos National Laboratory has prepared ceramic-grade plutonium dioxide in production quantities by purifying impure plutonium metal to plutonium oxide.[1] Large quantities of americium and other impurities are removed from the plutonium as peroxide filtrates in this process. Because of the increasing demand for the use of americium in oil-well logging instruments and other uses, routine operations to recover the americium have been developed and implemented.[2] Figure 1 shows partial flow diagrams for a plutonium purification process based on selective precipitation and an americium recovery and purification process based on ion exchange and oxalate precipitation.

The solutions generated from the plutonium purification and americium recovery processes have a wide range of total (plutonium and americium) concentrations and Am/Pu ratios: for solutions generated from the plutonium purification process, the total concentrations range from 0.1 to 500 g/L and the Am/Pu ratios vary from a few parts per million to 10; for solutions generated from the americium recovery process, the total concentrations range from 0.1 to 50 g/L and the Am/Pu ratios vary from 0.5 to 100.

It is important to both special nuclear material control and process control to determine the plutonium and americium content of these solutions accurately and rapidly. The assay procedure needs to be as simple as possible for routine operation by process technicians. An in-line solution assay instrument (SAI) that satisfies these criteria has been designed at Los Alamos and installed in the plutonium purification and americium recovery process area in the Los Alamos Plutonium Processing Facility. Solution types, with total concentration and Am/Pu ratios, are shown at the SAI measurement points in Fig. 1.

MEASUREMENT METHOD

The SAI is based upon high-resolution gamma-ray measurements. Because the plutonium in the purification process is of known isotopic composition, the total plutonium concentration of the solutions can be determined by using the 413.7-keV gamma rays from ^{239}Pu. The americium concentration is determined by a weighted average based on the measured intensities of the 376.6-keV (after removal of the contribution from ^{239}Pu at 375 keV) and 419-keV gamma rays from ^{241}Am. The reason for not using high-intensity low-energy gamma rays (for example, 125 keV, 129 keV) is because the correction factors and uncertainties become very large; the transmission of low-energy gamma rays decreases dramatically as the total concentration increases up to 200 g/L. Furthermore, as the ^{241}Am/^{239}Pu ratios and/or ^{237}U/^{239}Pu ratios in the solutions become very high, the Compton continuum from the intense 208-keV gamma ray makes the lower energy unusable. To maximize the SAI's sensitivity and precision at both low and high concentrations for such high ratios, a 0.76-mm-thick tungsten filter was installed in front of the detector. The filter reduces the lower energy portion of the gamma-ray spectrum and provides adequate reduction of the 416-keV sum peak that results from pileup of the 208-keV gamma rays and interferes with the 413.7-keV ^{239}Pu peak. The transmission correction is made by counting gamma rays emitted from an external transmission source (a 20-g nickel-plated plutonium metal disk) through the sample. Corrections for rate-related counting losses as a result of deadtime and pile-up are made by counting the 88-keV gamma rays

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emitted from a ^{109}Cd source attached directly to the detector housing.

The gamma-ray net peak areas are calculated by using a straight-line background subtraction method. Both the 413.7- and 419-keV gamma rays are clean single peaks, while the 376.6-keV gamma rays are part of an unresolved doublet that includes the contribution from ^{239}Pu at 375 keV. The americium content determined from the unresolved doublet can be expressed as follows:

$$Am\ (g) = \frac{I}{I(376.6)}\left[\frac{R}{K} - \frac{I(375)}{I} \times {}^{239}Pu\ (g)\right] \quad ,$$

where

I(375), I(376.6) = specific activity of 375-, 376.6-keV gamma rays, respectively, (in γ/g/s),

$I = I(375) + I(376.6)$,

R = count rate of (375 + 376.6) unresolved peak (in counts/s) with the corrections of transmission and rate-related counting losses,

^{239}Pu = ^{239}Pu content (in g) in the sample as determined by the intensity of 413.7 keV,

K = calibration constant (in counts/G/s),

and

$$G = \frac{I(375)}{I} \times {}^{239}Pu(g) + \frac{I(376.6)}{I} \times {}^{241}Am(g).$$

The SAI hardware, software, and assay procedure have been described elsewhere.[3] Briefly, the SAI consists of a sample chamber, a germanium detector and associated electronics, a NOVA 2 (28K of 16-bit memory) minicomputer-based multichannel analyzer with a digitally stabilized 4K analog-to-digital converter, a dual magnetic-tape cassette unit, and a terminal. The sample chamber houses a polystyrene sample bottle and a rotating tungsten shutter. The sample bottle is a right circular cylinder (10 cm^2 by 4 cm) with a maximum solution volume of 40 mL. For routine assays, 25-mL solution samples are drawn through clean calibrated automatic pipettes by process technicians. The shutter is located above the sample bottle and is pneumatically operated under computer control; the transmission source is centered on one side of the shutter. The germanium detector, which has a resolution of 1.55 keV at 413.7 keV, is located outside the glovebox, directly under the sample bottle. No modifications were necessary to the 4.75-mm-thick stainless steel glovebox floor.

An automatic data-acquisition-and-analysis program written in interactive BASIC language gives simple instructions for the assay procedure and asks the operator to respond to displayed questions by entering numerical codes at the terminal.

The assay procedure includes a background run, a transmission-source run, a transmission-source-plus-sample run, and a sample-only run. The background run and the transmission-source run are required once a day; the data are stored in the computer. The transmission-source-plus-sample run and the sample-only run are performed for each sample; the system automatically combines the resulting data with the stored background and transmission-source data for calculating the final assay results. The data collection times for the concentrated solutions were 1000-s (500-s each for the transmission-plus-sample run and for the sample-only run). For low-concentration solutions, the data collection times were 2000-s (100-s for the transmission-plus-sample run and 1900-s for the sample-only run).

RESULTS AND DISCUSSION

The instrument was calibrated with solution standards prepared by the Analytical Chemistry Laboratory at Los Alamos. Six plutonium standards, having concentrations ranging from 0.45 to 261 g Pu/L, were used for the original plutonium calibration. The typical precision of the plutonium assay[3] was <0.75% for concentrations >30 g Pu/L within a 1000-s count time and ~4% at 0.5 g Pu/L within a 2000-s count time. Four americium standards, having concentrations ranging from 0.1 to 4.5 g Am/L, were used for americium calibration. The precision of the americium analysis was <1% for concentrations >4.5 g Am/L and ~4% at 0.3 g Am/L within a 2000-s count time.

The performance of the SAI in assaying plutonium process solutions[3] has been evaluated by comparing results from its analyses with results from chemical analyses (photometric titration). The results agreed very well for plutonium solutions that were free of particulate matter.

The SAI accuracy for simultaneous analysis of americium and plutonium in mixed solutions from process samples is tested by comparing the SAI results with those of radioanalysis. Radioanalysis, which is routinely used for analyzing process samples, determines (1) plutonium content by alpha counting after the plutonium is extracted with 2-thenoyl trifluoroacetone and (2) americium content[4] by integral counting gamma activity above 32 keV. The routine accuracy of the radioanalysis is ~1 to 5% for americium and ~5 to 10% for plutonium. Preliminary results for 15 process samples are summarized in Table I. The radioanalysis results and their associated uncertainties are the means and mean deviations of two measurements, respectively. Although the plutonium concentrations were relatively low (<1.2 g Pu/L) and Am/Pu ratios were relatively high (from 0.6 to 34.9), the average relative difference between the SAI and radioanalysis results was 0.21%, which indicates that there is no significant bias between them. However, an

TABLE I

COMPARISON OF SAI RESULTS WITH RADIOANALYSIS RESULTS FOR SIMULTANEOUS AMERICIUM AND PLUTONIUM MEASUREMENTS

	Am Concentration (g/L)			Pu Concentration (g/L)			
Sample No.	RAD[a]	SAI	Δ%[b]	RAD	SAI	Δ%	Am/Pu[c]
1	0.90 ± 0.02	0.86 ± 0.02	-4.4	0.88 ± 0.02	0.92 ± 0.04	4.6	0.9
2	0.41	0.39 ± 0.02	-4.9	0.098 ± 0.004	0.116 ± 0.04	18.4	3.4
3	3.10 ± 0.07	3.06 ± 0.03	-1.3	0.68	0.55 ± 0.07	-4.4	4.7
4	5.15	4.87 ± 0.05	-5.4	0.97 ± 0.02	0.89 ± 0.09	-8.3	5.5
5	3.10	2.68 ± 0.03	-13.6	0.83 ± 0.04	0.90 ± 0.07	8.4	3.0
6	1.56 ± 0.06	1.54 ± 0.02	-1.3	0.068 ± 0.02	0.053 ± 0.05	-22.1	29.1
7	2.39	2.20 ± 0.03	-7.9	0.99 ± 0.04	1.14 ± 0.06	15.2	1.9
8	3.95	3.87 ± 0.04	-2.0	1.02 ± 0.05	1.03 ± 0.08	1.0	3.8
9	1.90 ± 0.07	1.85 ± 0.02	-2.6	0.057 ± 0.002	0.053 ± 0.058	-7.0	34.9
10	2.36	2.39 ± 0.04	1.3	0.67 ± 0.02	0.80 ± 0.07	19.4	3.0
11	3.81	3.73 ± 0.04	-2.1	1.15 ± 0.05	0.93 ± 0.08	-19.1	4.0
12	4.41	4.10 ± 0.04	-7.0	0.91 ± 0.04	0.70 ± 0.08	-23.1	5.9
13	3.43 ± 0.04	3.35 ± 0.04	-2.3	0.54 ± 0.02	0.535 ± 0.076	-0.9	6.3
14	3.25	3.00 ± 0.03	-7.7	0.66 ± 0.01	0.59 ± 0.07	-10.6	5.1
15	0.049	0.044 ± 0.01	-10.2	0.060 ± 0.01	0.079 ± 0.035	31.7	0.6

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[a] Radioanalysis results and their associated uncertainties are represented by the means and mean deviations, respectively, of two measurements. Mean deviations <1% are not listed in the table.

[b] Δ = (SAI - RAD)/RAD

[c] According to SAI results

~5% negative bias was obtained between SAI and radioanalysis results for americium concentrations. The possible explanation for the higher radioanalysis results may be due to contribution of ^{237}U to the 59.5-keV gamma ray, which is commonly associated with ^{241}Am. To obtain the best results for americium from radioanalysis, the uranium needs to be separated from the americium. Investigation is now under way to compare the radioanalysis results obtained after the uranium is removed.

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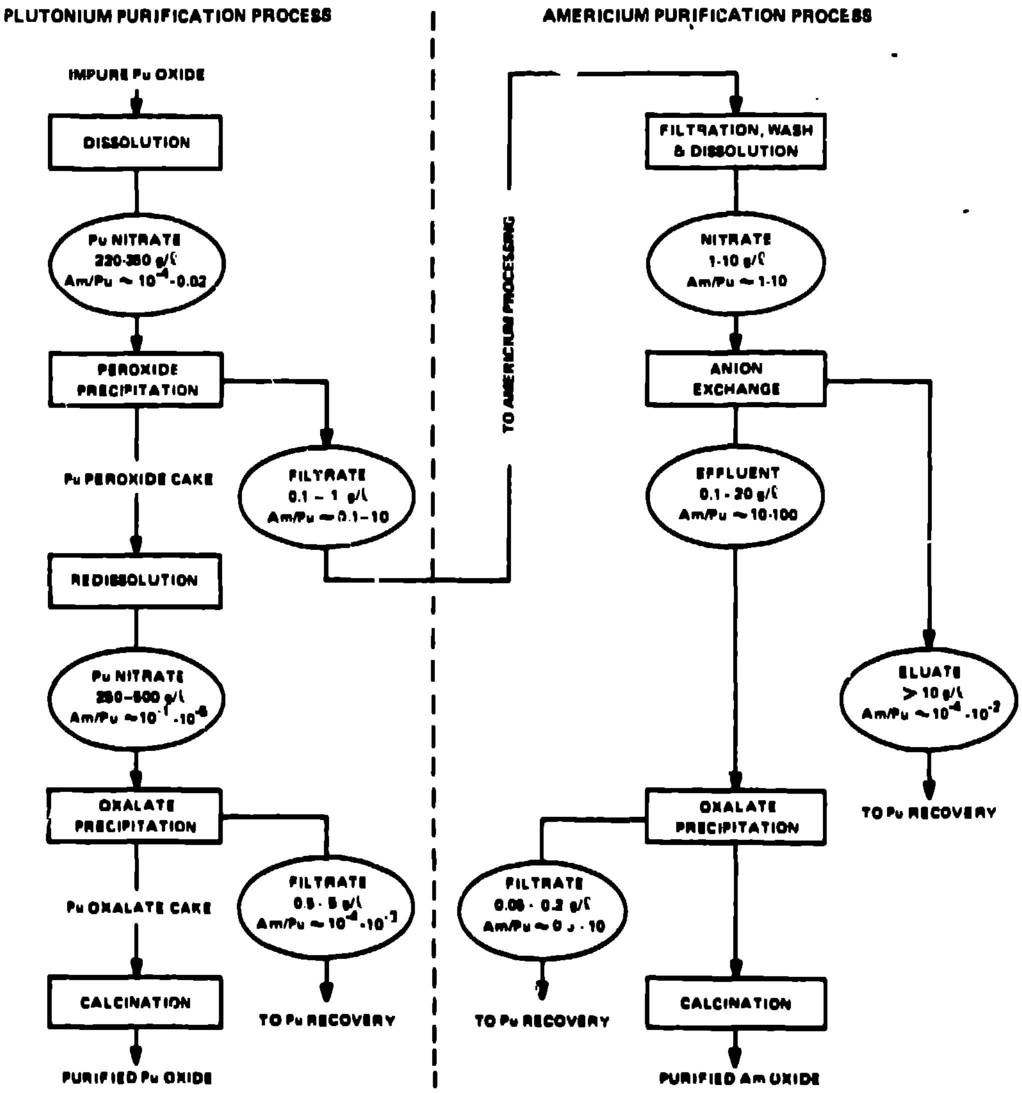

Fig. 1. Flow diagram of the plutonium purification process and the americium recovery and purification process. Solution types, with total (plutonium and americium) concentrations and Am/Pu ratios, are shown at the SAI measurement points.