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HYBRID CHEMICAL AND NONDESTRUCTIVE ANALYSIS TECHNIQUE*

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Abstract

A hybrid chemical/NDA technique has been applied at the Los Alamos National Laboratory to the assay of plutonium in ion-exchange effluents. Typical effluent solutions contain low concentrations of plutonium and high concentrations of americium. A simple trioctylphosphine oxide (TOPO) separation can remove 99.9% of the americium. The organic phase that contains the separated plutonium can be accurately assayed by monitoring the uranium L x-ray intensities.

1. Introduction

In the past, the use of nondestructive assay (NDA) techniques for rapid analysis of nuclear material has been limited because NDA instruments are usually designed for specific types of samples. However, prior chemical treatments can increase the versatility of the instruments by changing various sample types into an optimum form for the instrument or by removing radioactive components that interfere with the measurement. In this paper, we report the first application at the Los Alamos National Laboratory of a hybrid chemical/NDA technique to the assay of plutonium in ion-exchange effluents.

Plutonium scrap generated at the Los Alamos Plutonium Processing Facility is routinely dissolved in nitric acid in the plutonium recovery processes. Plutonium solutions of less than 1 g/l are routed to the lean-residue ion-exchange process; the more concentrated plutonium solutions go to the dissolver-solution ion-exchange process. Typical effluent solutions from the ion-exchange columns contain low concentrations of plutonium (1 to 200 mg/l) that the process fails to remove. Because all the americium and ^{237}U remain in the effluent solution, the ^{241}Am concentration can be as much as 20 times that of the plutonium in which case the americium activity would be 1000 times higher. Accurate and prompt measurement of plutonium in these large-volume effluents is required for process and accountability controls.

2. Materials and Methods

Measurement of low concentrations of plutonium by a passive NDA technique requires more abundant signals than those produced by the passive gamma rays of plutonium. (Table I lists the alpha, gamma-ray, and L x-ray specific activities of plutonium isotopes and ^{241}Am .) The 413.7-keV gamma ray of ^{239}Pu , for example, is suitable for determining plutonium only at concentrations greater than 1 g/l. Although the

TABLE I

SPECIFIC ACTIVITIES OF RADIOISOTOPES

Isotope	Alpha ($\mu/\text{s}\cdot\text{g}$)	γ Energy (keV)	Gamma-Ray ($\gamma/\text{s}\cdot\text{g}$)	L X Ray ^a (x rays/s·g)
^{238}Pu	6.33×10^{11}	43.5	2.5×10^8	7.21×10^{10}
		152.7	6.4×10^6	
^{239}Pu	2.30×10^9	51.6	6.2×10^5	1.06×10^8
		129.3	1.4×10^5	
		375.0	3.6×10^4	
		413.7	3.5×10^4	
^{240}Pu	3.34×10^9	45.2	3.8×10^6	8.42×10^8
		160.4	2.5×10^4	
^{241}Pu	9.15×10^7	148.6	7.3×10^6	1.03×10^7
^{242}Pu	1.45×10^8	---	---	1.23×10^7
^{241}Am	1.27×10^{11}	26.3	3.1×10^9	4.6×10^{10}
		59.5	4.5×10^{10}	
		208.0	1.0×10^6	

^aTabulated is the total L x-ray intensity. The L x-ray yield per alpha decay is obtained from Ref. 3.

alpha specific activity is much higher, alpha counting requires extensive and time-consuming sample preparation.

The L x rays induced from the plutonium alpha decay are nearly 100 times more abundant than plutonium gamma rays.^{1,2} Plutonium decay is followed by uranium x rays, whereas decay of americium and ^{237}U are followed by neptunium x rays. The uranium L x rays ($L_{\alpha 1}$, $L_{\beta 1}$, and $L_{\gamma 1}$) can therefore be used to monitor the plutonium concentration. Figure 1 depicts an L x-ray spectrum from a plutonium solution that contains an Am/Pu ratio of 0.002 and a superimposed spectrum from americium in the same energy region.

The major limitation of using uranium L x rays for the assay of plutonium in effluent solutions is interference of neptunium x rays. For an Am/Pu weight ratio of 1, the Np $L_{\beta 1}$ /U $L_{\beta 1}$ peak area ratio is approximately 290, which renders the measurement impossible to perform. Because the Am/Pu ratio in these effluent solutions is as high as 20, nondestructive assay of the plutonium cannot be performed based on uranium L x rays without prior chemical separation of plutonium from americium.

We demonstrated that a simple and rapid solvent extraction⁴ can effectively separate the plutonium from americium, such that the uranium

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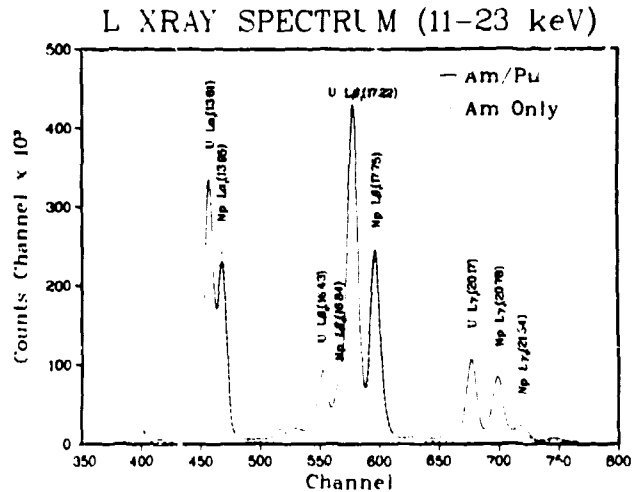


Fig. 1. Passive L x-ray spectrum from plutonium, americium, and ^{237}U . Plutonium emits uranium x rays after alpha decay, whereas americium and ^{237}U emit neptunium x rays.

x rays are measured with little interference. The extraction is based on the property that trioctylphosphine oxide (TOPO) forms complexes with plutonium that preferentially dissolve in the organic solvent, in this case kerosene. For 3% TOPO in kerosene, and with 5 min of mixing, the organic solvent extracts greater than 99% of the plutonium and less than 0.1% of the ^{241}Am . Following extraction of the plutonium (and uranium) in a 60-ml bottle (left side of Fig. 2), the solid cap of the bottle is replaced with a dispensing cap. The organic phase that contains the separated plutonium is dispensed into a smaller plastic vial (right side of Fig. 2) for assay.

An L x-ray spectrum from a plutonium sample that contained an Am/Pu ratio of 0.5 before extraction (lower curve in Fig. 3) shows that the uranium x rays are barely visible. The extracted plutonium from this sample (upper curve in Fig. 3) shows quite prominent uranium x-ray peaks whose area can be determined precisely. There are still some neptunium x rays resulting from the presence of ^{237}U in the organic phase, but the interfering neptunium x-ray peaks are small and can be subtracted. The chemical separation offers the added advantage of extracting plutonium into a substantially smaller volume of kerosene, thereby concentrating the plutonium and improving the measurement sensitivity.

An instrument based on the hybrid chemical/NDA technique has been developed to assay the plutonium concentration in ion-exchange effluents. This device, named the Low-Solution Assay Instrument (LOSAL), has been demonstrated to be capable of assaying plutonium concentrations ranging from 1 mg/l to several g/l. The instrument has been installed at one of the gloveboxes in the plutonium recovery section. With the LOSAL, effluents from the ion-exchange separation can be assayed without bag-out, 1 h after the separation (vs taking 2 days by destructive chemical analyses). The timely assay has been found

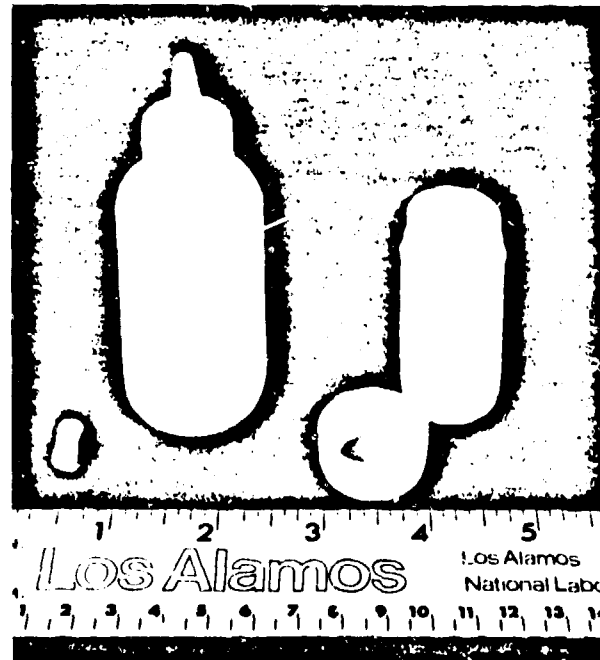


Fig. 2. Bottles used in the TOPO separation. The larger bottle on the left is used for mixing the effluent solution with TOPO. The smaller bottle on the right is used to hold the organic plutonium phase after the separation.

to be very useful in detecting process upsets in which an abnormally large amount of plutonium is found in the effluent stream; the assay can be performed before disposal of the effluent solutions.

After the separation, the plutonium and/or ^{241}Am are dispersed into separate vials for assay. The assay chamber and the Si(Li) detector, relative to the glovebox, are shown in

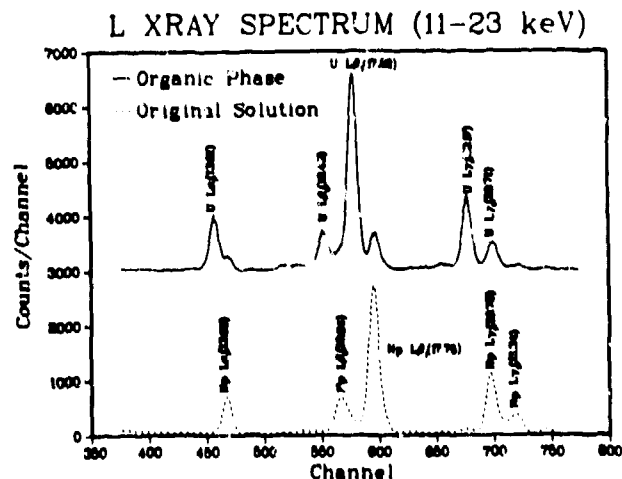


Fig. 3. The L x-ray spectrum from the original effluent solution (lower curve, Am/Pu 0.5) and from the organic phase containing plutonium (upper curve).

Fig. 4. There are two separate positions for plutonium and americium vials. The sample vials are inserted into the holder at the position shown and moved near the detector for assay. Because the instrument is intended for assay of low levels of plutonium, the sample vial holder within the chamber is designed so that it can be easily removed for decontamination in order to maintain a relatively low background. Signals from the detector are processed by linear electronics and analyzed by a Canberra Industries Series 85 multichannel analyser. A picture of the entire system before installation is shown in Fig. 5. Deadtime and pileup correction are based on the 5.9-keV peak from a ^{55}Fe source taped on to the detector. No attenuation correction is made. Calculations indicated that bias from the sample self-attenuation is less than 5% when the acid molarity varies from $2M$ to $7M$.

3. Results

The LOSAI has been installed for three months at one of the gloveboxes in the plutonium recovery section. It is presently undergoing a test-and-evaluation program in which process effluent solutions are assayed with the LOSAI and duplicate samples are sent to be analyzed chemically. The chemical analyses consist of 2-thenoyl trifluoroacetone (TTA) extraction and alpha counting to determine the plutonium concentrations. Table II summarizes the comparison between the two assay techniques. We found that, with the exception of three outliers, the ratios of the results have an average value of 0.95 and a standard deviation of 0.17. A plot of this ratio as a function of plutonium concentration is shown in Fig. 6b. The calculated precisions for various concentrations are shown in Fig. 6a.

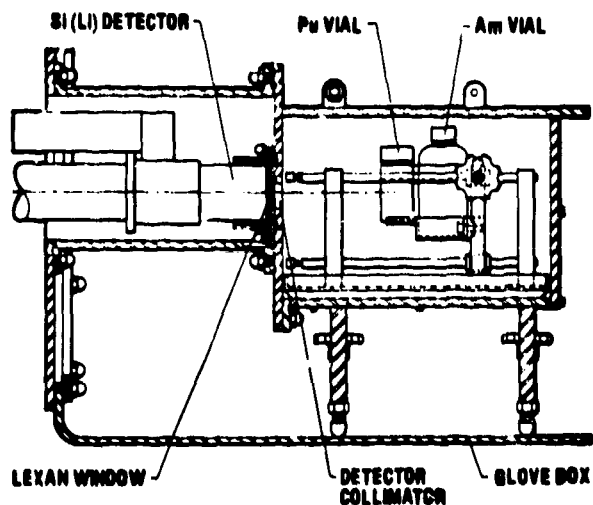


Fig. 4. Schematic of the Si(Li) detector and the assay chamber. There are two sample positions for plutonium and americium, respectively. The sample vials are inserted into the holder at the position shown and then moved near the detector for assay.

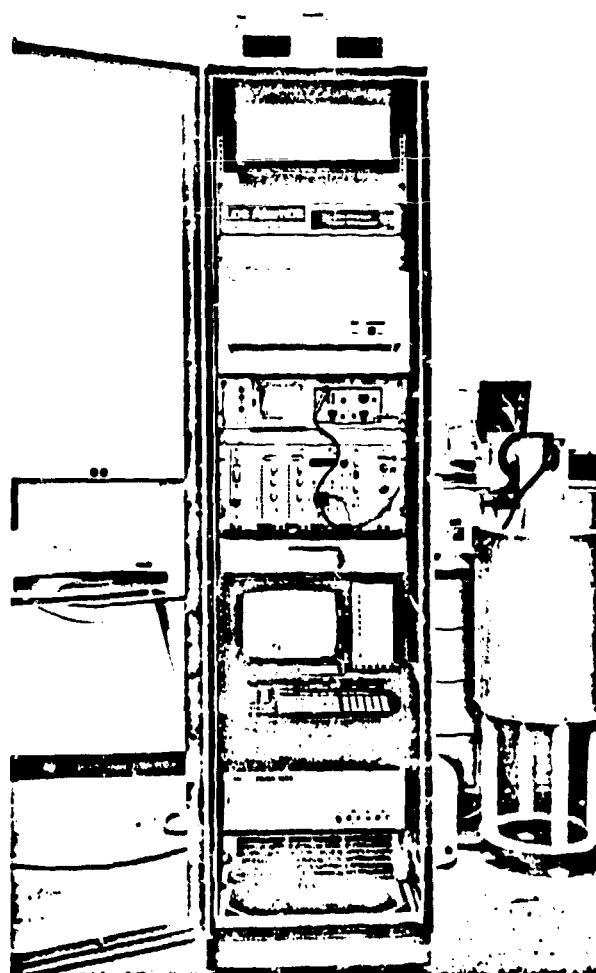


Fig. 5. The LOSAI electronics rack and the detector stand. The assay chamber is installed inside the glovebox.

The outliers could be due to other factors such as incomplete americium-plutonium separation and are being investigated.

4. Conclusion

The combined chemical separation/NDA technique has been shown to provide highly sensitive and precise measurements of plutonium under conditions where such measurements would otherwise be impossible. This hybrid technique can undoubtedly be applied beneficially to many safeguards assay problems.

5. Acknowledgments

The authors wish to thank D. F. Bowersox and B. S. Davis for their help in collecting the test and evaluation data.

TABLE II
COMPARISON BETWEEN ALPHA COUNTING AND LOSAI

Sample	Am/Pu Weight Ratio	Alpha (mg/k)	LOSAI (mg/l ± %)	Ratio LOSAI/Alpha
1	5.0	3.50	4.44 ± 9.8	1.26
2	2.3	9.22	2.85 ± 11.8	0.31 ^a
3	3.7	2.52	2.02 ± 23.0	0.80
4	2.8	6.26	5.15 ± 6.6	0.82
5	3.2	6.55	6.06 ± 4.7	0.93
6	13.7	2.07	2.05 ± 27	0.99
7	8.1	1.55	1.96 ± 23	1.27
8	2.0	5.78	5.94 ± 4.3	1.03
9	5.2	3.76	3.69 ± 12.2	0.98
10	3.1	8.79	4.89 ± 14.1	0.56 ^a
11	0.3	48.00	46.22 ± 0.9	0.96
12	7.9	1.97	1.75 ± 13.8	0.89
13	8.8	1.69	1.50 ± 47.4	0.89
14	0.6	13.40	2.98 ± 7.5	0.22 ^a
15	4.1	3.91	2.52 ± 20.0	0.64
16	6.5	1.56	1.31 ± 52.9	0.84
17	2.8	5.32	3.75 ± 32.7	0.70
18	4.3	3.59	2.65 ± 16.6	0.74
19	0.8	15.60	18.16 ± 2.8	1.16
20	5.4	2.35	2.57 ± 19.4	1.09
21	3.6	4.42	4.62 ± 9.5	1.04
22	1.4	8.88	8.79 ± 4.3	0.98
Average ratio				0.95
Std dev				0.17

^aExcluded in the average.

6. References

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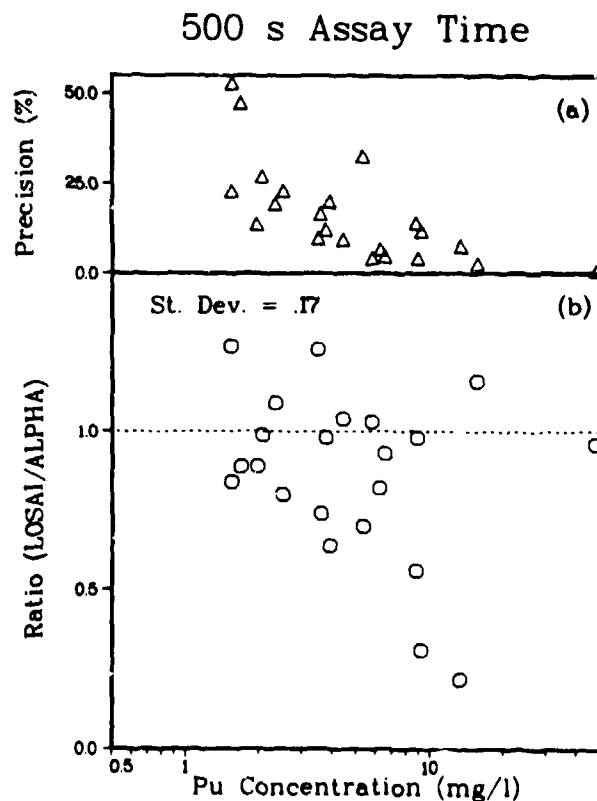


Fig. 6. (a) Precision of the LOSAI as a function of plutonium concentration. The precision includes the counting statistics only and does not include the separation process. (b) The ratio is obtained by comparing LOSAI assay results with alpha counting assay results.