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QUANTITATIVE ELECTRODEPOSITION OF ACTINIDES FROM ISOPROPYL ALCOHOL

M. Y. DONNAN & E. K. DUKES

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QUANTITATIVE ELECTRODEPOSITION OF ACTINIDES FROM ISOPROPYL ALCOHOL

CFSTI PRICES

by

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ABSTRACT

An electrodeposition method was developed for the preparation of thin, uniform alpha sources for precise counting and accurate pulse height analysis. The method employs an isopropanol electroplating medium and is applicable to deposition of actinides from both organic and aqueous media. Moderate amounts of aluminum and iron do not decrease deposition yields.

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QUANTITATIVE ELECTRODEPOSITION OF ACTINIDES FROM ISOPROPYL ALCOHOL

INTRODUCTION

Precise alpha counting and accurate energy measurements require that radioactive material be prepared as a thin, uniform layer, and absolute counting requires that the active material be deposited quantitatively. The three methods generally used to prepare alpha sources are direct evaporation, vacuum evaporation or sublimation, and electrodeposition. Direct evaporation is simple, rapid and quantitative but dissolved solids deposited with the active element cause self absorption. Sublimation produces thin, uniform deposits but fractionation of the actinides can occur and deposits are not quantitative. Electrodeposition also produces satisfactorily thin deposits; but, until recently, quantitative deposition required long times.

Development of a carrier technique for rapid, quantitative electrodeposition of actinides has been described.⁽¹⁾ In this method actinides are deposited from an aqueous solution of NH_4Cl to which natural uranium is added several times during deposition to obtain yields of 99.8% in 20 minutes. Although the method is used for analytical service work, it is limited to aqueous samples that are free from iron or aluminum.

A method for the preparation of counting plates that is applicable to a broader variety of sample types than either direct evaporation or aqueous electrodeposition was needed for routine use. Quantitative deposition from isopropanol and ethanol was reported by Parker.^(2,3) The method was applied to aqueous samples and deposition times were long; however, use of the organic plating medium suggested that the method might be modified for application to organic as well as to aqueous samples.

SUMMARY

A rapid, quantitative method was established for electrodepositing actinides from aqueous and organic solutions onto alpha counting plates. Isopropanol was an excellent plating medium for most samples tested. Satisfactory deposition rates and yields were achieved by operating at high current density (10 ma/cm^2). Addition of uranium carrier gave increased deposition rates for aqueous samples but not for organic samples.

In tests with ^{239}Pu , a 10-minute deposition period gave yields of 99.4% for aqueous samples and 99.0% for organic samples. The presence of up to 100 μg of either Al or Fe caused no significant decrease in deposition yield.

DISCUSSION

Deposition from Aqueous Samples

In initial trials of Parker's method with isopropanol as the plating medium, uranium in aqueous samples was deposited quantitatively in 30 minutes. The apparatus consisted of a glass deposition cell, a platinum anode-stirrer, a cathode (nickel plated stainless steel planchet), and a high voltage supply. Parker reported deposition times of 10 to 60 minutes for quantitative yields. Deposition time decreased as the current was increased.

Our tests with ^{239}Pu in nitric acid solution confirmed that deposition rate increased with increasing current density. The practical upper limit on current density was about 10 ma/cm^2 for isopropanol. Above 10 ma/cm^2 , boiling and subsequent loss of isopropanol was observed. Acetone and ethanol were unsuitable as plating media because of their low boiling points.

Deposition rates were increased further by adding natural uranium during deposition, as shown in Table I. The beneficial effect of high current density and uranium carrier was confirmed by making five 10-minute depositions of ^{239}Pu . The results in Table II show that deposition was quantitative (99.41%), and that the precision was satisfactory.

TABLE I

Deposition of ^{239}Pu from Isopropanol^(a)

<u>Current Density,</u> <u>ma/cm^2</u>	<u>Voltage,</u> <u>volts</u>	<u>Yield,</u> <u>%</u>
3.3	500	63
5.0	500	75
6.6	500	87
6.6	500	96 ^(b)

(a) Five-minute deposition time.

(b) Ten micrograms of uranium added.

TABLE II

Electrodeposition of ^{239}Pu in Aqueous Samples^(a)

<u>Alpha Count Rate, c/m (multiplied by 10^{-4})</u>	<u>Recovery,^(b) %</u>
3.47	99.91
3.44	99.16
3.46	99.74
3.45	99.42
3.43	98.80
Average 3.45	99.41

(a) Ten micrograms of uranium added.

(b) Relative standard deviation = $\pm 0.48\%$.

Increased tolerance for Fe and Al was one of the important advantages of the isopropanol plating medium. Table III shows that there was no significant decrease in deposition yields of ^{239}Pu when up to 100 micrograms of Fe or Al was present. In comparison, as little as 25 micrograms of either element decreased yields in the aqueous ammonium chloride system.

TABLE III

Effect of Aluminum and Iron on Deposition Yield

<u>Al^{3+}, μg</u>	<u>Yield, %</u>	
	<u>NH_4Cl</u>	<u>Isopropanol</u>
25	91	99.4
50	82	99.3
100	50-60	98.8
250	20-30	89
<u>Fe^{3+}, μg</u>		
25	98	99.4
50	90	99.2
100	70-80	98.9
250	40-50	96

Deposition from Organic Samples

Preliminary experiments showed that isopropanol was a satisfactory medium for quantitative deposition of americium, curium, neptunium, and plutonium present in organic samples. In confirmatory tests, plutonium was electrodeposited from six organic phosphates that are representative of different classes of organic phosphates under study as new extractants at the Savannah River Laboratory. Quantitative deposition (99%) was achieved in 10 minutes with five of the organic solutions (Table IV). Deposition from the sixth organic solution was only 50% complete after 10 minutes.

TABLE IV

Electrodeposition of ^{239}Pu from Organic Phosphate Samples

	<u>Recovery, %</u>
Tetraamyl methylene diphosphonate	99
Tetrabutyl methylene diphosphonate	99
Tetrahexyl methylene diphosphonate	99
Dihexyl-N,N-diethyl carbamyl diphosphonate	99
Bis(4-methyl-2 amyl) -N,N-di-2 propyl carbamyl methylene phosphonate	99
Dibutyl-N,N-diethyl carbamyl-1, 1-ethane phosphonate	50

With one exception, diluents commonly used for organic extractants had no effect on deposition yield. In tests of diluents, plutonium was extracted from nitric acid into tetraamyl methylene diphosphonate; the extract was then diluted in various diluents and the plutonium was deposited from the dilutions. Toluene was the only diluent tested that showed less than quantitative deposition. Results of the tests are summarized in Table V.

TABLE V

Effect of Common Diluents on Deposition*

	<u>Yield, %</u>
Diethylbenzene	100
Xylene	100
N-dodecane	100
Toluene	93

* 10% tetraamyl methylene diphosphonate in diluents.

Contrary to results obtained with aqueous samples, uranium carrier had no effect on deposition yields for organic samples. However, it was necessary to add small amounts of water to the isopropanol to maintain the high current density required for rapid deposition.

The excellent quality of the electrodeposits of organic samples was demonstrated by comparing pulse height scans with those of evaporated mounts, as shown in Figure 1.

FIG. 1 ALPHA PULSE HEIGHT SCAN
(Organic Samples)

The counting precision for electrodeposited organic samples was excellent, relative to that obtained with mounts prepared by direct evaporation. Table VI compares data obtained from the evaporated and electrodeposited mounts of ^{239}Pu in tetraamyl methylene diphosphonate.

TABLE VI

Comparison of Counting Data
for Electrodeposited and Evaporated Mounts^(a)

	Evaporated, c/m	Electrodeposited, c/m
	1.81	3.01
	1.94	3.06
	2.23	3.02
	2.43	3.04
Relative Standard Deviation	14%	0.77%

(a) Multiplied by 10^{-4} .

Results of a detailed precision study of the analysis of ^{239}Pu in one organic sample are shown in Table VII. Dihexyl-N, N-diethyl carbamyl phosphate containing ^{239}Pu was diluted with N-dodecane and 1 ml aliquots were used for analysis to minimize the error in pipetting.

TABLE VII

Precision Study of Organic Sample

Aliquot	c/m ^(a)	Recovery, (b) %
1	2.617	99.67
2	2.635	100.35
3	2.614	99.54
4	2.615	99.57
5	2.621	99.82
6	2.613	99.52
7	2.630	100.16
8	2.628	100.07
9	2.618	99.68
Average	2.621	99.82

Relative Standard Deviation = $\pm 0.28\%$.

(a) Multiplied by 10^{-4} .

(b) Yields were verified by evaporating and counting aliquots of the plating media after deposition.

The electrodeposited activity strongly adhered to the counting planchets. Ten deposits of ^{239}Pu (10^4 d/m) from organic phosphate samples were tested. Each mount was rubbed with a filter paper (1-3/4 inches in diameter) and the papers were then counted for alpha activity. The test was repeated with filter paper moistened with acetone. The average amount of activity removed was only 0.04% for dry smears and 0.03% for wet smears.

Recommended Procedure

Add an aliquot of sample to the deposition cell that contains 20 ml of isopropanol; stir the solution until it is thoroughly mixed. Position the anode stirrer ~15 mm above the cathode and rotate it at 100 rpm. Apply a constant current of 55-60 ma (10 ma/cm^2) for 5 to 15 minutes. After deposition turn off the current, immediately decant the isopropanol, and remove and flame the planchet.

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