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QUANTITATIVE SEPARATION OF AMERICIUM AND PLUTONIUM USING CUPFERRON

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ABSTRACT

Americium and plutonium are separated quantitatively by chloroform extraction of plutonium cupferrate from hydrochloric acid solution. This separation is successful from tracer concentrations up to gram quantities of plutonium, and milligrams of americium.

In this Laboratory, the separation is made routinely at two widely different Am/Pu ratios: (1) during americium purification where the Am/Pu ratio is of the order of 1/10; and (2) for americium assays on plutonium solutions where the Am/Pu ratio varies from 10 - 250 ppm.

For separation of macro-amounts, no carrier is needed. For small amounts, iron and lanthanum are used, the former as a plutonium carrier and the latter as a holdback for americium. Satisfactory plates for counting plutonium can be made directly from aliquots of the chloroform extract of plutonium cupferrate.

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QUANTITATIVE SEPARATION OF AMERICIUM AND PLUTONIUM USING CUPFERRON

I. INTRODUCTION

Even though the specific alpha activity of americium is about 50 times that of plutonium, it is difficult to determine small amounts of americium in plutonium by alpha analysis. For example, only 0.5% of the total alphas from a plutonium sample containing 100 ppm of americium are emitted by americium. A method was needed to separate the two elements quantitatively, so that each could be counted separately. Cupferron (ammonium nitrosophenyl-hydroxylamine) was the reagent chosen. The specific activity of 400 g/T plutonium[1] is taken as 7.66×10^7 c/min/mg and that of americium as 3.54×10^9 c/min/mg at 51% geometry.

The extraction of plutonium cupferrate has been the subject of several reports[2-6] in which it is stated that recovery of plutonium in small amounts (10^3 c/min) is consistent at HCl acidities 0.2 to 1.0 N. An average recovery of 90% was obtained with 2N HCl.[6]

In the present study, 10 to 15 mg of plutonium ($\sim 10^9$ c/min) was used, since the emphasis was on the recovery of small amounts of americium. In every case, an alpha analysis was made of the counting plates to determine if a pure emitter was present. Using the sweep-type, differential alpha-energy analyzer,[7] 1 to 2% of plutonium alphas could not be detected in the presence of 98 to 99% americium alphas. Since the specific activities of Pu/Am are in the ratio of about 1/50, the lower limit on the weight of plutonium detectable by this method is equal to that of americium. However, on a 10-mg plutonium sample, containing 200 ppm of americium, this would still amount to 99.9% removal of plutonium.

The use of the cupferron technique is shown first as an analytical tool for the determination of small amounts of americium in plutonium; and, secondly, its use is outlined as a separation method for macro-amounts of americium and plutonium.

II. USE OF CUPFERRON FOR THE QUANTITATIVE DETERMINATION OF AMERICIUM IN PLUTONIUM

This method was developed primarily for the assay of americium in solutions of 400 g/T plutonium from which americium is currently being separated. The effectiveness of the cupferron extraction is indicated by Figs. 1 and 2, which show the alpha distribution in an original plutonium solution containing about 200 ppm of americium compared with the distribution in the aqueous solution after extraction of plutonium from the sample.

The procedure finally adopted is described below. It is followed by a summary of some pertinent observations noted in the development of the method, and by results obtained from its use.

Reagents

Chloroform
Lanthanum nitrate solution (1 mg of La/ml)
Ferrous ammonium sulfate solution (10 mg of Fe/ml)
Cupferron (6% aqueous solution, slightly ammoniacal)
Hydrochloric acid, 1 N

[redacted]

[redacted]

Equipment

Separatory funnels, 125 ml
Graduated cylinders, 50 ml
Micro-pipets, 25, 50, 100 μl
Volumetric flasks, 10, 25, 100 ml
Hypodermic syringe, 1 ml
Platinum plates
Alpha counter
(For this investigation, an alpha-energy analyzer was also used)

Procedure

(For the determination of americium in the range 10 to 10^3 ppm in plutonium)

Twenty ml of 1 N hydrochloric acid, 2ml of lanthanum nitrate, and 1 ml of ferrous ammonium sulfate solution are added to a 125-ml separatory funnel, followed by 10 to 15 mg of plutonium in solution ($\sim 10^9$ c/min.). (The exact amount should be chosen so as to give a reasonable number of americium counts in a 25- to 100-μl aliquot of the final aqueous solution - - $\sim$ 35 ml.) Five ml of 6% cupferron solution is added, the mixture is agitated and allowed to stand for 30 minutes in a refrigerator. The plutonium and iron cupferrates are then extracted with 5-ml portions of chloroform until no color is observed in the last chloroform layer (approximately six extractions). One ml of ferrous ammonium sulfate solution and 5 ml of 6% cupferron solution are again added, the slurry allowed to stand an additional 20 minutes, and extracted as before. The water layer is transferred to the graduated cylinder and the volume noted. An aliquot (25 to 50 μl) is dried on a platinum plate, ignited to red heat, and alpha-counted. (In the present study, a 300-watt induction heater was used for ignition of the samples, and each plate was analyzed in the alpha analyzer.) The chloroform solution is diluted to a convenient volume, and an aliquot is treated in a similar manner. The americium content is calculated from the ratio of total americium and plutonium counts.

Sample Calculation

A 500-μl aliquot of a plutonium solution to be analyzed was treated according to the procedure just described. After extraction, the volume of the water layer was 32.6 ml and a 100-μl aliquot gave 1656 c/min. The volume of the chloroform phase was 100 ml; a 10-μl aliquot gave 24,120 c/min.

$1.656 \times 10^3 \times 10 \times 32.6 = 5.40 \times 10^5$ total americium c/min. in the aqueous layer.

$\frac{5.40 \times 10^5}{3.54 \times 10^6} = 0.153$ micrograms of americium.

$2.412 \times 10^4 \times 10^2 \times 10^2 = 2.41 \times 10^8$ total plutonium c/min. in the chloroform extract.

$\frac{2.41 \times 10^8}{7.66 \times 10^{10}} = 3.15 \times 10^{-3}$ grams of plutonium.

$\frac{0.153}{3.15 \times 10^{-3}} = 48.6$ micrograms of Am/g of Pu = 48.6 ppm of americium.

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To check on the recovery of plutonium, 10 µl of the original plutonium solution was diluted to 10 ml and a 25-µl aliquot gave 12,170 c/min. This yields a value of

$$1.217 \times 10^4 \times 400 \times 50 = 2.43 \times 10^8 \text{ c/min.}$$

in 500 µl of the original solution which is (within experimental error) in agreement with 2.41×10^8 c/min. found in the chloroform phase. The contribution from americium alphas in the original solution is negligible.

Recovery of Plutonium from the Chloroform Extract

When the amount of americium in the plutonium exceeds 200 ppm, americium contributes more than 1% of the total alphas. Above this level, these alphas constitute an error that is greater than the average counting error if a direct plate is made of the original plutonium solution. It is therefore necessary to make a plate of the chloroform extract to determine plutonium. Several methods are described

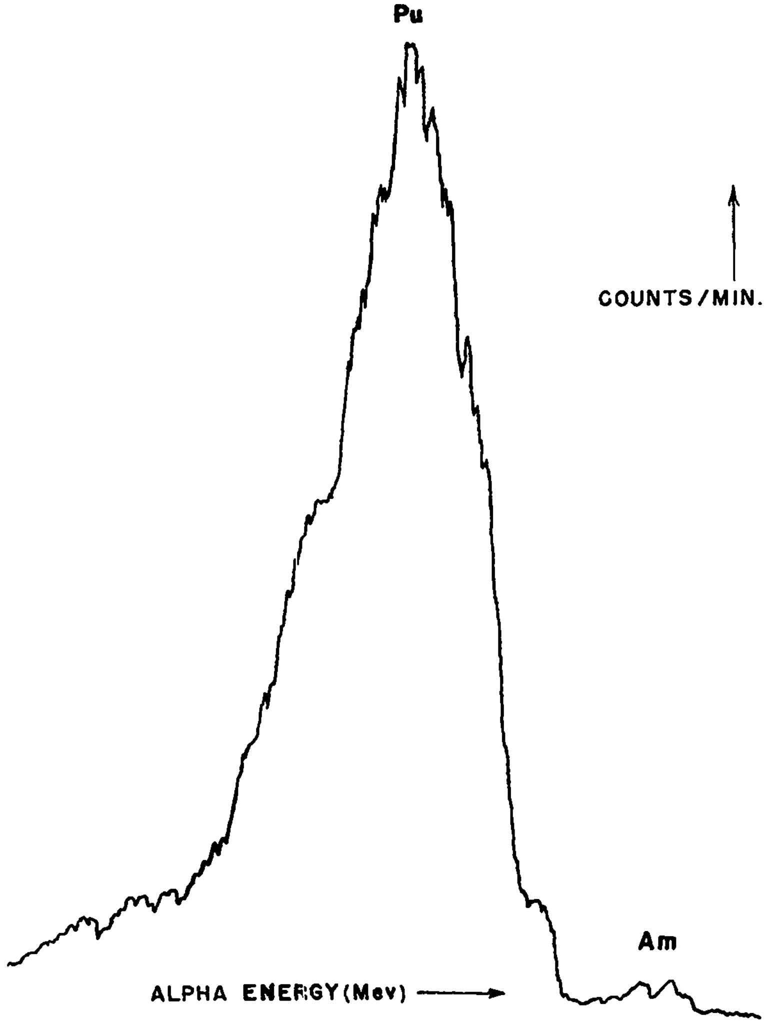

Fig. 1 α-analysis of Pu-Am solution before extraction, 99% plutonium, 1% americium.

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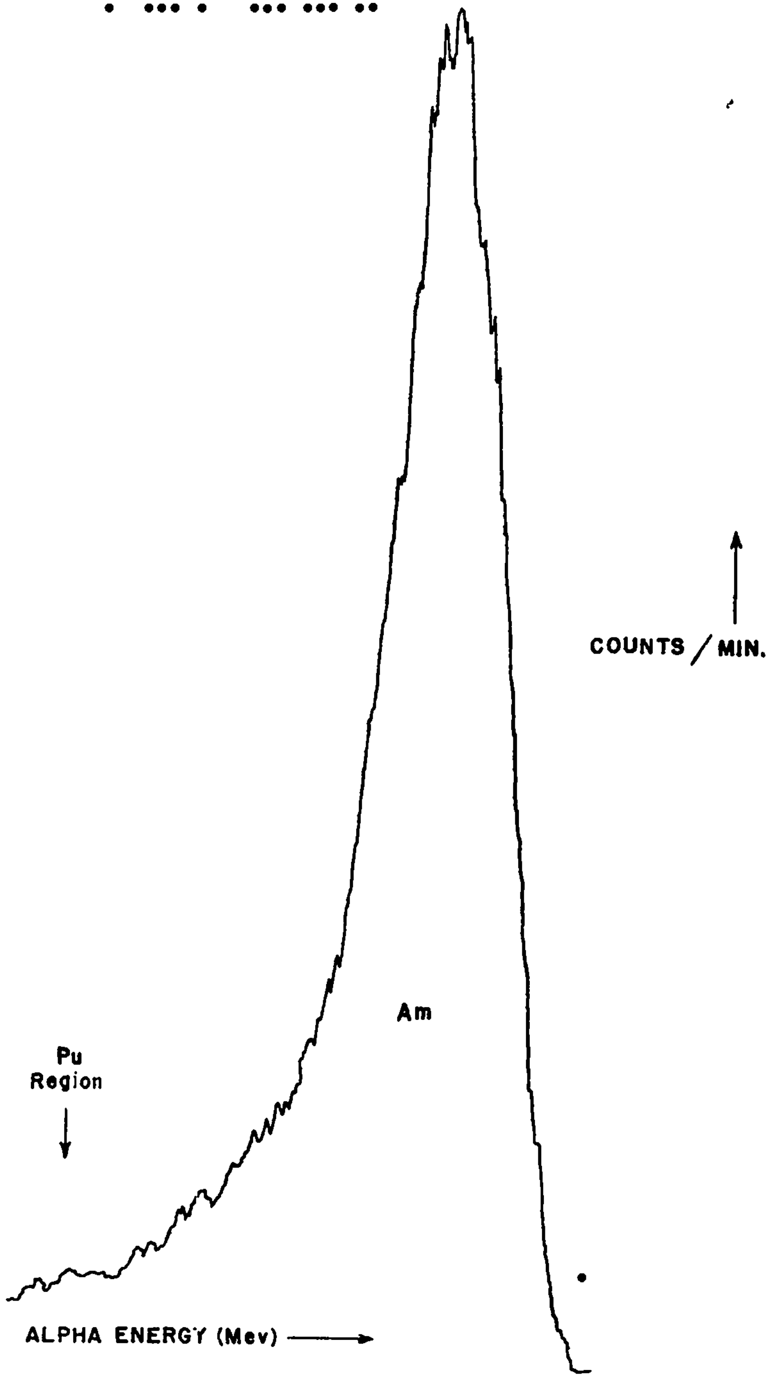

Fig. 2 α-analysis of aqueous layer after extraction, 100% americium.

[redacted]

for oxidation of the cupferron extract using nitric, sulfuric and perchloric acids.[5,8] These methods are time-consuming. Sufficiently satisfactory results are obtained by taking a direct aliquot of the chloroform extract. The pipet is rinsed onto the plate with chloroform, and the plate is treated in the usual manner for counting purposes. Since the coefficient of expansion for chloroform is appreciable, it is necessary to avoid large temperature variations. Further, somewhat greater care is necessary when taking an aliquot of the chloroform extract, since it has a tendency to creep. Table I shows the recovery of plutonium from the chloroform extract using this direct technique.

TABLE I

RECOVERY OF PLUTONIUM FROM CHLOROFORM EXTRACT

Pu taken (mg)	Pu recovered (mg)
23.0	22.2
22.6	22.1
9.75	9.58
9.63	(8.36)
3.17	3.15
3.17	3.03
0.354	0.366

Effect of Lanthanum Holdback on the Recovery of Small Amounts of Americium

Preliminary experiments indicated that americium tracer (10^5 c/min.) was apparently extracted unless a similar ion was present. A series of americium determinations was performed on a stock plutonium solution, and a duplicate set was repeated with the addition of lanthanum. An increase of about 6% in americium remaining in the aqueous solution was found when one mg of La per 25 ml was present. Increasing the amount to 2 mg of La per 25 ml did not increase the americium recovery. The results are collected in Table II. Using 1 to 2 mg of La per 25 ml, the recovery of americium is quantitative within counting accuracy.

Quintuplicate analyses were performed according to the described procedure on a stock plutonium solution, using 13.0 mg of plutonium per analysis. From three of the results, an average recovery of 0.28 μg of americium was found. Duplicate analyses were then performed after the addition of 2.07 μg of americium to each. In this set, 2.35 and 2.34 μg of americium was found, showing that the recovery of americium is quantitative within counting accuracy.

Effect of Single Versus Double Extraction

After a single extraction, a variable percent of plutonium activity remains in the aqueous layer, so that a direct alpha count is useless (without alpha-energy analysis) for determining the americium present. A double treatment with iron and cupferron removes this last trace of plutonium. This double extraction is recommended in the procedure.

Effect of Temperature

It was found that allowing the mixture to stand at room temperature after addition of cupferron causes coagulation of the precipitate into particles that are difficult to dissolve in chloroform. To avoid this, the solutions are placed in a refrigerator for approximately one-half hour after addition of cupferron. On the other hand, if

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the solutions are precooled to 5°C prior to the addition [redacted] plutonium is extracted, unless a much longer period is [redacted] An example of this is shown in Table III. Six solutions containing plutonium and americium were cooled to 5°C and treated with cupferron. They were allowed to stand one-half hour in the refrigerator and then extracted. The solutions were extracted in series at intervals of about fifteen minutes, so that one and one-fourth hours elapsed between extraction of sample No. 1 and sample No. 6. Following this period, iron and cupferron were again added and the solutions were re-extracted.

TABLE II

EFFECT OF LANTHANUM HOLDBACK ON AMERICIUM RECOVERY

Mg of Pu Taken	μg of Am in Aqueous Layer After Extraction (no lanthanum)	μg of Am in Aqueous Layer After Extraction (1 mg of La per 25 ml)
Lot A		
3.19	0.144	0.163
3.19	0.148	0.157
3.19	0.146	0.154
3.19	0.146	0.153
3.19	0.146	0.147
3.19	0.146	0.149
3.19	0.126	
3.19	0.146	
3.19	0.145	
	Avg. 0.144	0.154

TABLE III

DISTRIBUTION OF ACTIVITY IN AQUEOUS LAYER AS FUNCTION OF TIME AT 5°C

	Percent of Alphas		Time Before Extraction
	Pu	Am	(min.)
Sample 1	65	35	30
Sample 2	55	45	45
Sample 3	25	75	60
Sample 4	18	82	75
Sample 5	0	100	90
Sample 6	0	100	105

Effect of Aqueous Volume

When extraction is run using a small water- to -chloroform ratio (20 ml aqueous/5 ml $CHCl_3$), some of the americium is extracted. However, at a chloroform-to -water ratio of about 1/6, good results are obtained.

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Effects of Acidity

The extraction of plutonium was satisfactory at hydrochloric acid normalities of 0.2, 0.6, 1.0 and 2.0.

Comparison of Americium Process Yield with Calculated Yield from Cupferron Analyses

The accuracy of the cupferron method was checked by comparing the amount of americium removed from a large amount of plutonium by the peroxide process with the predicted yield based on cupferron analyses. For this comparison, the original plutonium solution was stirred for two hours and sampled. Duplicate cupferron analyses were made by the procedure described. The plutonium was then processed by the following procedure to remove americium. Plutonium peroxide was precipitated, washed, and filtered dry. Americium hydroxide was precipitated from the combined supernatants by gaseous ammonia diluted with nitrogen. The precipitate was filtered, dissolved in hydrochloric acid, and the actual americium yield determined by alpha count and alpha-energy analysis. The spent plutonium peroxide was dissolved, sampled carefully as before, and the residual americium content determined by another set of cupferron analyses. The difference in americium content of the original and spent plutonium was multiplied by the total amount of plutonium processed to give the calculated americium yield. A comparison of this figure and the amount of americium actually removed appears in Table IV.

TABLE IV

COMPARISON OF ACTUAL AMERICIUM PROCESS YIELD WITH RESULTS OF CUPFERRON ANALYSIS

Amercium Concentration (mg/kg of Pu) in Plutonium Process Solutions by Cupferron Analyses			Average Americium Yield (mg)	
Before Peroxide Precipitation	After Peroxide Precipitation	Kilograms of Pu Processed	Calc. from Cup. Analysis	Actual Process Yield
190	19.1	0.205		
	20.5		34.7	36.2
( )*	21.7			
	16.8			
228	12.7	0.1976	43.3	40.9
240				
	14.1			
170	13.8	0.2132	34.6	36.7
182				
	25.2	0.1916		
219	22.6			
223	22.1		37.8	37.1
			Total 150.4	150.9

*One analysis lost.

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III. SEPARATION OF MACRO AMOUNTS OF [redacted]
USING CUPFERRON

The success of the separation on a small scale prompted its use for the purification of americium. Even though only the americium and plutonium separation is shown in Table V, it should be noted that other chloroform-soluble cupferrates (such as iron) are also removed quantitatively. At these concentrations, no iron or lanthanum is used.

TABLE V

USE OF CUPFERRON FOR THE SEPARATION OF
PLUTONIUM AND AMERICIUM ON A MACRO-SCALE

Original Solution		Aqueous Layer		
Am(mg)	Pu(mg)	Am(mg)	Pu(mg)	Remarks
0.77	13.8	0.78	0(a)	$CHCl_3$ extraction
12.5	694.	12.1	0	Cupferrate ppt filtered
38.2	88.	39.5	0	Cupferrate ppt filtered
69.8	1660.	67.3(b)	0	Cupferrate ppt filtered

(a) It should be recalled that detection of plutonium by alpha analysis is not accurate to more than 1 to 2% in the presence of 98 to 99% americium alphas.

(b) Extensive caking of cupferron occurred, leaving only 56.5 mg of americium in first filtrate. Dissolution of the cake in chloroform and extraction with dilute acid recovered the remaining americium.

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