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A COMPARISON OF ANALYTICAL METHODS FOR AMERICIUM

BY

M. W. GIFT
TECHNICAL SECTION
ENGINEERING DEPARTMENT

OCTOBER 22, 1954

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Chemistry Unit
Applied Research Sub-Section

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By Authority of TID-1112,
pag. 239, 3-15-56
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A COMPARISON OF ANALYTICAL METHODS FOR AMERICIUM

INTRODUCTION

Two analytical methods for americium have been developed for use in the analytical laboratories supporting the Hanford separation processes. These methods represent two widely different approaches to the analysis of americium: (a) co-precipitation with a rare earth fluoride, and (b) extraction as an organic-soluble chelate.

The co-precipitation of americium and cerium fluorides, a method developed by Miller(1), is used for analysis of solutions containing americium and uranium. This method differs from most radiochemical procedures in that it requires an unusual amount of time in close contact with the sample. For highly radioactive samples the radiation exposures are excessive.

The extraction method, developed by Chetham-Strode(2), in which americium is extracted as an organic-soluble chelate of thenoyltrifluoracetone (TTA), is designed for the separation of americium and plutonium. Uranium, when present, interferes with the extraction. This method for americium has been modified by the author to include a tributylphosphate (TBP) extraction which eliminates the uranium interference. The TBP-TTA method was tested successfully on solutions containing uranium and americium. The americium recovery is 100 per cent with a standard deviation of three per cent.

SUMMARY

In a comparison of methods, the modified TBP-TTA method for americium shows higher recoveries than the better-known cerous fluoride method. The ratio of TBP-TTA to cerous fluoride recoveries is 1.05 with a standard deviation of ± 0.028. This deviation from unity may be due to absorption losses in the cerous fluoride method.

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Comparison of radiation exposures for each method indicates a better decontamination by the extraction method, with consequent lower exposures to the laboratory worker.

CHEMISTRY

Americium occurs in aqueous solution in the tripositive state, except under extreme oxidizing conditions where it occurs in the pentapositive or hexapositive state. In the tripositive valence state, its behavior is analogous to the tripositive rare-earths. The behavior of americium in the actinide series parallels the behavior of europium in the rare-earth series. The separation of americium from its actinide neighbors depends on carefully controlled reactions of different oxidation state. The difficulties encountered are in adjusting and holding each actinide in a different oxidation state. Two separations of americium from other transuranium elements are in use. These are an extraction method using a chelating agent, thenoyltrifluoroacetone, and a precipitation method involving ceric oxidations of the plutonium prior to precipitation of the americium on cerous fluoride.

The TTA Method and Modifications

A solvent extraction separation for the determination of americium in the presence of large amounts of plutonium has been investigated by Chetham-Strode(2). In this method, americium and all the plutonium are extracted from a solution of pH 4.5 into an organic phase as chelate complexes of thenoyltrifluoroacetone. Americium is selectively removed from the organic phase by back extraction into an aqueous phase of lower pH, i.e., 0.5M HNO_3, while Pu(III) and Pu(IV) remain in the organic phase. Pu(VI) will accompany americium in the back extraction. For this reason, plutonium was adjusted to the plus four oxidation state in the original procedure before the extraction with thenoyltrifluoroacetone. Although the thermodynamics of this system are favorable for the transfer of Pu(III) from the

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organic phase to the aqueous phase, the rate of transfer is quite slow, thus permitting an effective separation of Pu(III) from americium.

The application of this separation method to samples containing uranium is difficult. Under the conditions necessary to separate Am(III) and Pu(IV), uranium, as U(VI), will accompany americium. Although the chelation coefficients for Am(III) and U(IV) differ by the same magnitude as Am(III) and Pu(IV), the reduction of U(VI) to U(IV) is difficult under these conditions. For low concentrations of uranium comparable to the concentration of plutonium, Chetham-Strode(2) found that U(VI) was held in the organic phase by adding tributylphosphate to form a soluble uranium complex that does not back extract.

In many cases the concentration of uranium is the limiting factor in the separation of americium from plutonium and uranium. The situation occurs where micromicrograms of americium and plutonium are in solution with milligram quantities of uranium. The volumes and concentrations necessary to accommodate all the reactants become excessive, and the separation as an analytical method fails.

The interference of large quantities of uranium can be circumvented by separating uranium from americium and plutonium using tributylphosphate as an extractant. This treatment, followed by the separation of americium from plutonium using the TTA scheme, constitutes an analytical method for americium. A schematic diagram of the modified TTA method is shown in Figure 1.

TBP Extractions

Moore(3) has proposed that the extraction of U(VI) by tributylphosphate is accomplished according to the following reaction

$$UO_2{}^{++}_{(aq)} + 2\ NO_3{}^-_{(aq)} + 2\ TBP_{(org)} \rightleftharpoons UO_2(NO_3)_2 \cdot 2\ TBP_{(org)}.$$

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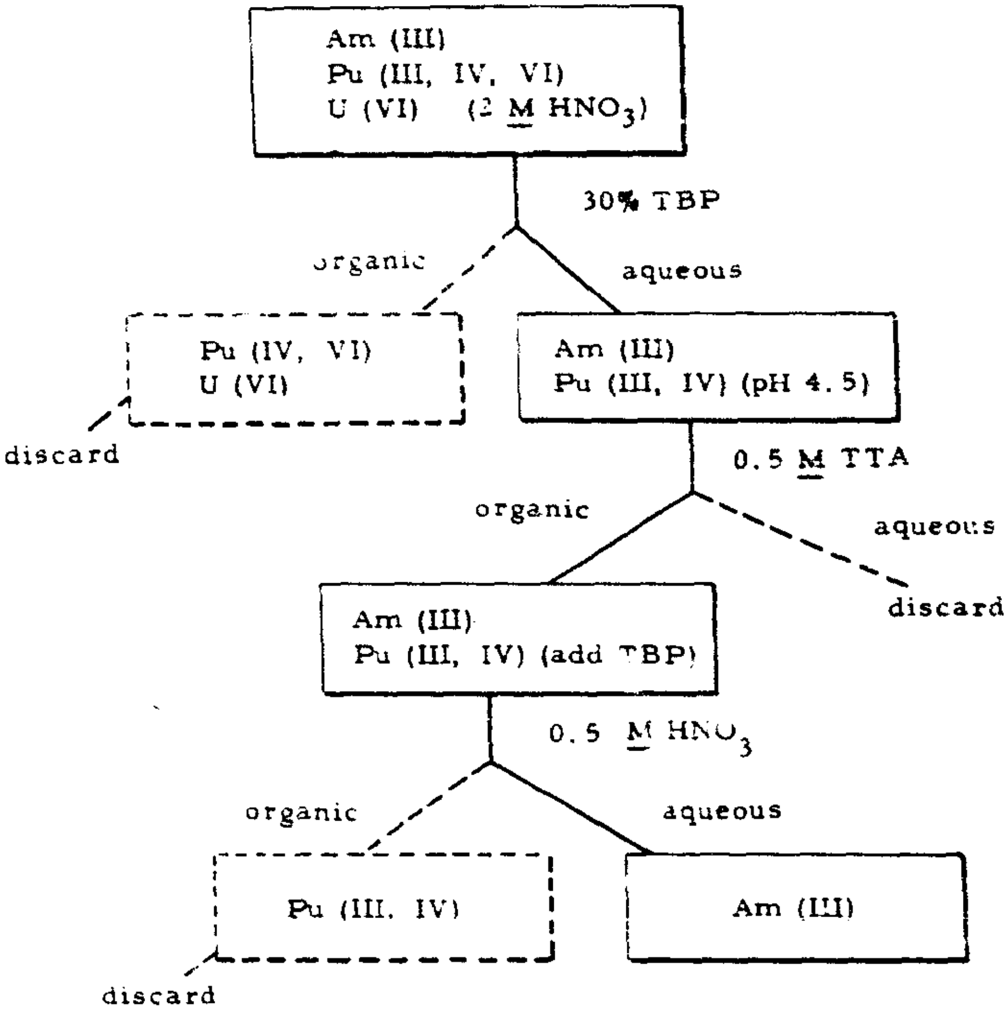

Figure 1
The TBP-TTA Separation of Americium

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The equilibrium constant, K_{eq}, is written

$$K_{eq} = \frac{\left[UO_2\,(NO_3)_2 \cdot 2TBP\right]}{(UO_2^{++})(NO_3^{-})^2(TBP)^2}$$

and molar distribution coefficient

$$E_a^o = \frac{\left[UO_2\,(NO_3)_2 \cdot (2TBP)\right]}{(UO_2^{++})} = K_{eq}\ (NO_3)^2\,(TBP)^2.$$

It is readily seen that the distribution of uranium into the organic phase is favored by increasing nitrate ion and tributylphosphate concentrations

McKay and Woodgate$^{(4)}$ found the PuO_2^{++} is extracted by the same mechanism, the distribution coefficient being much smaller. In addition, Pu(IV) and Pu(III) follow similar reactions resulting in $Pu\,(NO_3)_4 \cdot 2\ TBP$ and $Pu\,(NO_3)_3 \cdot 3TBP$.

A comparison of typical distribution coefficients for uranium, plutonium, and other elements under comparable conditions is present in Table I.

The reactions of Am(III) and Pu(III) with tributylphosphate are presumed to be similar. The distribution of americium has been measured at several acid concentrations and found to agree with the magnitude of the distribution of Pu(III) as predicted. The data is presented in Table II.

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TABLE I

A COMPARISON OF DISTRIBUTION COEFFICIENTS

M	M HNO3	M NO_3^- Salt	Total M NO_3^-	% TBP	E_a^o	
UO_2^{++}	2.0	-	2.0	25	12	(6)
	4.0	-	4.0	25	23	(6)
Pu(III)	2.00	-	2.00	20	0.0167	(4)
	5.00	-	5.00	20	0.0116	(4)
Pu(IV)	2.23	-	2.23	20	3.90	(4)
	5.00	-	5.00	20	16.6	(4)
Pu(VI)	2.00	-	2.00	20	1.54	(4)
	5.00	-	5.00	20	2.70	(4)
R.E.	4.50	-	4.50	25	0.005	(5)
Zr(IV)	-	2.0	2.0	15	0.4	(5)
	-	4.0	4.0	15	0.80	(5)
Ce(III)	-	2.0	2.0	15	0.003	(5)
	-	4.0	4.0	15	0.003	(5)

TABLE II

THE DISTRIBUTION OF Am IN 30% TBP IN XYLENE

M HNO_3	Total M NO_3^-	E_a^o
0.5	0.5	0.004
1.0	1.0	0.013
2.0	2.0	0.01
4.0	4.0	0.01
5.0	10.3*	0.010

*$Al(NO_3)_3$ added

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The TBP-TTA Separation of Americium

The combination of a TBP extraction and a TTA extraction in one method, requires the initial aqueous phase be of high nitric acid concentration. This same aqueous phase, after the extraction of uranium, must be buffered to a low acidity for the americium extraction. It was decided the initial aqueous phase would be held between 2.0 and 2.5 M HNO_3 in a minimum volume. Thus, the aliquot taken for the second extraction would not require excessive volumes of buffer solution to reach the proper pH.

The distribution of uranium has been measured using fixed volumes of aqueous and organic phases. The initial concentration of uranium in the aqueous phase was 0.0945 M. The acid concentration was varied between 0.5 M and 3.0 M HNO_3. The organic phase was 1.1 M TBP in xylene, (30 per cent TBP). It can be seen from the curve in Figure 2 that extraction coefficient becomes greater at higher acidities but reaches a maximum as the ratio of tributylphosphate to uranium in the organic phase approaches two, in accord with the equation for the reaction on page 6.

Holding the volume of each phase constant and the concentration of tributylphosphate constant, changes in the initial uranium concentration will change the distribution coefficient. This is confirmed by the curves in Figure 3 which have been calculated from Moore's data(3). In theory, maintaining a two to one mole ratio of tributylphosphate in the organic phase to uranium in the aqueous phase is sufficient for extraction. It can be seen, in Figure 3, that a three to one or four to one ratio is more desirable for a one-pass separation of uranium.

The effectiveness of the TBP separation of uranium and americium was tested using a solution of known americium content spiked with varying quantities of uranium. These solutions in 2 M HNO_3 were extracted with 2000 μl of 30 per cent TBP in xylene. Aliquots of the aqueous phase after TBP extraction were removed to clean equipment, and the americium determined by the TTA method. It was apparent that the uranium was removed

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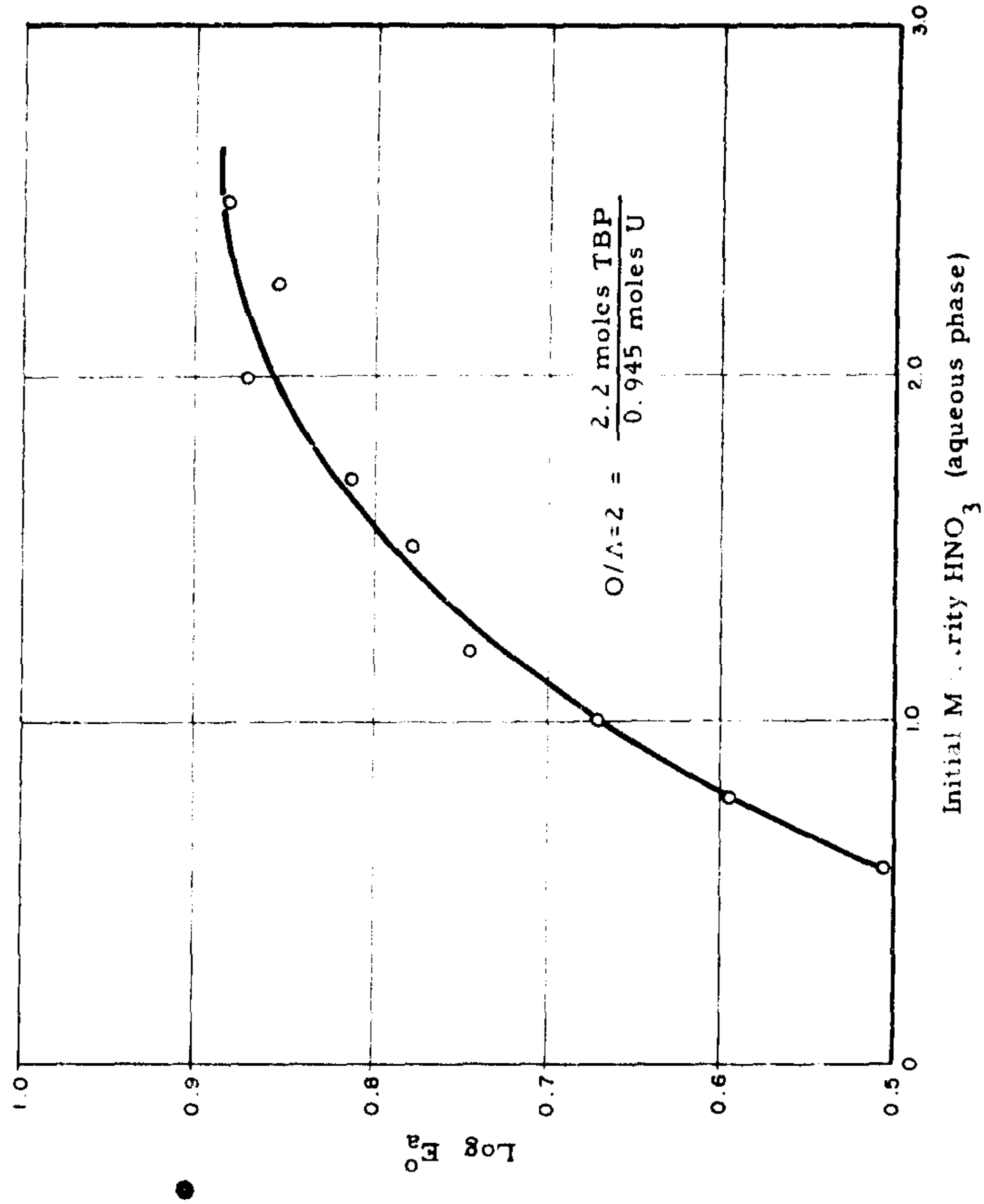

Figure 2
The Distribution of Uranium into TBP

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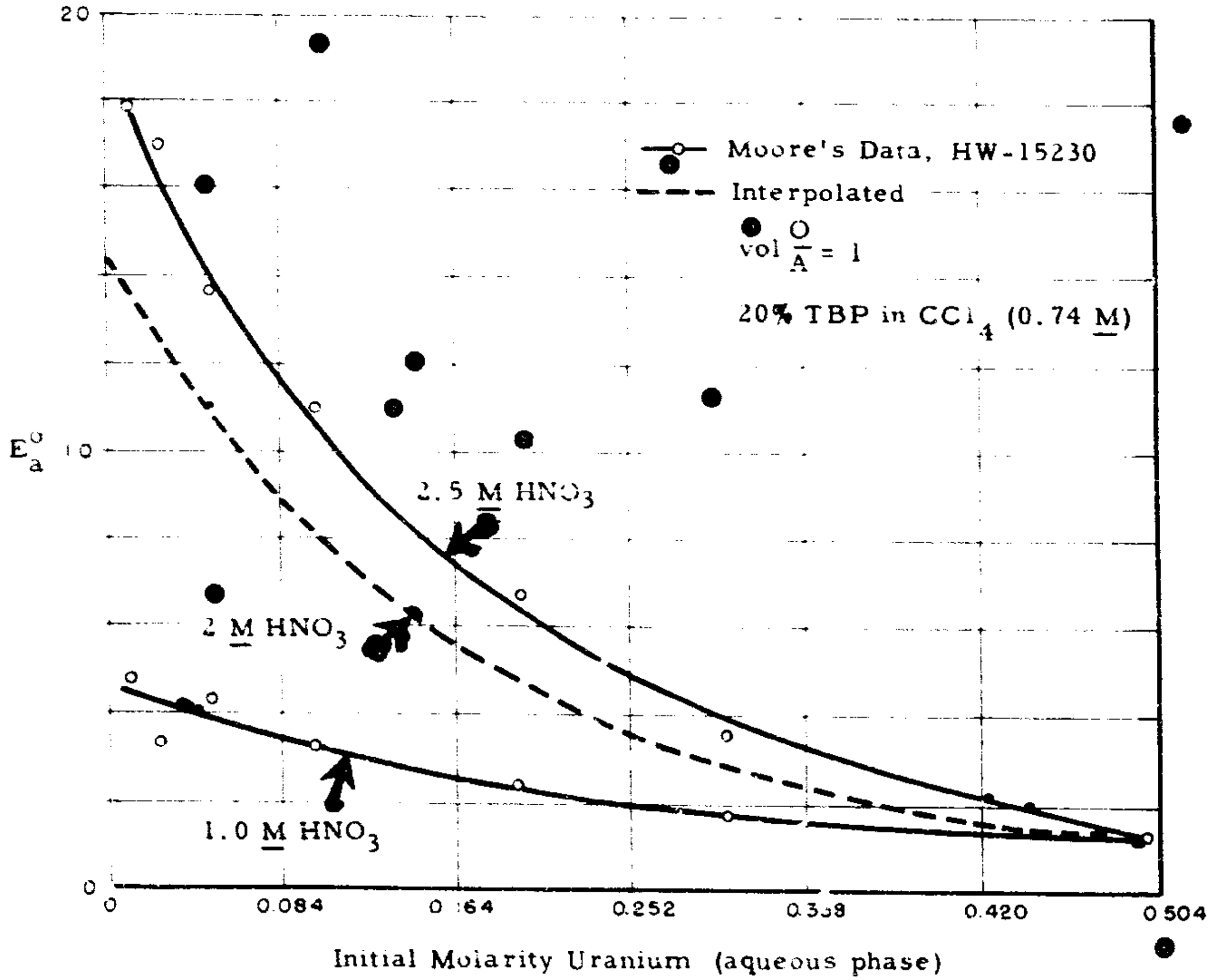

Figure 3
The Effect of Concentration on Distribution

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by the TBP extraction since the aqueous phase became colorless. In some cases microquantities of uranium carried through to the TTA extraction imparting the characteristic uranium-chelate color to the TTA phase. There was no evidence of uranium back-extracting with the americium. The data are presented in Table III.

TABLE III

EFFECT OF TBP EXTRACTION ON TTA AMERICIUM METHOD

Uranium mg added	HNO_3 M	Americium Recovery - %
0	2.00	99
1.5	2.00	96
10.5	1.96	103
*10.5	1.95	99
11.3	2.00	100
46.1	2.03	100
223.0	2.00	96

*0.3 mg $Al(NO_3)_3$ present

Avg. = 100 ± 3.3 (95% C.L.)

The fate of plutonium in the TBP extraction was not investigated. It is obvious from the data in Table I that some Pu(IV) and Pu(VI) will be separated with the uranium. The remaining plutonium will not interfere in the TTA extraction, since Pu(IV) will not back extract into 0.5 M HNO_3, and Pu(VI) will be held in the organic phase by tributylphosphate.

The TBP-TTA method will be affected by those ions which form complexes with uranium such as sulfate, phosphate, and fluoride. Other metals which will interfere to a certain extent are thorium, zirconium, and cerium. Curium will carry with americium.

The Cerium Fluoride Method

The separation of americium from uranium and plutonium on precipitated cerium fluoride has been investigated by H. W. Miller(1). In this method ceric ion is added to oxidize plutonium to Pu(VI). Cerous fluoride

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is then precipitated which carries Am(III). Pu(VI) and U(VI) remain in solution.

In application, the method has been modified to include the dissolution of the cerous fluoride precipitate with zirconium nitrate - nitric acid solution, followed by reprecipitation from a solution of greatly reduced plutonium concentration. This step serves to separate americium from absorbed or occluded plutonium from the first precipitation. Details of this dissolution - reprecipitation have been investigated by M. M. Jones(7).

Interferences in this method are those elements which are precipitated by fluoride, such as rare-earths. The ceric reagent used to oxidize plutonium may be reduced by impurities in the sample, in which case absorption losses will occur due to excess solid material on the counting disc. Macro quantities of aluminum and zirconium and other metals forming soluble fluoride complexes will interfere with the cerous fluoride precipitation. Curium will precipitate with americium.

Comparison of Methods

Solutions were analyzed by the TBP-TTA method and by the cerous fluoride method, including the double precipitation. Three or more determinations by each method were made on each sample. The time for analysis is the same for both methods. The results for comparison and description of the composition of the solutions are presented in Table IV.

TABLE IV

COMPARISON ON TBP-TTA AND CEROUS FLUORIDE METHODS

Sample	U	Pu Content	Am	Am(^{d}/m) TBP-TTA	Am(^{d}/m) CeF_3	Ratio TBP-TTA
1	med	low	high	5.14×10^4	4.76×10^4	1.08
2	high	---	high	3.45×10^5	3.37×10^5	1.02
3	high	high	low	1.42×10^6	1.33×10^6	1.07
4	high	high	low	8.96×10^5	8.60×10^5	1.04

Avg. = 1.05 ± 0.04
(95% C. L.)

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The extraction method is consistently higher than the precipitation method. This difference is probably due to losses in the dissolution step and absorption losses in the cerous fluoride method.

Samples 3 and 4 in Table IV were dissolver solutions from the Redox process, and contain fission product activity. These samples were monitored for analyst exposures. A comparison of exposures on sample 4 for the two methods is shown in Table V. The total exposure for each operation is calculated from the radiation reading and the time spent in manipulation.

TABLE V

COMPARISON OF EXPOSURES

	TBP-TTA (200 µl sample)			CeF$_3$ (100 µl sample)	
	total γ/sample	total β/sample		total γ/sample	total β/sample
Pipetting (pre TBP)	0.8 mr	16 mrads	Pipetting	0.8 mr	16 mrads
Pre TTA ext'n	0.8 mr	15 mrads	1st CeF$_3$ ppt'n	3.5 mr	175 mrads
Back ext'n	0.3 mr	8 mrads	2nd CeF$_3$ ppt'n	1.5 mr	85 mrads
Mounting	0.4 mr	18 mrads	Mounting	0.4 mr	33 mrads
Totals	2.3 mr	57 mrads		6.2 mr	309 mrads

The TBP-TTA extraction method involves less radiation exposure than the cerous fluoride method. This is due to the fact that the time spent in close contact manipulation is shorter for the TBP-TTA method.

ACKNOWLEDGEMENTS

The author wishes to thank A. Chetham-Strode, Jr. and E. M. Kinderman for their contribution to this work.

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ANALYTICAL PROCEDURES

The TBP-TTA Method

A procedure for the TBP-TTA method is outlined as follows:

1. Pipet the sample into a test tube and adjust the volume to exactly 1000 µl, 2 N in HNO_3.
2. Add 2000 µl of 30 per cent TBP in xylene and stir for 15 minutes. Centrifuge and discard the TBP phase.
3. Pipet exactly 500 µl of the aqueous phase into a clean test tube. Wash the pipet twice with 2 M $NaC_2H_3O_2$.
4. Add 100 µl 6 M NaOH.
5. Add exactly 1000 µl of 0.5 M TTA in xylene and stir for 15 minutes. Centrifuge and discard the aqueous phase.
6. Pipet exactly 500 µl of the TTA phase into a clean test tube. Wash the pipet once with 30 per cent TBP in xylene.
7. Add exactly 500 µl of 0.5 M HNO_3 and stir for 15 minutes. Centrifuge and discard TTA phase.
8. Mount an aliquot of the aqueous phase for counting.
9. Calculations:

$$^{c}/m/\text{sample} = {}^{c}/m\,(A)\,(B)\,(C)$$

where

$$A = \frac{\text{volume of 2N aqueous phase}}{\text{volume of 2N phase removed}}$$

$$B = \frac{\text{volume of TTA added}}{\text{volume of TTA removed}}$$

$$C = \frac{\text{volume of 0.5 M HNO3 added}}{\text{volume of 0.5 M HNO3 mounted}}$$

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The CeF_3 Method

A procedure for the CeF_3 method is outlined as follows:

1. Pipet the sample into a centrifuge cone and dilute to 2 ml with 2 N HNO_3.
2. Heat in water bath at 95° C for 10 minutes.
3. Add one drop 0.05 M $Cr_2O_7^=$ and heat for 5 minutes.
4. Add 250 µl 0.1 M Ce^{+4} solution and heat for 15 minutes. Cool to room temperature.
5. Add 10 drops of 27 M HF which has been previously treated with a few drops of 0.05 M $Cr_2O_7^=$ and stored in a platinum container. Stir and digest 5 minutes.
6. Centrifuge and discard the supernate.
7. Add one drop 0.05 M $Cr_2O_7^=$ and 3 drops 0.1 M $ZrO(NO_3)_2$ and stir vigorously.
8. Add 2 ml of 2 N HNO_3 and stir till the precipitate dissolves.
9. Add 10 drops of 27 M HF as before. Stir and digest 5 minutes.
10. Centrifuge and discard the supernate.
11. Wash the precipitate 3 times with 1 N HF - 1 N HNO_3 solution.
12. Slurry the precipitate and transfer to a platinum disc using wash solution.
13. Dry, flame and count.

[redacted]

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