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# THE SOLVENT EXTRACTION OF PLUTONIUM AND AMERICIUM BY TRI-n-OCTYLPHOSPHINE OXIDE

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THE increasing use of organophosphorus compounds (such as TOPO, tri-n-octylphosphine oxide) in solvent extraction is due to their selectivity and efficiency in removing metal ions from aqueous solutions. TOPO dissolved in an inert hydrocarbon solvent is outstanding amongst the newer reagents. Ross and WHITE<sup>(1)</sup> studied the extraction of several metal ions by TOPO, and published a preliminary qualitative survey. Later quantitative results,<sup>(2)</sup> and a detailed study of the extraction of thorium,<sup>(3,4)</sup> iron,<sup>(5)</sup> zirconium,<sup>(6)</sup> chromium,<sup>(7)</sup> and technetium<sup>(8)</sup> confirmed its effectiveness and new analytical methods for chromium,<sup>(9)</sup> titanium,<sup>(10)</sup> uranium,<sup>(11)</sup> zirconium<sup>(12)</sup> and thorium<sup>(13)</sup> involve a TOPO solvent-extraction stage.

Although TOPO will extract at least twenty-three different metal ions, the conditions for extraction vary considerably. Normally extraction is from acidic solutions. when the nature and strength of the acid are critical factors, e.g. TOPO extracts ferric iron from hydrochloric acid solutions but not from nitric, sulphuric, perchloric or phosphoric acid solutions. The charge on the metal ion is another critical factor; TOPO extracts ferric but not ferrous iron from hydrochloric acid, and hexavalent (i.e. chromate) but not di- or tri-valent chromium. In addition, a single extraction with TOPO under optimum conditions gives a quantitative separation.

The versatility outlined above indicated that TOPO might be of use in the separation of plutonium from other metal ions. This paper describes the extraction of plutonium in three valency states (III, IV, and VI) from nitric and hydrochloric acids of various strengths, and the properties of the plutonium (IV and VI)-TOPO complexes extracted into the organic phase from nitric acid. The extraction of americium (III) from nitric acid is also described.

# **EXPERIMENTAL**

Preparation of 0.1 M-TOPO in cyclohexane

In the first experiments TOPO was prepared by the reaction of phosphorus oxychloride with the

<sup>(1)</sup> W. J. Ross and J. C. WHITE, Report ORNL-CF-56-9-18 (1956).

(2) J. C. WHITE, A.S.T.M. Special Technical Publication 238, 27 (1958).

<sup>(1)</sup> J. C. WHITE, A.S.I.M. Special recrifted rubication 236, 27 (1938).
 <sup>(3)</sup> W. J. Ross and J. C. WHITE, Report ORNL-2627 (1958).
 <sup>(4)</sup> R. A. ZINGARO and J. C. WHITE, J. Inorg. Nucl. Chem. 12, 315 (1960).
 <sup>(5)</sup> J. C. WHITE and W. J. Ross, Report ORNL-2382 (1957).
 <sup>(6)</sup> J. C. WHITE and W. J. Ross, Report ORNL-2498 (1958).
 <sup>(7)</sup> J. C. WHITE and W. J. Ross, Report ORNL-2326 (1957).
 <sup>(8)</sup> C. D. Burn and O. V. Locand, Blue, Chem. 6498 (1960).

(8) G. E. BOYD and Q. V. LARSON, J. Phys. Chem. 64, 988 (1960).
 (9) C. K. MANN and J. C. WHITE, Analyt. Chem. 30, 989 (1958).
 (10) J. P. YOUNG and J. C. WHITE, Analyt. Chem. 31, 393 (1959).

(11) J. C. WHITE and C. A. HORTON, Analyt. Chem. 30, 1779 (1958).
 (12) J. P. YOUNG and J. C. WHITE, Talanta 1, 263 (1958).

(13) J. C. WHITE, Analyt. Chem. 31, 1847 (1959).

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Grignard reagent prepared from 1-bromoöctane and magnesium.<sup>(14)</sup> Acidic impurities such as dioctylphosphinic acid were removed from the product by shaking the mixture in petroleum ether with activated alumina, and TOPO was not finally recrystallized until shown to be free of acids by titration with sodium hydroxide using phenolphthalein as the indicator. Later experiments employed material (m.p.  $50-52^{\circ}$ C) supplied by Albright and Wilson (Mfg.) Ltd.; the two batches of TOPO had the same m.p. and mixed m.p. Cyclohexane was supplied by L. Light and Co. Ltd., and was distilled (b.p.  $81^{\circ}$ C). TOPO was always recrystallized from cyclohexane before use, and the 0.1 M solution then prepared was stored in an opaque container. Recrystallization of TOPO immediately before use was essential to obtain a clear solution.

#### Preparation of plutonium (IV)

A recently-prepared standard solution of plutonium (IV) (100 mg/ml in 10.0 N nitric acid) was used after dilution with 1.0 N nitric acid.

#### Preparation of plutonium (VI)

Plutonium entirely in the six-valent state was prepared by anodic oxidation of plutonium (IV), using the method described by HEALY and GARDNER.<sup>(15)</sup> The solution was examined for plutonium (IV) every day, and was only used if it contained no detectable amount of the latter (<0.5%).

#### Preparation of plutonium (III)

A stock solution of plutonium (III) in hydrochloric acid was prepared by dissolving 12.5 mg of plutonium metal in 2.0 N hydrochloric acid. The solution was stabilized by addition of hydroxylamine hydrochloride. Solutions of plutonium (III) nitrate were prepared by reduction of 1.0 mg/ml plutonium (IV) nitrate in 0.5 N nitric acid with either hydroxylamine nitrate, hydroxylamine nitrate and sulphamic acid or ferrous sulphamate. After adding the reducing agent, the solutions were allowed to stand overnight before extraction with 0.1 M TOPO in cyclohexane.

#### Method of equilibration

Throughout this work 1 ml of aqueous solution was shaken for 10 min with 1 ml of organic solution (0·1 M TOPO conditioned with acid of the same strength as the aqueous solution). The degree of extraction did not change if the solutions were shaken for longer periods. The phases separated rapidly after shaking, and the aqueous layer was analysed for plutonium by  $\alpha$ -counting. The activity of the aqueous phase before equilibration was also measured, and so gave by difference the activity of the organic phase. In the americium (III) experiments the organic and aqueous layers were both counted after equilibration. Reproducibility of results was the criterion of stability of a valency state, and the instability of plutonium (III) in nitric acid was clearly demonstrated by lack of consistent results. With the more concentrated solutions (1 mg/ml) it was possible to check some of the plutonium (IV and VI) valency states spectrophotometrically (see below).

All experiments were carried out at room temperature (about 20°C).

#### Spectrophotometric measurements

All measurements were made with a Hilger Mark II H700 Uvispek spectrophotometer, the solutions being contained in 10 mm fused silica cells with ground-glass stoppers.

#### The determination of nitric acid in 0.1 M TOPO

Five millilitre of nitric acid (0.30-11.0 N) was shaken with 5 ml of 0.1 M TOPO in cyclohexane for 10 min. After the phases had separated 4 ml of the organic layer was removed and shaken with a known excess of sodium hydroxide solution. The excess sodium hydroxide was titrated with standard hydrochloric acid using screened methyl orange as indicator.

(14) K. B. BROWN, Report ORNL-2399 (1957).

<sup>(15)</sup> T. V. HEALY and A. W. GARDNER, J. Inorg. Nucl. Chem. 7, 245 (1958).

#### RESULTS

# Results are expressed in terms of an extraction coefficient, $E_a^{0}$ , defined:

$$E_a^0 = \frac{\text{Concentration of plutonium in organic phase}}{\text{Concentration of plutonium in aqueous phase}}$$
 at equilibrium

or

$$E_{\alpha}^{0} = \frac{\alpha - \text{Activity of plutonium in organic phase}}{\alpha - \text{Activity of plutonium in aqueous phase}}$$

## Extraction of plutonium (III, IV, and VI) and americium (III) nitrates

The extraction coefficients of americium (III) and plutonium (IV and VI) nitrates from nitric acid by 0.1 M TOPO are recorded in Table 1, and plotted in Fig. 1. For comparison the extraction coefficients of chromium (VI) and uranium (VI) from the paper by  $WHITE^{(2)}$  are also shown in Fig. 1.

In these experiments the plutonium solutions contained americium-241 formed by  $\beta$ -decay of plutonium-241. On account of its high specific activity and stability in the trivalent state compared with plutonium, traces of americium lead to appreciable errors in the experimentally-determined extraction coefficients. Using the extraction coefficients of americium (III), the plutonium (IV and VI) extraction coefficients were corrected for small known amounts of americium.

Over the range of acidities examined 0.1 M TOPO extracted at least 99.5 per cent of the plutonium (IV) nitrate and 99.5 per cent of the plutonium (VI) nitrate from 0.3 to 0.7 N nitric acid. The extraction of plutonium (III) nitrate from 0.2 to 2.0 N nitric acid was studied, but reproducible results could not be obtained.

### Extraction of plutonium (III, IV, and VI) chlorides

The extraction coefficients of plutonium (III, IV, and VI) chlorides from hydrochloric acid by 0.1 M TOPO are recorded in Table 2 and plotted in Fig. 2 which also shows the extraction coefficients for chromium (VI) and uranium (VI).

No correction for americium-241 was necessary in this case as the stock solution was made from freshly-separated plutonium. At acidities less than 5.0 N, plutonium (IV and VI) chlorides were not extracted as efficiently as the nitrates. At acidities greater than 5.0 N, however, the extraction was again virtually quantitative. The extraction coefficient of plutonium (III) from hydrochloric acid increased with acid strength, but was always less than unity.

#### Variation of extraction with TOPO concentration

A study of the chemical nature of the complexes extracted into cyclohexane by TOPO was limited to those derived from plutonium (IV and VI) nitrates. Maximum extraction occurs at the acidity at which the complex is most stable, viz.  $6\cdot0-7\cdot0$  N for the plutonium (IV) complex and less than 1N for the plutonium (VI) complex. The acidities used in these experiments were  $7\cdot0$  N (plutonium IV) and  $0\cdot69$  N (plutonium VI).

Solutions containing 1 mg/ml of plutonium (IV) in 7.0 N nitric acid were shaken with varying molar excesses of TOPO in cyclohexane using a 1:1 phase ratio. The extraction coefficients are shown in Fig. 3. The formation of the extractable complex may be written as:

Pu(IV) + n TOPO  $\rightleftharpoons Pu(IV)$  (TOPO)<sub>n</sub>.



FIG. 1.-Extraction of metal ions from nitric acid by 0.1 M TOPO in cyclohexane.

ignoring the effect of complexing by nitrate ions, which also occurs. The stability constant for the reaction is then:

$$K = \frac{[\operatorname{Pu}(\operatorname{IV})(\operatorname{TOPO})_n]}{[\operatorname{Pu}(\operatorname{IV})][\operatorname{TOPO}]^n}$$
$$\log K = \log \frac{[\operatorname{Pu}(\operatorname{IV})(\operatorname{TOPO})_n]}{[\operatorname{Pu}(\operatorname{IV})]} - n \log [\operatorname{TOPO}]$$

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Nitric acid molarity	Extraction coefficients		
	Am (III)	Pu (IV)	Pu (VI)
0.30		· ·	224.9
0.50	—	211.0	_
0.60	1.03	— ,	_
0.69	—	'	238.4
1.50	$2\cdot42$ $ imes$ $10^{-1}$	— ,	110.4
2.00		309.6	
3.00	$1.59 \times 10^{-2}$	_ '	29.3
4.00	_	514.0	25·0
5.00	$3\cdot 30 \times 10^{-3}$	. — :	28.3
6.00		567-1	32.3
7.00	$1.89 \times 10^{-3}$	567.1	24.2
9.00	$1.36 \times 10^{-3}$	404.9	14.9
11.00	$1.26 \times 10^{-3}$	272.3	6.4

Table 1.—The extraction of Americium (III) and plutonium (IV and VI) nitrates by  $0{\cdot}1$  m topo



FIG. 2.--Extraction of metal ions from hydrochloric acid by 0.1 M TOPO in cyclohexane

At equilibrium all the complex is in the organic phase, and all the uncomplexed plutonium (IV) is in the aqueous phase, so that:

$$\log K = \log E_a^{\ 0} - n \log [\text{TOPO}]$$
$$\log E_a^{\ 0} = n \log [\text{TOPO}] + \log K$$
$$n := \frac{\log E_a^{\ 0}}{\log [\text{TOPO}]}$$

whence

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When  $\log [TOPO] = 0$ 

$$\log K = \log E_a^{C}$$

TABLE 2.—THE EXTRACTION OF PLUTONIUM (III, IV, AND VI)
CHLORIDES BY 0.1 M TOPO

Hydrochloric acid molarity	Extraction coefficients		
	Pu (III)	Pu (IV)	Pu (VI)
0.43	0.11	·	
1.00	0.12	7·0	19-1
2.90	0.15		
3.00		11.1	27.2
3.85	<b>0</b> ∙19		—
4.80	0.25		
5.00	—	50.4	271.6
7.00	_	172.6	329.4
7.65	0.68	_	—
8.60	0.76		_
9.00		342.6	250.3
11.00	—	280.0	109.7

The effect of nitrate complexing will be discussed later in this paper. By plotting  $\log E_a^0$  vs. log [TOPO] as in Fig. 4 the slope gives a value for *n*, and the intercept on the  $\log E_a^0$  axis a value for log K. For the plutonium (IV) complex these values were n = 2.02, log K = 5.10,  $K = 1.26 \times 10^5$ .

A similar treatment of the plutonium (VI) complex extracted from 0.69 N nitric acid gave n = 1.98, log K = 4.50,  $K = 3.16 \times 10^4$ .

Thus the ratio of plutonium: TOPO is 1:2 in both of the complexes. The stability constants are tentative values, owing to the long extrapolation to log [TOPO] == 0 (all the results are for values of log [TOPO] between -1 and -2). Fig. 4, however, shows quite definitely that the plutonium (IV) complex is more stable than the plutonium (VI) complex.

#### Visible absorption spectrum of the plutonium (IV and VI)-TOPO complexes

The absorption spectrum of the plutonium (IV)-TOPO complex extracted from 7.0 N nitric acid into cyclohexane was measured from 400 m $\mu$  to 1000 m $\mu$ , using cyclohexane as a "blank". The region from 440 m $\mu$  to 860 m $\mu$ , containing the important absorption peaks, is shown in Fig. 5 together with the spectrum of plutonium (IV) nitrate in 7.0 N nitric acid. The characteristic absorption maximum of

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FIG. 3.—Effect of varying molar excesses of TOPO on the extraction coefficient of plutonium (IV) nitrate from 7.0 N nitric acid.



FIG. 4.—The greater stability of the plutonium (IV)-TOPO complex compared with the plutonium (VI)-TOPO complex.

plutonium (IV) nitrate at 476 m $\mu$  is shifted to 491 m $\mu$  in the TOPO complex (as also in concentrated nitric acid) and the absorption is greater throughout.

Fig. 6 shows a similar comparison of the plutonium (VI)-TOPO complex extracted from 0.69 N nitric acid and plutonium (VI) nitrate in 0.5 N nitric acid. The 830 m $\mu$ 



FIG. 5.—The spectra of plutonium (IV) nitrate in 7.0 N nitric acid, and of the plutonium (IV)-TOPO complex formed from 7.0 N nitric acid.



FIG. 6.—The spectra of plutonium (VI) nitrate in 0.5 N nitric acid, and of the plutonium (VI)-TOPO complex formed from 0.69 N nitric acid.

peak of plutonium (VI) nitrate is shifted to 847 m $\mu$  with some diminution of intensity. At other wavelengths the TOPO complex absorbs light more strongly than the ordinary nitrate complex.

As shown in Fig. 6 plutonium (VI) nitrate in dilute nitric acid does not absorb light in the region 670–720 m $\mu$ , so that any absorption in this region can be ascribed to plutonium (IV) impurity. The absence of absorption in this region was in fact used as the criterion of purity of the valency of plutonium (VI) nitrate solutions. The application of Job's "continuous variation method" to plutonium-TOPO complexes

JOB's method of continuous variation<sup>(16)</sup> is widely used in the identification of complex compounds formed in solution, but fails if more than one complex is formed from the same components. By means of spectrophotometric measurements JOB's method has been improved so that several complexes in the same solution can be differentiated.<sup>(17)</sup> By measuring the optical densities of a series of solutions of the



FIG. 7.—JoB's continuous variation method applied to the plutonium (IV)-TOPO complex.

same total concentration of ion plus ligand at several different wavelengths the formula of the complex may be obtained, or alternatively the existence of several complexes is apparent.

To confirm the formula of the plutonium (IV)-TOPO complex, a series of solutions of the complex was prepared by extraction of plutonium (IV) nitrate from 7.0 N nitric acid into TOPO in cyclohexane. All the solutions had the same total molarity initially (0.0336 M), but the actual plutonium (IV) and TOPO concentrations were varied. The optical densities of each solution were measured at wavelengths selected from Fig. 5—namely 435, 491, 500, 550 and 662 m $\mu$ , and are plotted in Fig. 7. From this we see that

$$\frac{[Pu (IV)]}{[Pu (IV)] \div [TOPO]} = 0.33$$

$$Pu (IV) : TOPO = 1 : 2.$$

(13/)

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The experiment was repeated with plutonium (VI) nitrate in 0.69 nitric acid and TOPO in cyclohexane. The total concentration was 0.0336 M initially and the optical densities were measured at 410, 470, 830, 840, 845 and 850 m $\mu$ . This gave

<sup>(16)</sup> P. JOB, Ann. Chim. 9, 113 (1928).

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<sup>(17)</sup> W. C. VOSBURGH and G. R. COOPER, J. Amer. Chem. Soc. 63, 437 (1941).

Pu(VI):TOPO = 1:2, again confirming the ratio determined previously and proving that only one complex is formed.

### The extraction of nitric acid by 0.1 M-TOPO in cyclohexane

The results are shown in Fig. 8. One molecule of TOPO extracts one molecule of nitric acid from 4.45 N acid. Between 2.0 N and 8.0 N nitric acid the number of



FIG. 8.--The extraction of nitric acid by 0.1 M TOPO in cyclohexane.

moles of nitric acid extracted per mole of TOPO increases linearly, but above 8.0 N the amount of acid increases very rapidly. A recent paper<sup>(18)</sup> dealing with the extraction of nitric acid by tributyl phosphate has shown that the organic phase contains only associated "HNO<sub>3</sub>". At low acidities most of the nitric acid is present as the 1:1 complex TBP·HNO<sub>3</sub>, while at higher acidities the effect of associated nitric acid extracted into the organic phase is considerable.

The extraction of nitric acid by 0.1 M TOPO follows a similar pattern, and the experimentally-determined curve may be divided into two portions, one due to the formation of TOPO·HNO<sub>3</sub>, and the other due to the partition of associated nitric acid. ZINGARO and WHITE<sup>(4)</sup> showed that from 0 to 0.4 N nitric acid extraction is consistent with the formation of a 1:1 complex.

<sup>(18)</sup> F. L. BOYER and L. J. BIRCHER, J. Phys. Chem. 64, 1328 (1960).

### DISCUSSION

# The variation of extraction coefficient with acidity

The shape of the extraction curve for plutonium (IV) nitrate by TOPO (Fig. 1) is a familiar one, and is characteristic of the extraction of plutonium (IV) by uncharged reagents. Electromigration<sup>(19)</sup> and ion-exchange measurements<sup>(20)</sup> show that in nitric acid plutonium (IV) may be present as a cation, an uncharged molecule or an anion, depending on the strength of the acid. There are, however, no sharply defined acidity limits for the existence of any particular species. Thus in nitric acid below 1 N,  $Pu(NO_3)^{3+}$ ,  $Pu(NO_3)_2^{2+}$  and  $Pu(NO_3)_3^{+}$  are stable, whilst from 1 to 8 N uncharged  $Pu(NO_3)_4$  predominates.  $Pu(NO_3)_5^-$  is also present in increasing amounts, and at higher acidities,  $Pu(NO_3)_6^{2-}$ . As the extraction maximum for plutonium (IV)-TOPO coincides with the acidity corresponding to the maximum stability of uncharged  $Pu(NO_3)_4$ , the extractable complex could be  $Pu(NO_3)_4 \cdot 2$  TOPO.

The decrease in extraction coefficient from nitric acid stronger than 7 N is due partly to the formation of anionic plutonium (IV) complexes and partly to the competition between plutonium (IV) and nitric acid for TOPO. Above 8 N the concentration of associated "HNO3" in nitric acid increases rapidly<sup>(20)</sup> so displacing the equilibrium to the right in the following equation:

### $TOPO + HNO_3 \rightleftharpoons TOPO HNO_3$

Consequently at high acidities there will be less TOPO available for complexing plutonium (IV).

In the case of plutonium (VI) a similar maximum occurs in extraction from 6.0 N nitric acid. The principal maximum, however, is from 0.69 N nitric acid, and the reason for this is not clear. The removal of acidic impurities from TOPO, ensures that the first extraction peak (apparently hydrogen ion-dependent) cannot be due to the formation of a plutonium (VI)-dioctylphosphinate complex. Furthermore, the plutonium (VI) concentration  $(4.2 \times 10^{-3} \text{ M})$  is too high for the observed effect to be caused by reaction of plutonium (VI) with traces of impurity. In the extraction of plutonium (IV and VI) nitrates by tributyl phosphate,<sup>(21)</sup> another neutral reagent, the two curves show the same simple peak shape, plutonium (VI) extraction being the lower.

The extraction of plutonium (IV and VI) chlorides (Fig. 2) is apparently similar to that described for plutonium (IV) nitrate. The low extraction of plutonium (III) from chloride solutions is characteristic of trivalent actinides. The weak complexing of plutonium (III) by chloride ions<sup>(22)</sup> is insufficient to form uncharged PuCl<sub>a</sub>, which may be necessary for quantitative extraction.

### The instability of plutonium (III) in nitric acid

The instability of plutonium (III) in nitric acid is well known and DUKES<sup>(23)</sup> has studied the oxidation of plutonium (III) by nitrous acid. CARLESON<sup>(24)</sup> has shown

<sup>(19)</sup> C. K. MCLANE, J. S. DIXON and J. C. HINDMAN. The Transuranium Elements (Edited by G. T. SEABORG, J. J. KATZ and W. M. MANNING), NNES, Division IV, Plutonium Project Record, Vol. 14B, p. 364. McGraw-Hill, New York (1949).

 <sup>(20)</sup> J. BROTHERS, R. G. HART and W. G. MATHERS, J. Inorg. Nucl. Chem. 7, 85 (1958).
 (21) G. F. BEST, H. A. C. MCKAY and P. R. WOODGATE, J. Inorg. Nucl. Chem. 4, 315 (1957).

 <sup>&</sup>lt;sup>(32)</sup> M. WARD and G. A. WELCH, J. Inorg. Nucl. Chem. 2, 395 (1956).
 <sup>(23)</sup> E. K. DUKES, J. Amer. Chem. Soc. 82, 9 (1960).

<sup>&</sup>lt;sup>(24)</sup> G. CARLESON, Proceedings of the Second International Conference on the Peaceful Uses of Atomic Energy, Geneva, 1958, Vol. 17, p. 111. United Nations (1959).

that the partition coefficient of plutonium (III) between nitric acid and 36 per cent tributyl phosphate (TBP) in olefin-free kerosene depends on the reducing and stabilizing agents used. Other extraction systems for plutonium (III) in nitric acid are:

Extracting reagent	Strongest acid used	Reference
100 % TBP	2.5 N	(25)
20% TBP in odourless kerosene	5.0 N	(21)
10% Tri-n-octylamine in xylene	8.0 N	(26)

Each author claimed to use the strongest acid in which plutonium (III) is stable. This discrepancy may be due to the use of different solvents and extracting agents. As described earlier, pure plutonium (III) could not be extracted with TOPO from nitric acid at any acidity, partial oxidation to plutonium (IV) always occurred. This is unfortunate, as stable plutonium (III) with a low extraction coefficient would be of considerable analytical importance.

### Analytical applications

In determining the solvent extraction properties of plutonium and americium ions by TOPO, the advantages and limitations of TOPO in the analysis of plutonium and americium became apparent. The single disadvantage is the ease with which TOPO extracts the higher valency states of other actinide ions (e.g. uranium (VI) and thorium (IV)), so making a separation from plutonium (IV and VI) difficult. On the other hand, when the trivalent actinide is stable as in the case of americium, separation from plutonium (IV and VI), uranium (VI), and thorium (IV) is a simple matter. In addition TOPO could simplify the separation of plutonium from most metal ions other than the actinides, and it is to be recommended for this purpose. Extraction with TOPO is nearly always quantitative, and a large aqueous to organic phase ratio may be used.<sup>(10)</sup>

(25) G. F. BEST, E. HESFORD and H. A. C. MCKAY, J. Inorg. Nucl. Chem. 12, 136 (1960).
 (26) W. E. KEDER, J. C. SHEPPARD and A. S. WILSON, J. Inorg. Nucl. Chem. 12, 327 (1960).