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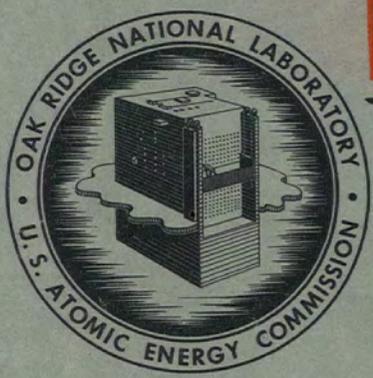
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THE USE OF TRI-n-OCTYLPHOSPHINE OXIDE
IN THE SOLVENT EXTRACTION OF
THORIUM FROM ACIDIC SOLUTIONS

W. J. Ross
J. C. White

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OF THORIUM FROM ACIDIC SOLUTIONS

W. J. Ross and J. C. White

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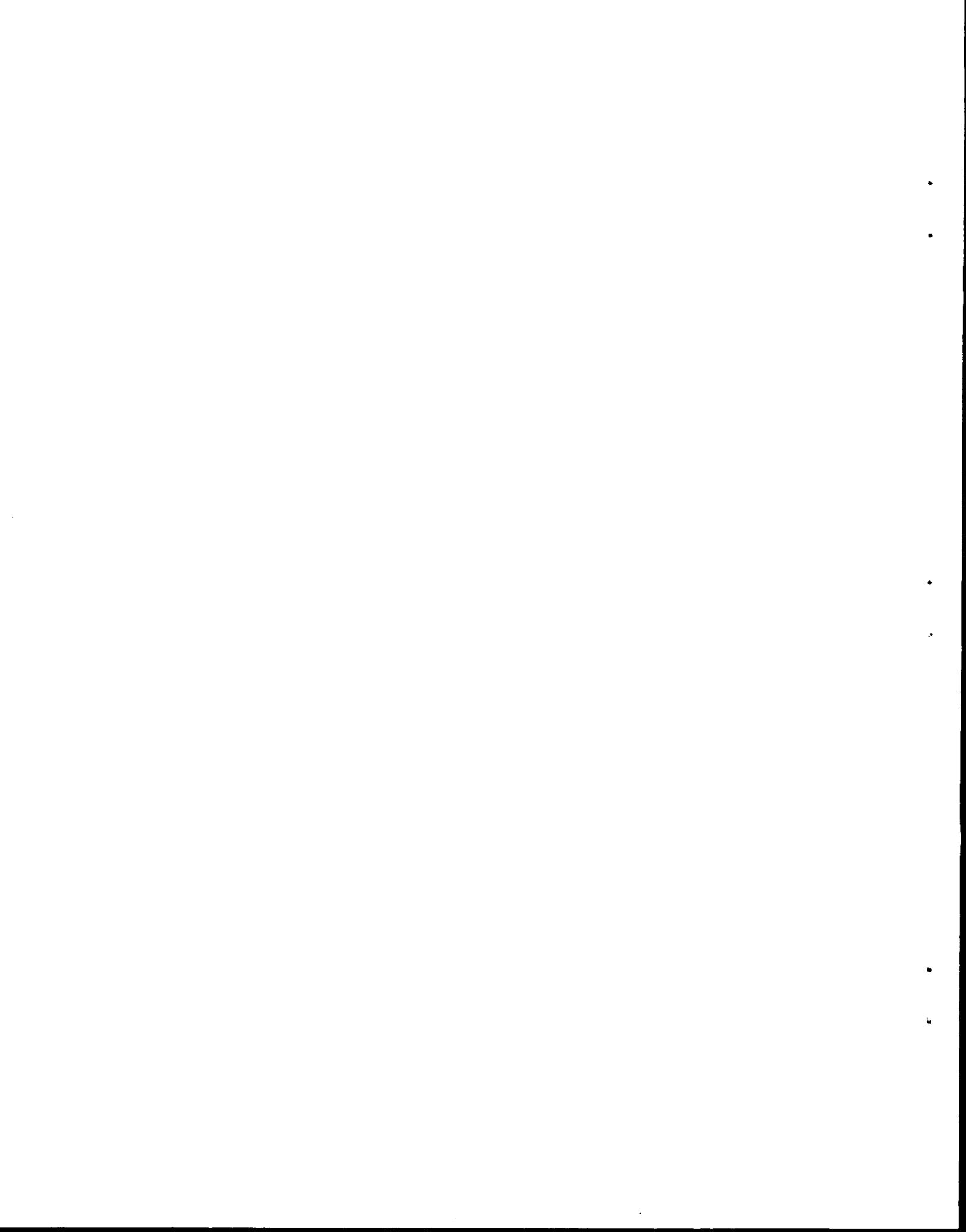


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ABSTRACT

Thorium is readily extracted by a solution of tri-n-octylphosphine oxide in cyclohexane from either acidic nitrate or chloride solutions. The maximum extraction coefficient in a nitrate medium is 380° as compared to 1300 for a chloride solution. In nitrate media the extraction coefficient is relatively unaffected by changes in the anion concentration. In chloride media, however, the coefficient varies directly with increasing chloride concentration, i.e. from about 0.4 in one molar chloride to the maximum in 7 to 10 molar. The acid concentration should be at least one molar.

Thorium is not appreciably extracted from sulfate solutions. The extraction coefficient is of the order of 0.3. The addition of nitrate or chloride increases the coefficient sufficiently so that essentially 99 per cent of the thorium can be extracted in a single equilibration. In perchlorate systems the extraction is most efficient in one molar acid. The maximum coefficient is about 80.

The amount of thorium that can be extracted to 99 per cent in a single 10-minute equilibration period is 46 mg in nitrate and 28 mg in chloride systems per millimole of TOPO. The extracted species are postulated to be $\text{ThCl}_4 \cdot \text{HCl} \cdot 3[\text{n}-(\text{C}_8\text{H}_{17})_3\text{PO}]$ and $\text{Th}(\text{NO}_3)_4 \cdot \text{HNO}_3 \cdot 3[\text{n}-(\text{C}_8\text{H}_{17})_3\text{PO}]$ wherein the concentration of the acid adduct is a function of the initial concentration of acid in the aqueous phase.

THE USE OF TRI-n-OCTYLPHOSPHINE OXIDE IN THE SOLVENT EXTRACTION
OF THORIUM FROM ACIDIC SOLUTIONS

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INTRODUCTION

In several communications^(4,7,8,9,10) from this laboratory the selectivity and the versatility of tri-n-octylphosphine oxide (TOPO) as a reagent for the solvent extraction of certain metals have been discussed. Systematic investigations of the solvent extraction of chromium,⁽⁸⁾ iron,⁽⁴⁾ and zirconium⁽⁹⁾ from acidic solutions with TOPO, dissolved in inert hydrocarbon solvents, have been reported previously. This report involves a similar study of the extraction characteristics of thorium in acidic systems.

In their preliminary survey test program,⁽⁷⁾ the authors reported that thorium was extracted by TOPO from acidic chloride, sulfate, nitrate and perchlorate solutions. These results were considered tentative inasmuch as the sensitivity of the spectrographic method used in these tests was less for thorium than for most of the other elements investigated. In this investigation more refined analytical techniques have been used to determine the fundamental extraction characteristics of thorium.

This report is limited to a description of these fundamental extraction characteristics. Several interesting and useful analytical separations of thorium have already been derived from applications of these basic data, however, and will be reported elsewhere.

REAGENTS

Thorium nitrate stock solution, approximately 233 mg of thorium per ml.

This solution was prepared by dissolving 26 g of reagent grade thorium oxide, ThO_2 , in 100 ml of 3 M HNO_3 .

Standard solutions of thorium nitrate, approximately 12 and 23 mg per ml.

These solutions were prepared by diluting 5 and 10 ml of the stock solution, respectively, to 100 ml with water. The solutions were standardized by analyzing them for thorium gravimetrically.⁽²⁾

Standard solutions of thorium chloride, approximately 11 and 113 mg per ml. These solutions were prepared by evaporating 25 ml of the thorium nitrate stock solution to dryness and dissolving the residue in 25 ml of concentrated hydrochloric acid which had been equilibrated with 0.1 M TOPO in cyclohexane to remove traces of iron(III). The evaporation and dissolution procedure was repeated four times to ensure complete removal of nitrate. The final residue was dissolved in 50 ml of 1 M HCl . The more dilute standard solution was prepared by diluting 10 ml of the concentrated thorium chloride solution to 100 ml with 1 M HCl . Both solutions were standardized by a gravimetric method.

Standard solution of thorium perchlorate, approximately 11 mg of thorium per ml. This solution was prepared by evaporating 10 ml of the thorium chloride solution (113 mg Th per ml) to dryness and then dissolving the residue in 10 ml of perchloric acid. The solution was evaporated to fumes of perchloric acid four times with intermittent dilutions with 10 ml of 2 M HClO_4 in order to remove chloride. After the final evaporation step, the solution of thorium was diluted to 100 ml with 1 M HClO_4 and standardized gravimetrically.

Tri-n-octylphosphine oxide (TOPO), $(C_8H_{17})_3PO$, 0.1 M solution. This solution was prepared by dissolving 38.6 g of TOPO in one liter of cyclohexane. The reagent was obtained from Eastman Organic Chemicals, EK7440; its purity exceeded 99 per cent $(C_8H_{17})_3PO$. The diluent was also obtained from Eastman, EK702 (M.P. 4-5.5°C).

GENERAL PROCEDURE

The experimental techniques that are described in this report have been reported previously.⁽⁸⁾ The test solution to be extracted in each experiment was prepared by combining the desired amounts of standard thorium solution with either nitric, hydrochloric, perchloric, or sulfuric acid. The volume of the solution to be extracted was usually 5 ml. In those tests where the effect of anion concentration was being investigated at constant hydrogen-ion concentration, neutral salts were dissolved in the acidic thorium solutions to yield the desired concentration of anion. The solutions were extracted with 5 ml of the cyclohexane solution of TOPO by agitating the two phases by means of a Kahn shaker for a predetermined period of time.

Following equilibration, the phases were allowed to stand until they separated completely. The degree to which thorium was distributed between the two phases was usually established through the determination of the thorium that remained in the aqueous phase. Test portions of the aqueous phase were removed by pipet and the concentration of thorium was determined by the gravimetric oxalate or spectrophotometric Thorin⁽⁶⁾ methods. The concentration of thorium in the organic phase was subsequently calculated by difference.

A non-aqueous colorimetric method⁽⁵⁾ was developed and applied to the determination of thorium in the organic phase of many of the test mixtures, usually as an independent method for checking the results of the indirect method. This non-aqueous method consisted of forming the red thorium-alizarin complex in an ethanol-acetone dilution of the organic phase and measuring the absorbance of this colored solution at a wavelength of 538 m μ . The intensity of the colored solution adheres to Beer's law at this wavelength and the molar absorbance index is about 11,000.

The concentration of chloride in the organic phase was determined by titrating the chloride in alcoholic dilutions of the organic phase by the Volhard method.⁽³⁾

The determination of nitrate in the organic phase was achieved by an ultraviolet spectrophotometric method⁽⁵⁾ that was adapted from a method for the determination of nitrate in aqueous solutions.⁽¹⁾ This non-aqueous method involves the measurement of the absorbance of nitrate at 197 or 273 m μ . Beer's law is followed at both wavelengths with molar absorbance indices of 18,000 and 10 respectively. The TOPO that was used in most of the studies that required the determination of nitrate in the organic phase was re-purified to reduce the cut-off wavelength of 0.1 M solutions to below 190 m μ . This degree of purification is not required for absorbance measurements at 273 m μ , but is necessary for accurate measurements at 197 m μ .

The results of all the extraction tests are reported either as thorium extracted, per cent, or as the extraction coefficient, E_a^O . This term is defined as:

$$E_a^O = \frac{\text{concentration of thorium in the organic phase}}{\text{concentration of thorium in the aqueous phase}}$$

EXPERIMENTAL

Effect of Concentration of Acids

The effect of acid concentration on the extraction of thorium from chloride, nitrate, sulfuric, and perchlorate solutions was determined. Solutions that contained approximately 11 mg of thorium in 5 ml of various concentrations of either nitric, hydrochloric, perchloric, or sulfuric acid were equilibrated for 10 minutes with 5 ml of 0.1 M TOPO in cyclohexane. The results of these tests are given in Table I and Figure 1.

TABLE I

EFFECT OF ACID CONCENTRATION ON EXTRACTION OF THORIUM
WITH TOPO FROM ACIDIC SOLUTIONS

Thorium present, 11.3 mg ThCl_4 , $\text{Th}(\text{ClO}_4)_4$,
11.5 mg $\text{Th}(\text{NO}_3)_4$
TOPO, 0.1 M in cyclohexane, 5 ml
Equilibration time, 10 minutes
Phase ratio, 1

Acid, Molarity	Thorium, mg		E_a^0		
	Organic	Aqueous			
HCl, 1	3	2.3	9.00	0.26	
	5	10.4	0.930	11	
	7	11.2	.077	145	
	8	11.2	.054	208	
	9	11.1	.177	64	
	10	10.9	.390	28	
		11.0	.344	32	
	HClO ₄ , 0.5	.8	11.2	0.135	82
		1.0	10.9	.353	31
		1.6	10.9	.425	26
2.0		10.4	.890	12	
2.4		10.3	1.04	9.9	
3.0		10.2	1.13	9.1	
3.2		10.1	1.22	8.3	
4.0		10.1	1.23	8.2	
5.0		10.1	1.21	8.3	
6.0		10.7	0.663	16	
HNO ₃ , 1	2	11.1	.200	56	
	3	11.5	.0055	2100	
	4	11.5	.028	420	
	5	11.4	.103	112	
	6	11.4	.147	78	
	7	11.2	.338	33	
	10	11.1	.415	27	
		11.0	.490	22	
		10.5	1.01	10	
	*H ₂ SO ₄ , 1	2	2.7	8.81	0.3
3		2.6	8.87	.3	
		3.2	8.30	.4	

* Thorium added as the nitrate salt. Total nitrate concentration, 0.02 M.

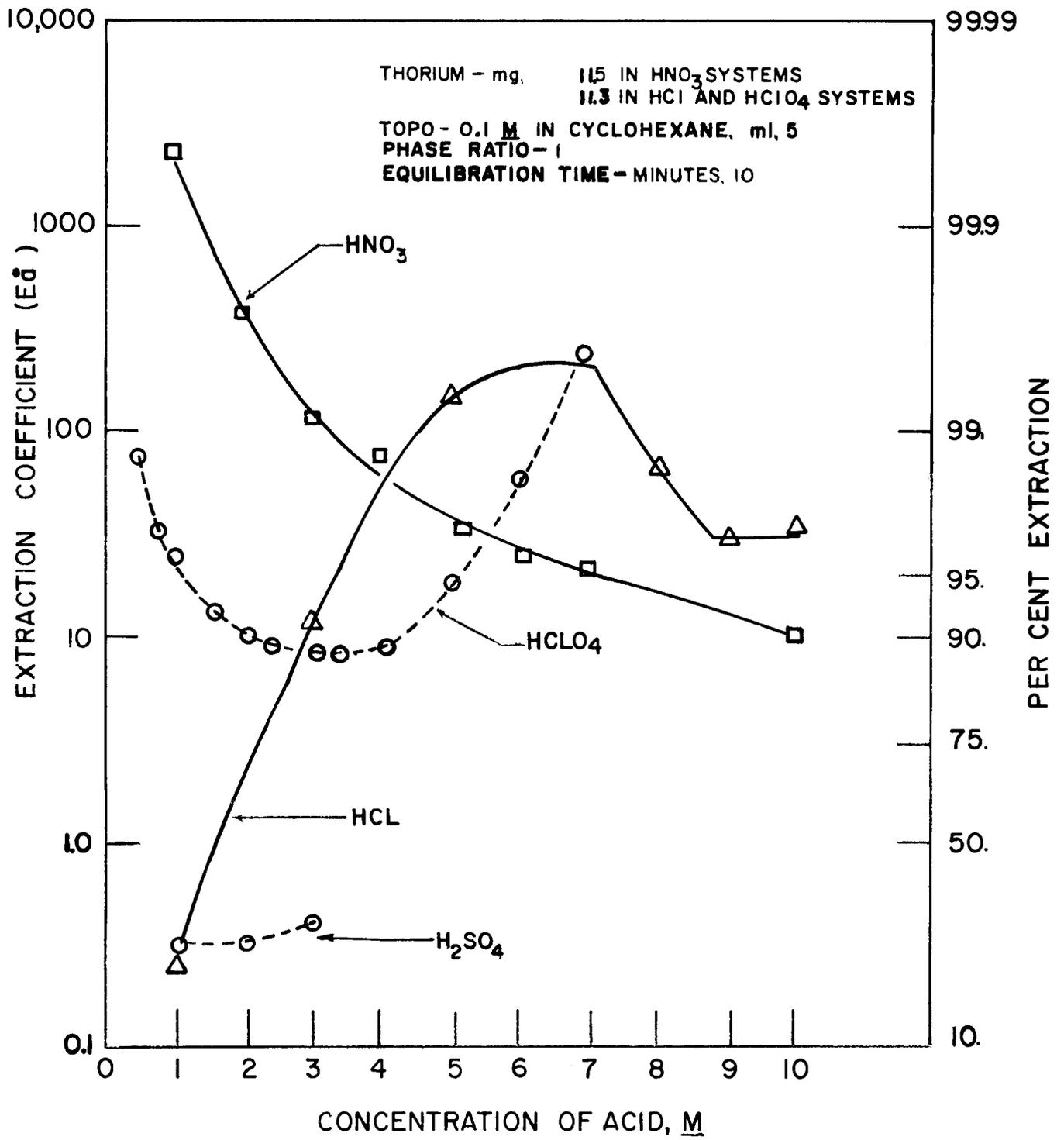


FIGURE 1

EFFECT OF CONCENTRATION OF ACID ON THE EXTRACTION OF THORIUM WITH TRI-n-OCTYLPHOSPHINE OXIDE

Hydrochloric Acid. The extraction of thorium from chloride solutions is enhanced as the concentration of hydrochloric acid is increased from 1 to 7 M, and, then, decreased as the acid concentration is increased further. Thorium is extracted to a degree that exceeds 98 per cent from 4 to 10 M HCl solutions. The impairment in extraction from > 7 M acidic solutions is probably caused by formation of non-extractable thorium chloride complexes in strong hydrochloric acid.

Perchloric Acid. In perchloric acid systems, the extraction coefficient of thorium passes through a minimum in 3 to 4 M HClO₄ media as the concentration of HClO₄ is varied from 1 to 6 M. The extraction of thorium from perchlorate systems is most efficient in 1 M acidic systems. Two immiscible organic phases are formed when 7 M HClO₄ and TOPO are equilibrated.

Nitric Acid. In nitrate systems, the extraction of thorium is continuously impaired as the concentration of nitric acid is increased. Extraction coefficients greater than 1000 are obtainable in 1 M HNO₃ systems; complete extraction, i.e. > 99 per cent, is achievable from < 4 M HNO₃ media. Extraction becomes incomplete, < 98 per cent, however, in more concentrated nitric acid systems.

The depression in the extraction of thorium that results from increased nitric acid concentration is contrary to the effect previously encountered in metal-TOPO extraction studies. This decrease in extraction is probably the result of formation of non-extractable complex species of thorium nitrate in solutions of high acid concentration rather than competition between the extraction of thorium and nitric acid. This hypothesis is supported by the fact that the extraction coefficient which was obtained when the TOPO had

been pre-equilibrated with 7 M HNO_3 prior to the extraction of thorium is identical to that obtained using TOPO that had not been pre-equilibrated with acid.

Sulfuric Acid. Thorium is extracted only to a small degree from sulfate solutions. The extraction is not materially affected by varying the concentration of sulfuric acid from 1 to 3 molar.

Effect of Concentration of Chloride and Nitrate

The extraction coefficients of zirconium⁽⁹⁾ in acidic chloride or nitrate solutions and iron⁽⁴⁾ in chloride solutions are dependent primarily on the anion concentration. The concentration of acid in the solution to be extracted must be relatively high, i.e. one molar, however, to achieve significant extraction by TOPO. In studying the anion effect on the extraction of thorium, the acid concentration was held constant at one molar. Solutions that contained either 11.3 mg of thorium as the thorium chloride or 11.5 mg of thorium as the thorium nitrate in 5 ml of 1 M HCl or HNO_3 were made 1 to 10 M with respect to the anion by the dissolution of various amounts of sodium chloride, aluminum chloride, or sodium nitrate. These solutions were equilibrated for 10 minutes with 5 ml of 0.1 M TOPO in cyclohexane, following which the thorium content of the aqueous phase was determined. The results are shown in Table II and Figure 2.

TABLE II

EFFECT OF CONCENTRATION OF CHLORIDE AND NITRATE ON EXTRACTION OF THORIUM

HCl (HNO₃), 1 M
 TOPO, 0.1 M in cyclohexane, 5 ml
 Phase ratio, 1
 Equilibration time, 10 minutes

Total Anion, M	NaNO ₃			NaCl			AlCl ₃		
	Organic	Aqueous	E _a ^o	Organic	Aqueous	E _a ^o	Organic	Aqueous	E _a ^o
2	11.5	0.003	3800	6.8	4.51	1.5	3.2	8.06	0.4
3	11.5	.006	1900	9.7	1.58	6.1	7.6	3.74	2.0
4	-	-	-	-	-	-	10.3	0.963	11
5	11.5	.008	1400	11.2	0.105	107	11.2	.117	102
6	-	-	-	11.3	.045	252	11.3	.025	450
7	11.5	.010	1200	-	-	-	11.3	.010	1100
8	-	-	-	-	-	-	11.3	.009	1300
9	-	-	-	-	-	-	11.3	.010	1100

Nitrate. The addition of sodium nitrate to 1 M HNO_3 solutions of thorium markedly enhances the extraction at all concentrations of nitrate over that attained in the absence of the salt. Maximum coefficients are found in 1 M HNO_3 -1 M NaNO_3 solutions. The extraction coefficients are extremely large, greater than 1000, at all concentrations tested. The coefficients decrease slightly, however, with increasing nitrate concentration. This trend is similar but not nearly so pronounced as that observed when the concentration of nitric acid is increased (Figure 1). Apparently the formation of non-extractable complex species of thorium nitrate in aqueous solution is more dependent on a high acid concentration rather than on high nitrate concentrations.

Chloride. The extraction coefficient of thorium increases linearly from about 0.5 to approximately 100 when the total chloride concentration is increased from one to five molar by the addition of either sodium chloride or aluminum chloride. This variation in extraction coefficient is identical, over this range of concentration, to that found for straight hydrochloric acid solutions.

In contrast to the extraction behavior in 7 to 10 M HCl , the coefficient remains in the vicinity of 1000 when the total chloride concentration is 7 to 10 molar as supplied by aluminum chloride. Some depression is noted but not to an appreciable extent. Sodium chloride would undoubtedly have a similar effect although such concentrations of chloride are not possible with sodium chloride due to its limited solubility in 1 M HCl .

A possible explanation for this difference in extraction as a function of whether the chloride is added as acid or salt is that in extremely strong

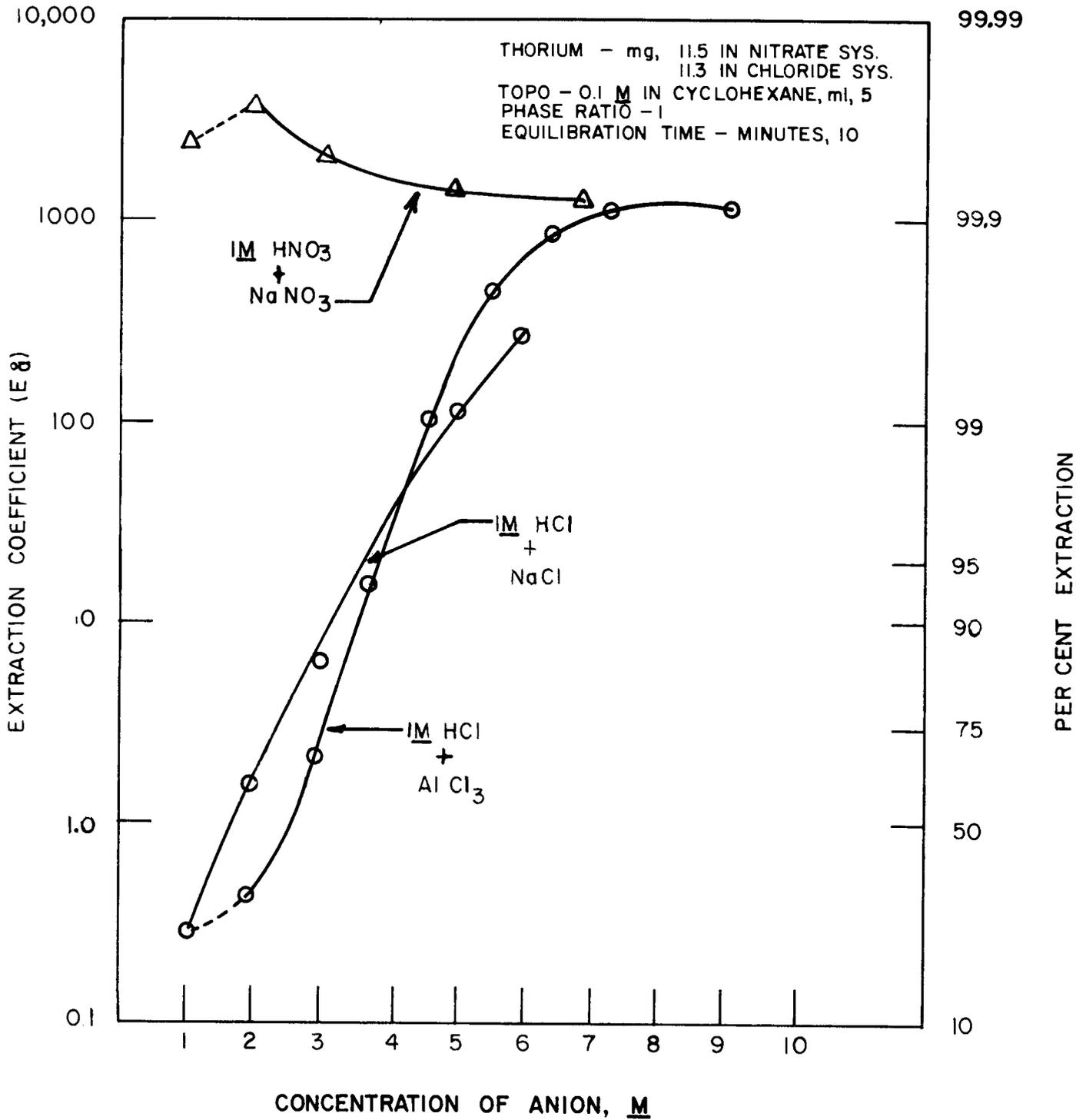


FIGURE 2

EFFECT OF CONCENTRATION OF CHLORIDE AND NITRATE ON THE
EXTRACTION OF THORIUM WITH TRI-n-OCTYLPHOSPHINE OXIDE

hydrochloric acid solutions there is some tendency for formation of non-extractable thorium chloride complexes. Such formation is not favored in much weaker acid solutions of equivalent chloride concentration, however.

Effect of Concentration of Thorium

The maximum amount of thorium that can be completely (> 99 per cent) extracted by TOPO in a single equilibration was determined for 7 M HCl and 1 M HNO₃ systems by adding various amounts of thorium to 5 ml of these acids, extracting the solutions for 10 minutes with 5 ml of 0.1 M TOPO in cyclohexane, and then determining the amount of thorium that remained in the aqueous phase. The degree to which these various amounts of thorium were extracted are given in Table III. The same results are presented graphically in Figure 3.

TABLE III

EFFECT OF CONCENTRATION OF THORIUM ON ITS EXTRACTION WITH TOPO

TOPO - 0.5 millimole
 Equilibration time - 10 minutes
 Phase ratio - 1

Acid	Thorium, mg			E_a^0	Per Cent Extracted
	Present*	Organic	Aqueous		
7 <u>M</u> HCl	6.9	6.9	0.022	310	99.7
	9.2	9.2	.036	260	99.6
	11.5	11.4	.068	170	99.4
	13.8	13.7	.130	106	99.1
	16.1	15.9	.235	68	98.5
	18.4	18.0	.437	41	97.6
	20.7	20.0	.705	28	96.4
	23.0	21.8	1.20	18	94.8
	25.3	23.2	2.12	11	91.2
	45.8	29.8	16.0	2	65.1
226	38	188	0.2	16.8	
1 <u>M</u> HNO ₃	11.5	11.5	0.003	4000	99.9
	18.3	18.3	.033	560	99.8
	22.9	22.8	.130	180	99.4
	27.5	27.0	.482	56	98.2
	32.1	30.6	1.54	20	95.2
	45.8	35.0	10.8	3	76.4
	233	39	194	0.2	16.7

* Thorium present as Th(NO₃)₄.

In 7 M HCl systems, about 28 mg of thorium is extracted completely, i.e. >99 per cent per millimole of TOPO, whereas 46 mg can be extracted to a degree that exceeds 95 per cent. The loading capacity of 1 millimole of TOPO in 7 M HCl systems is 76 mg of thorium.

The extraction capacity from 1 M HNO₃ solutions is even greater than that from 7 M HCl. Approximately 46 mg of thorium is extracted completely by 1 millimole of TOPO, while 64 mg can be extracted >95 per cent. The loading capacity of 1 millimole of TOPO is 78 mg of thorium.

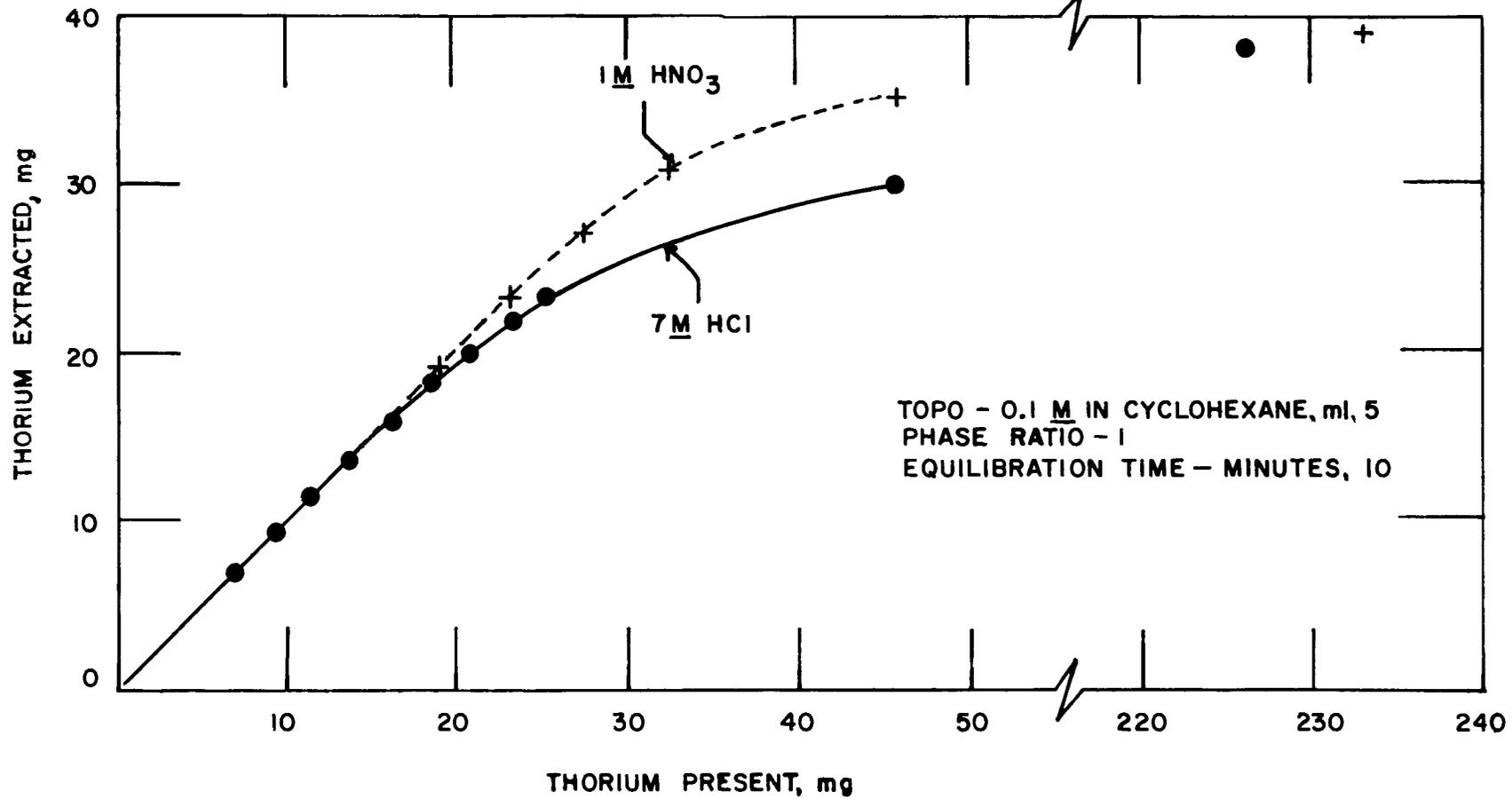


FIGURE 3
EXTRACTION OF THORIUM FROM CHLORIDE AND NITRATE
SOLUTIONS WITH TRI-n-OCTYLPHOSPHINE OXIDE

Effect of Phase Ratio

The efficiency of TOPO as a means of concentrating thorium through extraction from dilute solutions was investigated by varying the phase ratios of 7 M HCl and 1 M HNO₃ systems from 1 to 20. Solutions that contained 11.5 mg of thorium in 10 to 100 ml of 7 M HCl or 1 M HNO₃ were equilibrated for 10 minutes with 5 ml of 0.1 M TOPO. The aqueous phases were analyzed for thorium; the results are presented in Table IV.

TABLE IV

EFFECT OF PHASE RATIO ON THE EXTRACTION OF THORIUM

Nitrate, ~ 0.02 M
 Thorium present - 11.5 mg
 TOPO - 0.1 M in cyclohexane, 5 ml
 Equilibration time - 10 minutes

Acid	Va/Vo	Thorium, mg/ml		E _a ^o	Per Cent Extracted
		Organic	Aqueous		
7 <u>M</u> HCl	2	2.28	0.0145	157	98.7
	5	2.22	.016	138	96.5
	10	2.16	.0141	148	93.7
	20	2.06	.0118	175	89.7
1 <u>M</u> HNO ₃	2	2.30	.0049	470	99.6
	5	2.30	.0016	1430	99.6
	10	2.28	.0016	1420	99.2
	20	2.28	.0013	1750	98.9

The degree to which 11.5 mg of thorium is extracted from 1 M HNO₃ is diminished by less than one per cent when the aqueous to organic phase ratio is increased from 1 to 20. In 7 M HCl the extraction of thorium is depressed slightly by increasing the phase ratio, yet is 90 per cent complete when the ratio is 20.

These results indicate that thorium can be readily extracted from large volumes of aqueous solution, thus effecting the concentration as well as the separation of this element in a single step.

Effect of Extraction Time

Previous investigations have revealed that equilibrium between acidic solutions of metals and cyclohexane solutions of TOPO is attained in relatively short periods of time, i.e. 5 to 10 minutes. A series of extractions was conducted to establish the rate with which TOPO and acidic solutions of thorium attain equilibrium and also to determine if the variations in extraction coefficients that have been attributed to variations in acid concentration might be due in part to incomplete attainment of equilibrium. These tests consisted of extracting solutions that contained 11 mg of thorium (also 23 mg in 1 M HNO₃ systems) in 5 ml of 1 and 7 M HCl and HNO₃ for pre-determined periods of time and then determining the thorium that remained in the aqueous phase. The effects of these variable periods of time are shown in Table V.

TABLE V
EFFECT OF EXTRACTION TIME ON THE EXTRACTION OF THORIUM

TOPO, 0.1 M in cyclohexane, 5 ml
Phase ratio - 1

Acid	Equilibration Time, minutes	Thorium, mg			E _a ^o
		Present	Organic	Aqueous	
HNO ₃ , 1 <u>M</u>	1	22.9*	15.5	7.44	2.1
	3		22.6	0.330	68
	5		22.8	.128	180
	10		22.8	.130	180
	30		22.8	.128	180
	10	11.5*	11.5	.005	2300
	30		11.5	.005	2300
HNO ₃ , 7 <u>M</u>	10	11.5*	11.2	.329	34
	30		11.2	.330	34
HCl, 1 <u>M</u>	10	11.3**	2.2	9.09	0.24
	30		2.9	8.64	.34
HCl, 7 <u>M</u>	10	11.3**	11.2	0.051	220
	30		11.3	.021	540

* Thorium present as Th(NO₃)₄

** Thorium present as ThCl₄

An extraction time of five minutes is sufficient in 1 M HNO₃ systems, whereas in 7 M HCl systems slightly greater extraction is achieved by increasing the time from 10 to 30 minutes.

In 7 M HNO₃ systems no additional extraction is achieved by increasing the time from 10 to 30 minutes and only slight enhancement is attained in 1 M HCl media. Obviously, extraction time is not a critical factor in extraction of thorium.

Effect of Concentration of Tri-n-octylphosphine Oxide

The effect of concentration of TOPO on the extraction of thorium from nitric and hydrochloric acid solutions was investigated by equilibrating 5 ml of 0.01 to 0.20 M TOPO in cyclohexane with 5 ml of aqueous solutions that contained 233 mg of thorium in 7 M HCl or 1 M HNO₃. The results of these tests are presented in Table VI and Figure 4.

TABLE VI

EFFECT OF CONCENTRATION OF TRI-n-OCTYLPHOSPHINE OXIDE ON THE EXTRACTION OF THORIUM

Nitrate, ~0.4 M
 Th present - 233 mg (as Th(NO₃)₄)
 Equilibration time, 10 minutes
 Phase ratio, 1
 TOPO, 5 ml

Acid	TOPO, milli-moles	Thorium, mg			TOPO Th
		Aqueous	Organic		
			mg	mmoles	
HCl, 7 <u>M</u>	1.0	155	78	0.34	2.9
	0.75	177	56	.24	3.1
	.50	195	38	.16	3.1
	.25	214	19	.08	3.1
	.05	228	5	.02	2.5
HNO ₃ , 1 <u>M</u>	1.0	156	77	.33	3.0
	0.75	173	60	.26	2.9
	.50	194	39	.17	2.9
	.25	212	21	.09	2.8
	.05	232.5	0.5	.002	25

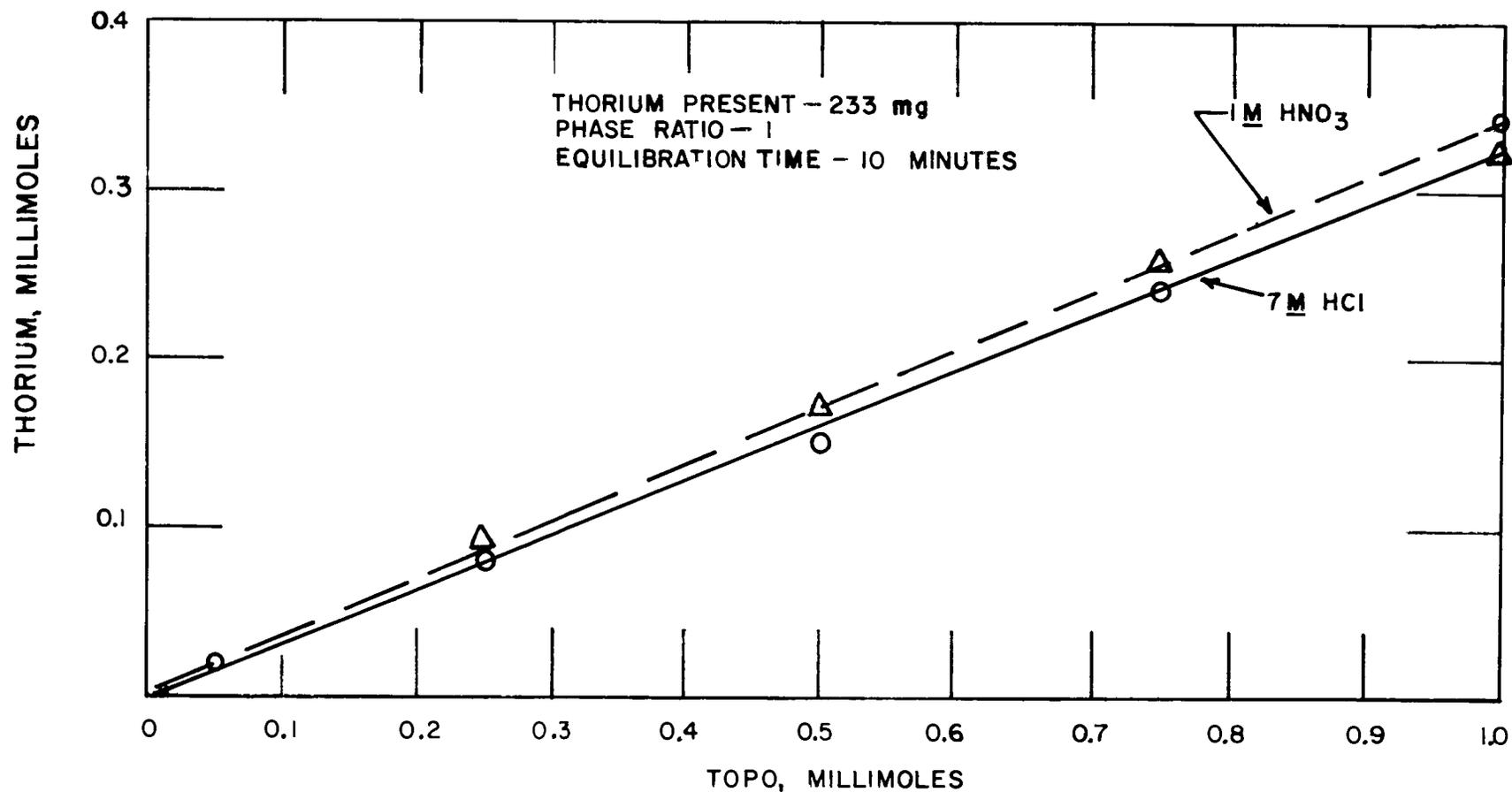


FIGURE 4
EXTRACTION OF THORIUM AS A FUNCTION OF THE
CONCENTRATION OF TRI-*n*-OCTYLPHOSPHINE OXIDE

The amount of thorium that is extracted from 1 M HNO₃ or 7 M HCl solutions increases linearly as the concentration of TOPO is increased. The ratios of TOPO to thorium in the organic phases are approximately 3 except in the least concentrated TOPO systems. The relationship of this molar ratio to the actual stoichiometry of the extracted species will be discussed in the next section.

Investigation of the Species of Thorium Extracted from Chloride and Nitrate Solutions

The nature of the species of thorium and mineral acid that are extracted into 0.1 M solutions of TOPO in cyclohexane was investigated in 1 to 9 M HCl and 1 M HNO₃ systems.

Chloride. A series of solutions that contained 226 mg of thorium in 5 ml of 1 to 9 M HCl was extracted with 5 ml of 0.1 M TOPO for 20 minutes. The amount of thorium taken was about six times the loading capacity of the TOPO present. This amount was so chosen to minimize extraction of free acid. The thorium that remained in the aqueous phase was determined gravimetrically by the oxalate method and the thorium that was extracted was calculated by difference. The chloride in the organic phase was determined by titration with silver nitrate solution. The TOPO concentration in the organic phase was assumed to be the same as that taken, i.e. 0.5 millimole. The molar ratios of thorium to chloride and thorium to TOPO in the organic phase were calculated from these data and are presented in Table VII.

TABLE VII

MOLAR RATIOS OF THORIUM TO CHLORIDE AND TOPO AS A
FUNCTION OF ACID CONCENTRATION

Thorium present - 226 mg
 TOPO, 0.1 M in cyclohexane - 5 ml
 Phase ratio - 1
 Equilibration time - 10 minutes

<u>Total Cl</u>	<u>Molarity</u>		<u>Molar Ratio</u>	
	<u>HCl</u>	<u>AlCl₃</u>	<u>Cl/Th</u>	<u>TOPO/Th</u>
1	1	-	3.8	5.0
2	1	0.3	5.4	9.6
3	3	-	3.7	3.6
	1	0.6	4.2	5.5
4	1	1.0	4.2	4.5
	5	-	4.0	3.1
5	1	1.3	4.4	3.6
	6	1	1.7	4.2
7	7	-	4.2	3.1
	1	2.0	4.1	3.1
9	9	-	6.1	3.8

The molar ratio of chloride to thorium is four, which indicates that ThCl_4 is the species of thorium extracted by TOPO. In strong hydrochloric acid, a medium that yields high extraction coefficients, thorium exists predominantly as ThCl_4 . In more dilute acid solution, where coefficients are low, the ThCl_4 species is correspondingly less concentrated. Since the Cl/Th ratio greatly exceeded four in the 9 M HCl test, acid must be extracted also by the TOPO. This is confirmed by previous experiments (10) in which it was shown that HCl·TOPO adducts are readily formed when strong acid and TOPO are equilibrated.

The limiting ratio of TOPO to thorium is three. The nature of the extracted species probably is more accurately defined, however, by a formula

such as $\text{ThCl}_4 \cdot \text{HCl} \cdot 3(\text{TOPO})$, wherein the amount of the acid adduct present is a function of the concentration of hydrochloric acid in the aqueous phase.

Nitrate. The study of the thorium species extracted from nitric acid solutions was restricted to 1 M acid systems since considerable co-extraction of nitric acid occurs at higher concentrations. The determination of nitrate in the organic phase was performed by spectrophotometric measurements of cyclohexane dilutions at 197 and 273 μ .⁽⁵⁾ The results of these analyses are presented in Table VIII.

TABLE VIII

MOLAR RATIOS OF THORIUM TO NITRATE AND TO TOPO
IN ORGANIC EXTRACTS

HNO_3 , 1 M
 Thorium present - 233 mg
 Phase ratio - 1
 Equilibration time - 10 minutes
 TOPO - 0.1 M in cyclohexane

TOPO, mmoles	Extracted, mmoles		$\frac{\text{NO}_3}{\text{Th}}$	$\frac{\text{TOPO}}{\text{Th}}$
	Nitrate	Thorium		
0.5	0.88	0.168	5.2	3.0
	.93	.168	5.5	3.0
0.7	1.24	.259	4.8	2.7
	1.24	.259	4.8	2.7
	1.17	.259	4.5	2.7
	1.13	.259	4.4	2.7

The average nitrate to thorium ratio, 4.9, indicates that nitrate in excess of that required to combine with thorium as $\text{Th}(\text{NO}_3)_4$ has been extracted. This excess nitrate presumably is present in the organic phase as an adduct of nitric acid and TOPO. Inasmuch as nitric acid is readily extracted from 1 M HNO_3 solutions by TOPO, it is postulated that two species are extracted, $\text{Th}(\text{NO}_3)_4$ and HNO_3 or $\text{Th}(\text{NO}_3)_4 \cdot \text{HNO}_3 \cdot 3(\text{TOPO})$.

Effect of Nitrate on the Extraction of Thorium from Sulfate and Phosphate Solutions

As shown in Table I, the extraction of thorium from sulfuric acid solutions is very small. The detrimental effect on the extraction of thorium that is caused by sulfate is due to the predominance of non-extractable thorium sulfate species in the aqueous solution. The nature of these species is considered to be similar to that observed in zirconium sulfate systems.⁽⁹⁾

Previous studies have revealed that the extraction of metals from sulfate solutions can be enhanced appreciably by the addition of nitrate to the aqueous phase.

This technique, consequently, was tested in an effort to enhance the extraction of thorium from sulfate solutions. At the same time, these tests were also designed to determine the effect of nitrate on the extraction of thorium from phosphate solutions since phosphate is very frequently encountered in the refining of thorium-bearing ores. The solubility of thorium in phosphoric acid solutions is sufficiently large to permit the dissolution of various phosphate ores in acidic solutions. Synthetic solutions of thorium in phosphoric acid were readily prepared and the extraction of thorium from these solutions investigated. When 11 mg of thorium was added to 5 ml of 1 to 7 M H_3PO_4 solutions a white precipitate formed instantaneously and, subsequently, no thorium was extracted by 0.1 M TOPO.

Inasmuch as either sulfate or phosphate seriously interferes with the determination of thorium by the gravimetric oxalate or colorimetric Thorin methods, an indirect method was developed to establish the degree to which thorium was extracted from these systems. Thorium was readily back-extracted from cyclohexane solutions of TOPO by equilibration with

0.3 M H_2SO_4 . Subsequently, thorium in the aqueous phase can be determined by the Thorin method after the sulfuric acid has been expelled by evaporation. This method was applied to the determination of thorium in all the following extraction tests.

The first series of extraction tests, the results of which are presented in Table IX, was designed to establish the effects of various concentrations of nitrate on the extraction of thorium from either 0.1 to 4 M H_2SO_4 or H_3PO_4 . The desired amount of nitrate, as HNO_3 or NaNO_3 , was added to sulfate and phosphate solutions of thorium so that the final volume was 5 ml. This solution was then extracted for 10 or 20 minutes with 5 ml of 0.1 M TOPO in cyclohexane. After equilibration, aliquots of the organic phase were removed by pipet and then back-extracted for 20 minutes with 5 ml of 0.3 M H_2SO_4 . Thorium in the aqueous phase was subsequently determined by the Thorin method.

TABLE IX

EFFECT OF NITRATE ON THE EXTRACTION OF THORIUM FROM SULFATE
AND PHOSPHATE SOLUTIONS BY TRI-n-OCTYLPHOSPHINE OXIDE

TOPO, 0.1 M in cyclohexane - 5 ml
Phase ratio - 1
Equilibration time - 20 minutes

Thorium Present, mg	Molarity				Thorium Extracted, Per Cent
	HNO ₃	NaNO ₃	H ₂ SO ₄	H ₃ PO ₄	
0.570	1	-	-	-	99
11.5	1	-	-	-	100
0.690	1	1	-	-	100
11.5	1	-	0.5	-	91*
	-	1	0.5	-	95*
	1	-	1.0	-	78*
	-	1	1.0	-	86*
	1	-	2.0	-	60*
	-	1	2.0	-	62*
	1	-	3.6	-	34*
0.690	1	1	1	-	78
			-	0.3	86
0.345	-	2	1	-	93
	0.5	2	-	0.3	92
	-	4	0.5	-	99
	-	4	1.0	-	102
	-	4	2.0	-	103
	0.5	4	-	0.24	98
				0.50	94
				1.0	81
				2.0	28
	0.5	4	0.5	0.1	110
			1.0	0.1	92
			0.5	0.3	95
			1.0	0.3	64
			0.5	0.6	41
			1.0	0.6	43
11.5	1	4	0.5	-	100
			1.0	-	97
			2.0	-	63

* Equilibration time, 10 minutes.

As revealed in Table IX, thorium can be extracted completely, under certain conditions, from sulfate or phosphate solutions if nitrate is added to the aqueous solution. The addition of nitrate in the form of the neutral salt has a more beneficial effect on the extraction of thorium from sulfate solutions than is obtained with nitric acid. Inasmuch as most metals are extracted only to a slight degree from weakly acidic, i.e. $< 1 \text{ M}$, solutions, nitric acid as well as sodium nitrate was added in most tests to maintain the acidity of the aqueous solution at 1 M .

The extraction of thorium is increasingly depressed when the concentration of sulfate or phosphate is increased. Phosphate inhibits the extraction to a greater extent than does sulfate. This impairment can be partially overcome by increasing the concentration of nitrate by the addition of NaNO_3 . Sub-milligram amounts of thorium are extracted to an extent that exceeds 95 per cent from solutions 2.0 M in H_2SO_4 , 0.5 M in H_3PO_4 , or $< 0.8 \text{ M}$ with respect to a mixture of the two acids when the solution is 0.5 M in HNO_3 and 4 M in NaNO_3 . Eleven mg of thorium is likewise extracted readily by 5 millimoles of TOPO from 1 M H_2SO_4 solutions that are 1 M in HNO_3 and 4 M in NaNO_3 .

The above results represent a great improvement in the extraction of thorium from sulfate or phosphate solutions; however, definite limitations are still imposed by the maximum permissible concentrations of sulfuric and phosphoric acids.

A second series of extraction tests was conducted to ease these limitations on the versatility of this method of extracting thorium by reducing the concentrations of sulfuric acid and phosphoric acid through

dilution with 1 M HNO_3 . Solutions that contained 0.345 or 0.069 mg of thorium in 5 ml of 1 M H_2SO_4 and various concentrations of phosphoric acid were diluted to 50 ml with a 1 M HNO_3 solution. Weighed amounts of sodium nitrate were added to some test solutions. These solutions were extracted for 20 minutes with 5 ml of 0.1 M TOPO in cyclohexane, following which aliquots of the organic phase were back-extracted with 5 ml of 0.3 M H_2SO_4 , and the thorium content of the acidic solution determined colorimetrically by the Thorin method. The results of these tests are presented in Table X.

TABLE X

EXTRACTION OF THORIUM FROM DILUTE SOLUTIONS OF SULFATE AND PHOSPHATE THAT CONTAIN NITRATE

HNO_3 - 1 M
 H_2SO_4 - 0.02 M
 TOPO, 0.1 M in cyclohexane - 5 ml
 Phase ratio, V_a/V_o - 10
 Equilibration time - 20 minutes

Thorium, mg	Present		Thorium Extracted, Per Cent
	NaNO_3 , M	H_3PO_4 , M	
0.345	-	0.0012	93
	1	.0012	99.9
	1	.0006	99.9
	2	.0006	99.9
	2	.0012	99.9
0.069	-	.0004	98*

* Equilibrations of 5-minute duration.

Sub-milligram amounts of thorium are readily extracted from such systems as listed in Table X. The concentrations of sulfate and phosphate are reduced to negligible amounts, while the extraction of thorium is not impaired by dilution of the aqueous phase to 50 ml. Analyses of samples

of thorium ores, the thorium content of which had been determined by other methods, prove that as much as 5 mg of thorium is completely extracted from these dilute solutions. (It is interesting to note that cerium(III) and the other rare-earth elements are not extracted under these conditions.)

The applicability of TOPO to the separation of thorium from sulfate and phosphate solutions greatly increases the versatility of TOPO as an extractant of thorium.

SUMMARY

Thorium is extracted readily from acidic chloride and nitrate solution by cyclohexane solutions of TOPO. In nitric acid systems the extraction coefficient is 2000 in 1 M HNO_3 but decreases to 75 in 10 M HNO_3 with increasing nitric acid concentration. A somewhat similar behavior of the extraction coefficient occurs when the nitrate concentration of 1 M HNO_3 solutions is increased by the addition of neutral salts; however, the extraction coefficient of thorium remains greater than 1000. In hydrochloric acid systems, the extraction coefficient increases from 0.3 to 200 as the acidity is increased from 1 to 7 M and then decreases to 30 in 10 M. The addition of chloride to 1 M HCl solutions of thorium enhances the extraction to a greater extent than is achieved with hydrochloric acid alone.

The loading capacity of 1 millimole of TOPO is 76 and 78 mg of thorium in 7 M HCl and 1 M HNO_3 respectively. The molar ratio of TOPO to thorium is three in 7 M chloride systems; the stoichiometry of extracted species is postulated to be $\text{ThCl}_4 \cdot \text{HCl} \cdot 3(\text{TOPO})$. In nitrate systems two species are extracted simultaneously by TOPO, i.e. $\text{Th}(\text{NO}_3)_4 \cdot 2(\text{TOPO})$ and $x \text{HNO}_3 \cdot (\text{TOPO})$.

The composition of the acid adduct is $\text{HNO}_3 \cdot (\text{TOPO})$ in 1 M HNO_3 and is a function of the initial concentration of acid.

As much as 46 mg of thorium can be extracted per millimole of TOPO from 1 M HNO_3 to an extent that exceeds 99 per cent, while 28 mg can be extracted from 7 M HCl . Equilibrium is attained rapidly in nitrate systems, 5 minutes being sufficient for extraction, whereas in chloride systems 10 minutes is required. Essentially complete extraction from 1 M HNO_3 solutions is achieved at a phase ratio, V_a/V_o , of 20; however, the extraction from 7 M HCl is decreased by 10 per cent as the phase ratio is increased from 1 to 20.

Thorium is extracted from sulfuric and phosphoric acids only to a very slight extent. By reduction of the concentrations of sulfuric and phosphoric acid to less than 2 M and 0.5 M respectively and the addition of sufficient nitric acid and sodium nitrate to make the solution 1 M in HNO_3 and 5 M in nitrate, the extraction of thorium can be made essentially quantitative. Milligram amounts of thorium can be extracted completely from solutions that are < 0.1 M in sulfate and phosphate if the solution is 1 M with respect to HNO_3 and 2 M in nitrate.

The extraction of thorium is readily achieved from solutions of perchloric acid; however, these systems frequently contain two immiscible organic phases, which complicate the recovery of the extracted thorium.

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