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THORIUM NITRATE DISTRIBUTION IN TRIBUTYL PHOSPHATE-CARBON TETRACHLORIDE SOLUTIONS

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THORIUM NITRATE DISTRIBUTION IN  
TRIBUTYL PHOSPHATE-CARBON TETRACHLORIDE SOLUTIONS

R. H. Gercke

October 9, 1951

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Thorium Nitrate Distribution in

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Tributyl Phosphate-Carbon Tetrachloride Solutions

R. H. Gercke  
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University of California, Berkeley, California

October 9, 1951

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ABSTRACT

The extraction of thorium nitrate by tributyl phosphate-carbon tetrachloride solutions has been studied. Aqueous solutions containing 0.0 M to 3.0 M  $\text{HNO}_3$  and 0.0 M to 2.0 M  $\text{Th}(\text{NO}_3)_4$  were equilibrated with both 60 percent and 80 percent by volume TBP (tributyl phosphate) solutions in carbon tetrachloride, and the effect of nitric acid concentration and thorium nitrate concentration are discussed. Equilibrium data are presented and conclusions concerning the mechanism of extraction of thorium nitrate have been made.

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Thorium Nitrate Distribution in  
Tributyl Phosphate-Carbon Tetrachloride Solutions

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October 9, 1951

INTRODUCTION

Although it has long been known that tributyl phosphate has the ability to extract thorium, it was felt that more detailed equilibrium data were needed, especially in the higher TBP (tributyl phosphate) concentration range, to supplement that which is now available. This information would be particularly useful in the calculation of column behavior.

EXPERIMENTAL

Ten milliliters of aqueous thorium nitrate solution and ten milliliters of TBP in carbon tetrachloride were shaken at room temperature ( $21^{\circ}\text{C} - 27^{\circ}\text{C}$ ) in a 75 milliliter separatory funnel on a mechanical agitator for 20 minutes to insure reaching equilibrium. After shaking, the phases were either separated by centrifuging or allowed to separate under the influence of gravity, depending upon the disengaging time of the particular sample. After the separation of phases, both the aqueous and organic phases were analyzed for thorium and, where necessary, for acidity.



The technical grade tributyl phosphate used was given two ten percent sodium hydroxide equal volume washes followed by three equal volume water washes. The carbon tetrachloride was Baker and Adamson's reagent grade. The thorium nitrate used was Baker and Adamson's reagent grade  $\text{Th}(\text{NO}_3)_4 \cdot 4\text{H}_2\text{O}$ . After a 2.0 M solution of this material was prepared, it was filtered several times to remove suspended material and then analyzed for thorium and hydrogen ion concentrations. It was necessary to add concentrated nitric acid to the thorium nitrate solutions to make them neutral (with respect to pure thorium nitrate).

#### DISCUSSION

The main portion of the experimental work is represented by four equilibrium curves for the distribution of thorium between a TBP-Carbon tetrachloride solution and an aqueous solution (Figure I and Table I). Equilibrations were carried out with both 60 percent TBP and 80 percent TBP by volume and the initial acidity was both neutral and 1 M  $\text{HNO}_3$ . It is seen that the curves are very similar in shape to those for uranium extracted with TBP.<sup>1</sup> The two neutral equilibration curves fit well onto a plot of the distribution data for thorium between aqueous and TBP-hexane solutions reported by Oak Ridge National Laboratory<sup>2</sup> which might be expected since R. L. Moore<sup>1</sup> and L. L. Burger<sup>2</sup> report the particular nonpolar solvent for TBP has little effect on uranyl nitrate distribution. It is interesting to note that the 1 M  $\text{HNO}_3$  curves cross the neutral curve of the same TBP extractant. This may be explained by a competition of nitric acid and thorium nitrate for TBP.

Specific gravities of the organic phases were obtained and it is seen that specific gravity is a linear function of the thorium concentration where no nitric acid is present (Figure V).

The effect of initial nitric acid concentration on the shape of the equilibrium curve in the region of low thorium concentration is demonstrated in Figure II. The initial slope of the curve increases rapidly with increasing nitric acid concentration. Here again the effect is very similar to that found in the case of uranium.<sup>1</sup>

It is probable that, in actual operation of a thorium-TBP extraction process, the system will contain some fluoride ion from the dissolving step. Therefore, effect of the presence of fluoride ion in a thorium-TBP system was determined. This effect is to lower the distribution ratio,  $E_D^0$ , at low thorium concentrations, but it is small and largely disappears at higher thorium concentrations (Figure III). In a 2.00 M  $\text{Th}(\text{NO}_3)_4$  solution with 0.05 M HF present only 2.5 percent of the thorium will be present as  $\text{ThF}^{+3}$ , and higher fluoride complexes may be disregarded. In column operation it may, therefore, be necessary to add a small quantity of aluminum nitrate or boric acid to tie up the fluoride in the dilute thorium part of the contactor.

The ratio of TBP to thorium concentration in the organic complex was of interest in establishing an extraction mechanism. An experiment was carried out to determine this ratio experimentally by equilibrating a known TBP-carbon tetrachloride solution with an equal volume of concentrated thorium nitrate solution. Thorium was added to the system in the form of solid thorium nitrate and when the system was saturated, the top phase was analyzed for thorium and a ratio of TBP to thorium was readily obtained. This was done

Table I. Thorium Equilibrium Distribution Between Aqueous and TBP-Carbon Tetrachloride Solutions at Approximately 25° C.

	(Th) <sub>aq</sub>	(Th) <sub>org</sub>	(H <sup>+</sup> ) <sub>aq</sub>	(H <sup>+</sup> ) <sub>org</sub>	$\rho_{4}^{25}$ <sub>org</sub>	E <sub>a</sub> <sup>0</sup> (V)	K <sub>1</sub> *	E <sub>a</sub> <sup>0</sup> (HNO <sub>3</sub> )
2.13 M TBP	0.128	0.022	0.016	0.082	1.232	0.171	0.329	
Neutral	0.216	0.093	0.012	0.000	1.259	0.430	0.122	
	0.281	0.174	0.020	---	1.287	0.620	0.094	
	0.423	0.329	0.006	---	1.335	0.779	0.064	
	0.708	0.503	0.022	---	1.396	0.710	0.461	
	1.000	0.591	0.006	---	1.428	0.591	0.052	
	1.231	0.627	0.024	---	---	0.509	0.057	
	1.349	0.653	0.000	0.020	---	0.484	0.114	
	1.371	0.665	---	---	1.443	0.485	0.209	
2.88 M TBP	0.117	0.035	0.006	0.010	1.110	0.299	0.311	
Neutral	0.175	0.129	0.005	---	1.145	0.738	0.201	
	0.222	0.230	0.006	---	1.181	1.036	0.158	
	0.323	0.416	0.005	---	1.248	1.285	0.109	
	0.554	0.643	0.009	---	1.327	1.160	0.056	
	0.822	0.764	0.004	---	1.372	0.929	0.041	
	1.025	0.833	0.000	---	1.399	0.813	0.044	
	1.120	0.841	---	---	---	0.751	0.041	
	1.131	0.877	---	---	---	0.775	0.048	
2.13 M TBP	0.070	0.077	0.756	---	1.257	1.096	0.225	
1.00 M HNO <sub>3</sub>	0.136	0.164	0.76	0.29	1.283	1.200	0.209	342
(Initial)	0.200	0.246	0.76	---	1.310	1.229	0.149	
	0.359	0.381	0.85	0.20	1.406	1.063	0.080	2355
	0.676	0.528	0.866	0.184	1.356	0.781	0.102	2125
	1.018	0.579	0.885	0.165	1.432	0.569	0.080	1865
	1.149	0.581	---	---	---	0.506	0.063	
	1.154	0.585	0.89	0.16	1.433	0.507	0.056	1798
2.88 M TBP	0.051	0.093	0.66	0.45	1.137	1.834	0.322	681
1.00 M HNO <sub>3</sub>	0.101	0.199	0.66	0.36	1.175	1.970	0.226	545
(Initial)	0.151	0.296	0.72	0.30	1.207	1.963	0.139	416
	0.263	0.477	0.75	0.27	1.269	1.811	0.112	36
	0.503	0.700	0.86	0.21	1.340	1.391	0.117	244
	0.809	0.787	---	---	1.379	0.972	0.101	
	0.912	0.813	---	0.14	---	0.891	0.098	
	0.930	0.819	0.86	0.14	1.385	0.870	0.092	1628
	1.202	0.842	0.844	0.134	---	0.700	0.112	1589
	1.432	0.877	0.860	0.129	---	0.612	0.243	150
2.13 M TBP	0.043	0.116	1.42	0.58	---	2.685	0.254	408
2.00 M HNO <sub>3</sub>	0.092	0.210	1.52	0.48	---	2.295	0.182	316
(Initial)	0.170	0.321	1.63	0.37	---	1.889	0.142	227
2.13 M TBP	0.026	0.125	2.19	0.81	---	4.850	0.231	370
3.00 M HNO <sub>3</sub>	0.063	0.225	2.28	0.72	---	3.562	0.249	316
(Initial)	0.137	0.338	2.37	0.63	---	2.468	0.342	266

$$*K_1 = \frac{[\text{Th}(\text{NO}_3)_4(\text{TBP})_3]_{\text{org}}}{(\text{Th})_{\text{aq}}(\text{NO}_3^-)_{\text{aq}}^4(\text{TBP})_{\text{org}}^3}, \text{ the formation of } (\text{HNO}_3 \cdot \text{TBP})_{\text{org}} \text{ being taken into account.}$$

for two TBP concentrations.

Table II.

	Tributyl Phosphate <u>M</u>	
	2.193 <u>M</u>	3.070 <u>M</u>
(Th) <sub>aq</sub>	2.109	2.415
(Th) <sub>org</sub>	0.728	1.027
TBP/Th <sub>org</sub>	3.01 ± 0.25	2.99 ± 0.28

The uncertainty in the TBP/Th<sub>org</sub> ratio is due to the uncertainty in the TBP concentration. The ratio of three agrees with the finding of the Oak Ridge National Laboratory.<sup>4</sup>

If the extraction is assumed to be represented by the reaction



an equilibrium constant may be written (neglecting activity coefficients):

$$\frac{[\text{Th}(\text{NO}_3)_4(\text{TBP})_3]_{\text{org}}}{(\text{Th})_{\text{aq}}(\text{NO}_3^-)_{\text{aq}}^4(\text{TBP})_{\text{org}}^3} = K_1$$

where (TBP)<sub>org</sub> is the molar concentration of uncomplexed TBP in the organic phase. In calculating K<sub>1</sub> from the data in Table I, the following relationships were used:

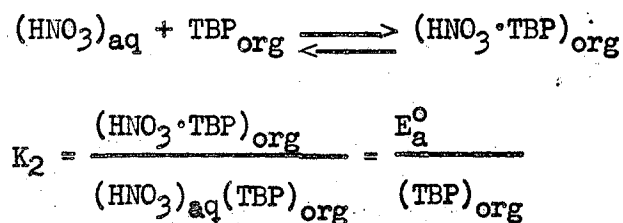
- (1)  $[\text{Th}(\text{NO}_3)_4(\text{TBP})_3] = (\text{Th})_{\text{org}}$
- (2)  $(\text{NO}_3^-)_{\text{aq}} = 4(\text{Th})_{\text{aq}} + (\text{H}^+)_{\text{aq}}$
- (3)  $(\text{TBP})_{\text{org}} = (\text{TBP})_{\text{initial}} - [3(\text{Th})_{\text{org}} + (\text{H}^+)_{\text{org}}]$

The equilibrium constant  $K_1$  can be calculated from thorium concentrations and acidities of the two phases. When this is done for all the data in Table I, there is a definite trend of  $K_1$  with  $\text{Th}_{\text{aq}}$  (Figure IV), though  $K_1$  is fairly constant at higher thorium concentration. A value of  $K_1 = 0.064$  can be assigned in the region between  $0.45 \text{ M Th}_{\text{aq}}$  and  $1.25 \text{ M Th}_{\text{aq}}$ . Almost all the data can be described by the empirical relationship

$$K_1 = 0.40 - 0.46 \sqrt{0.60 - (\text{Th}_{\text{aq}} - 0.80)^2} \pm 30\%$$

The correlation does not improve if various forms of the ionic strength are used rather than  $(\text{Th})_{\text{aq}}$ . It is felt that  $K_1$ , as given, is sufficiently constant so that it will be an aid to the prediction of column behavior.

When the data are used to calculate an equilibrium constant for the nitric acid extraction,

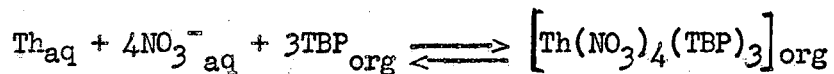


it is seen that  $K_2$  varies with  $(\text{Th})_{\text{aq}}$ . The value of  $K_2$  seems to approach the value assigned to it by R. L. Moore<sup>1</sup> at zero ionic strength. It is not surprising that  $K_2$  does vary because of the large range of ionic strength which is covered.

## SUMMARY

(1) The effect of fluoride ion on the thorium extraction (from the dissolving step) is to lower slightly the amount extracted into the organic phase. This is true at low thorium concentrations only. The effect largely disappears at higher thorium concentrations.

(2) The extraction of thorium and nitric acid into 60 percent and 80 percent TBP-carbon tetrachloride from aqueous thorium-nitric acid solutions was studied. The results indicated that the mechanism of thorium extraction is one of simple complex formation, the reaction being:



The equilibrium constant for this reaction is about 0.064 at  $\sim 25^\circ \text{C}$  over a fairly wide range.

BIBLIOGRAPHY

1. Robert L. Moore, Hanford Works Report HW-15230 (September 1, 1949)
2. Oak Ridge National Laboratory Chemistry Division Quarterly Progress Report (for the period ending December 31, 1949) ORNL-607 (March 7, 1949).
3. L. L. Burger, Hanford Works Report HW-19065 (October 6, 1950).
4. W. K. Eister, editor, Oak Ridge National Laboratory Chemistry Division Quarterly Progress Report (for the period ending August 31, 1949) ORNL-467 (October 20, 1949).

## APPENDIX - Analytical Methods

### Thorium

1. Aqueous phase after equilibration and separation: evaporate an aliquot to dryness under a heat lamp, then ignite in furnace at 900° C for one hour. Calculate contents of the crucible as ThO<sub>2</sub>.

2. Organic phase after equilibration and separation: dilute an aliquot to 5 percent TBP with the organic solvent (in this case carbon tetrachloride). Extract three times with an equal volume of water. Adjust the hydrogen ion to 1 N with concentrated hydrochloric acid and add 100 percent excess oxalic acid while boiling. Let precipitate settle overnight and filter precipitate. Ignite and weigh as ThO<sub>2</sub>.

### Determination of Acid in the Presence of Thorium

To a measured amount of thorium solution add enough NaF solution to precipitate ThF<sub>4</sub> and give 20 percent excess. Titrate electrometrically with 0.100 M NaOH.

### Tributyl Phosphate

A relationship between concentration of TBP in carbon tetrachloride and density for pure solutions was experimentally determined for the whole range of TBP concentration. This relationship agreed excellently with that of L. L. Burger.<sup>3</sup> It was felt that the TBP concentration could be determined more accurately from a density measurement than an actual TBP analysis.



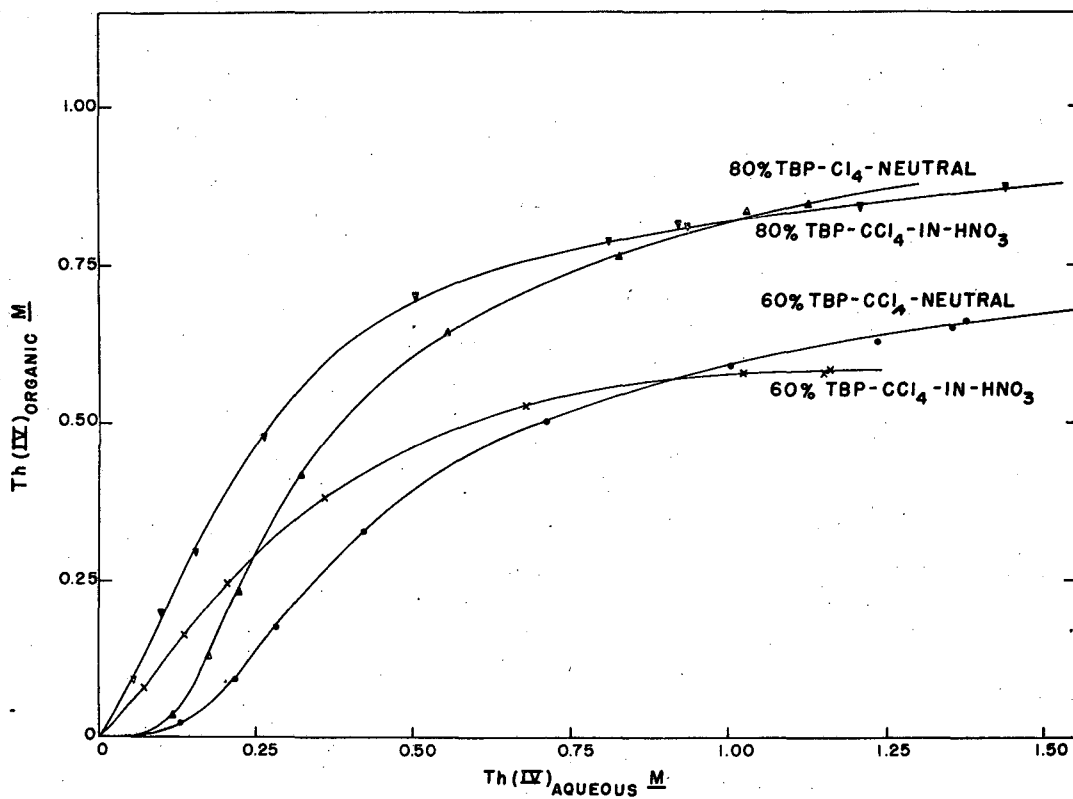
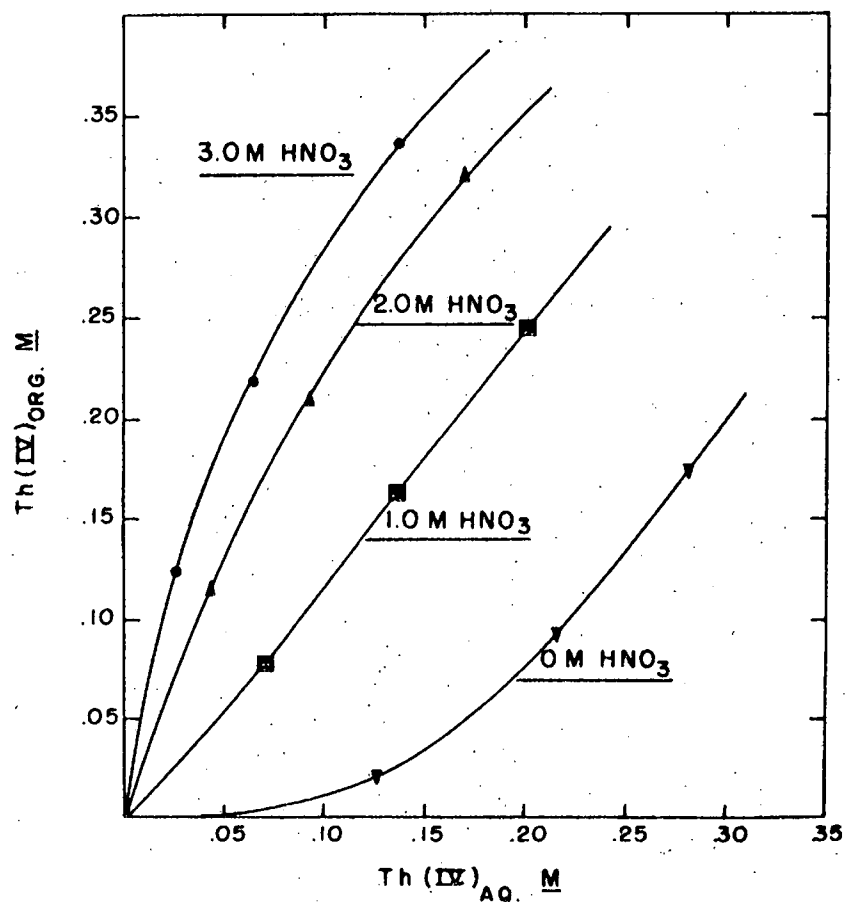
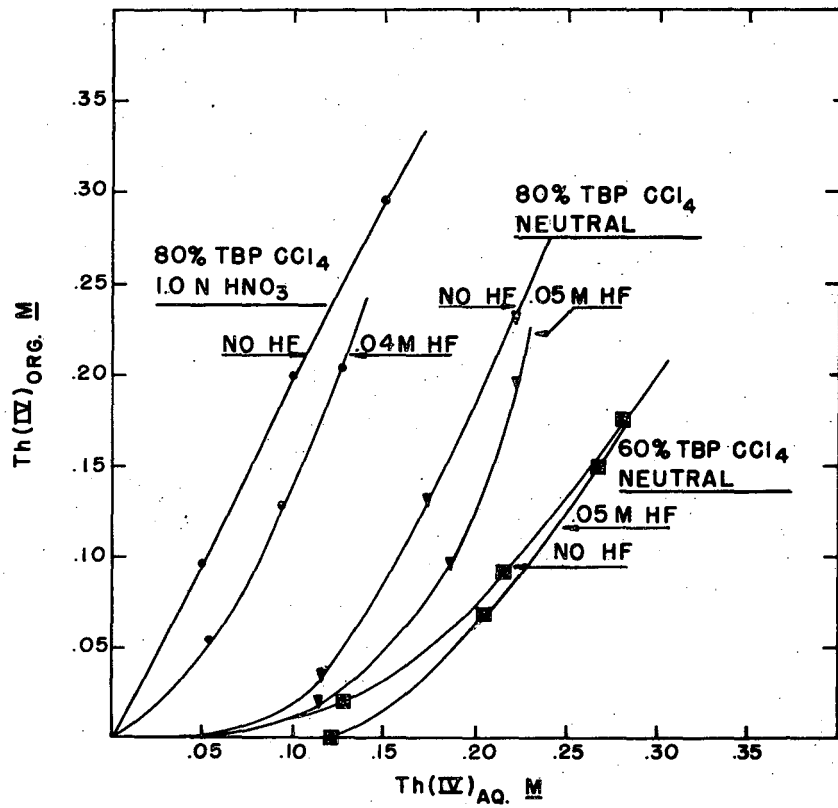


Figure I. THE DISTRIBUTION OF THORIUM NITRATE BETWEEN AQUEOUS AND TBP- $CCl_4$  SOLUTIONS.



MU 2621

Figure II. EFFECT OF NITRIC ACID ON THORIUM DISTRIBUTION BETWEEN WATER AND 60% TBP IN  $\text{C Cl}_4$ . (Acid concentrations shown are the initial value in the aqueous phase.)



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Figure III. THE EFFECT OF HF ON THE THORIUM DISTRIBUTION BETWEEN WATER AND TBP- $CCl_4$ .

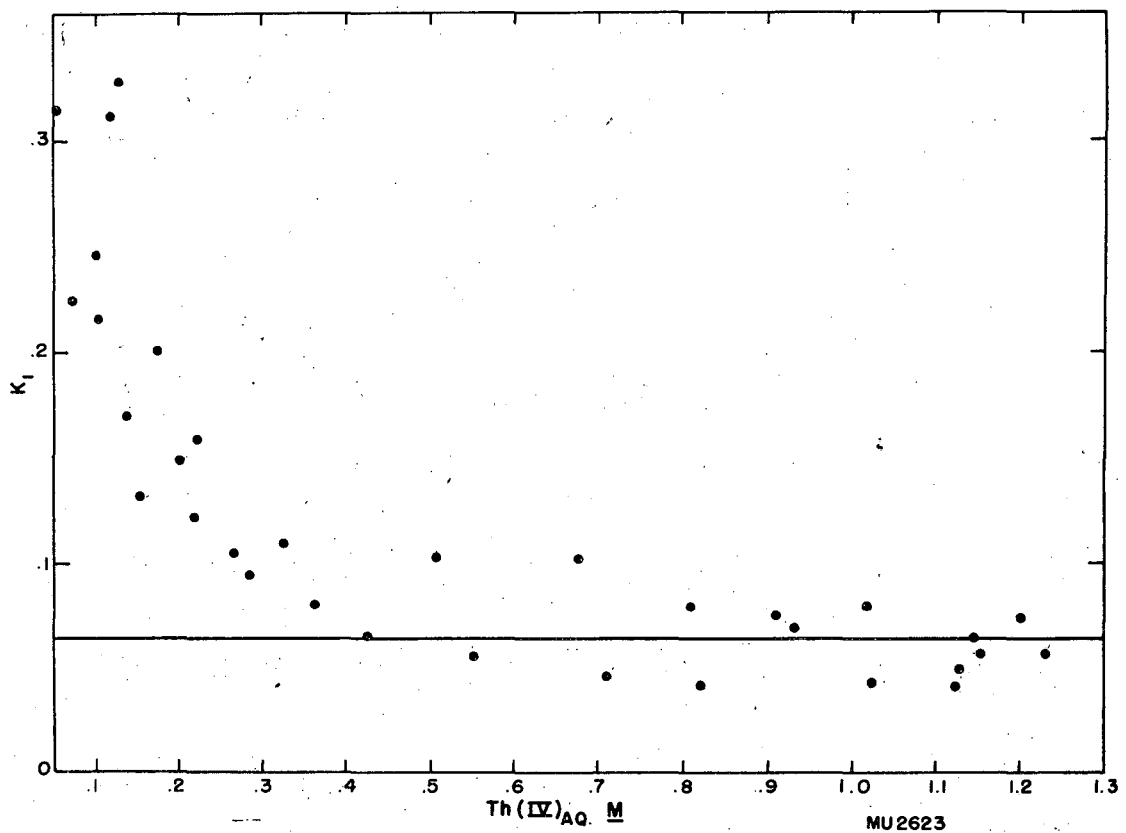
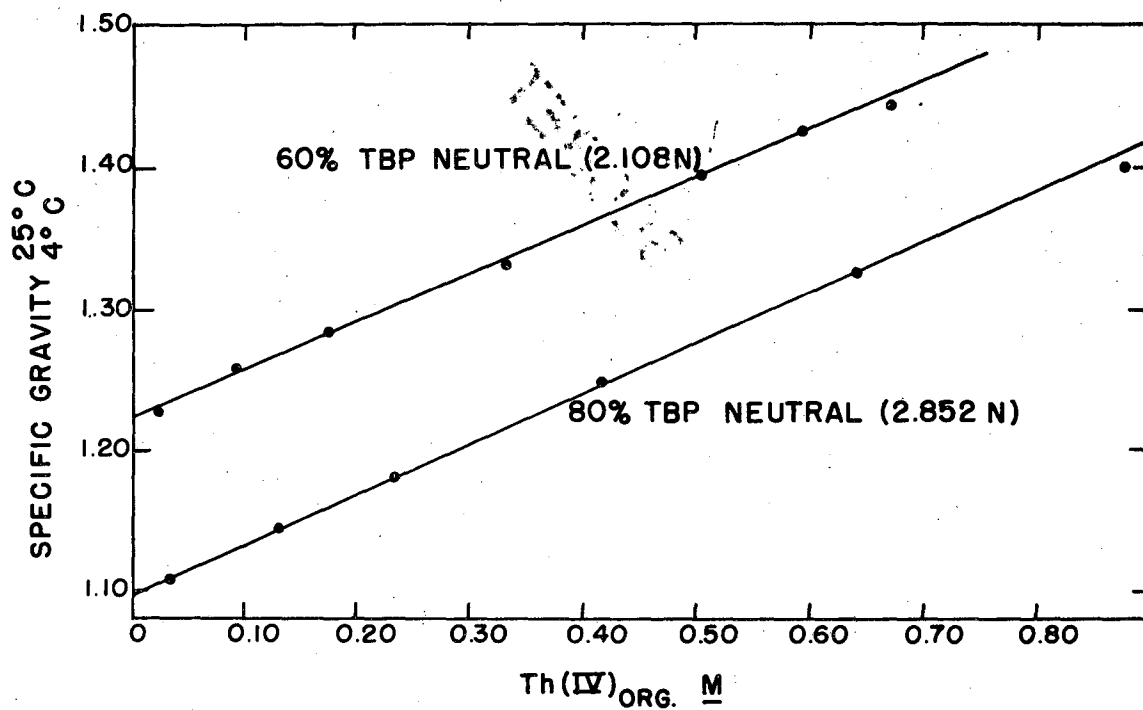


Figure IV.  $K_1$  versus  $\text{Th}(\text{aq})\underline{M}$

$$K_1 = \frac{[\text{Th}(\text{NO}_3)_4 \cdot \text{TBP}_3]}{(\text{Th})_{\text{aq}} (\text{NO}_3^-)_{\text{aq}}^4 (\text{TBP})_{\text{org}}^3}$$

CALCULATED FROM THE THORIUM DISTRIBUTION DATA BETWEEN 60% AND 80% TBP- C  $\text{Cl}_4$  SOLUTIONS AND 0 AND 1  $\underline{M}$   $\text{HNO}_3$  "(INITIAL)" AQUEOUS SOLUTIONS.



MU 2624

Figure V. SPECIFIC GRAVITY OF THORIUM NITRATE-TBP-C Cl<sub>4</sub> SOLUTIONS.