

*Chief's File*



CANADA

**STUDIES ON THE SEPARATION OF THE RARE  
EARTHS FROM THORIUM IN SULPHATE  
SOLUTIONS, USING CATION EXCHANGE RESINS**

4

01-7991790

by

**D. C. LEWIS & J. C. INGLES**  
**RADIOACTIVITY DIVISION**

**DEPARTMENT OF MINES AND  
TECHNICAL SURVEYS, OTTAWA**

**MINES BRANCH  
RESEARCH REPORT**

R 31

PRICE 25 CENTS

OCTOBER 6, 1958

Mines Branch Research Report R 31

STUDIES ON THE SEPARATION OF THE RARE EARTHS  
FROM THORIUM IN SULPHATE SOLUTIONS,  
USING CATION EXCHANGE RESINS

by

D. C. Lewis\* and J. C. Ingles\*\*

= = =

ABSTRACT

An ion exchange method for the separation of the rare earth elements from thorium has been investigated. The method is based on the difference in the extent of complexing of the metal ions by sulphate ions in aqueous solution. Variables investigated were: sulphate concentration, nature of the counter-ion (i. e. the cation whose sulphate salt supplies the sulphate for complexing), and resin type. Separation was not quantitative but it was found possible to obtain reasonable recoveries of thorium free of rare earths.

The application of the law of mass action to the solution and resin equilibria was undertaken in an attempt to explain the data. The theoretical expression obtained was not, however, in complete agreement with the experimental results.

---

\*Scientific Officer and \*\*Head, Analytical Chemistry Section, Radio-activity Division, Mines Branch, Department of Mines and Technical Surveys, Ottawa, Canada.

## CONTENTS

	<u>Page</u>
Abstract .....	i
Introduction .....	1
Experimental .....	3
Outline of Tests Performed .....	3
Absorption of Cations Separately .....	3
Absorption of Cations from Common Solutions...	3
Elution of Cations .....	4
Materials and Apparatus .....	4
Procedure .....	7
Analytical Method for Rare Earths and Thorium..	7
Test Work .....	7
Absorption of Cations Separately .....	7
Absorption of Cations from Common Solutions...	8
Elution of Cations .....	9
Results .....	10
Elution Tests .....	13
Discussion .....	13
Preliminary Testwork .....	13
Separation of Lanthanum and Thorium from a Common Solution Containing Sulphate Ions .....	13
The Distribution Coefficient and the Separation Factor.	18
Elution .....	21
Summary of Results, and Conclusions .....	24

CONTENTS (cont'd) '

	<u>Page</u>
Appendix: Application of the Law of Mass Action to the Thorium-Lanthanum Data .....	25
References .....	39-40

(40 pages)

= = =

## INTRODUCTION

During the course of an investigation, in 1957, on the recovery of uranium and thorium from a uranothorianite concentrate using sulphuric acid leaching, H. J. Herbst and L. E. Shaheen of this Division postulated that it should be possible to recover a uranium-thorium solution free of rare earths by using a cation exchange resin. The basis for this hypothesis was the now well-known tendency of uranium and thorium to form un-ionized and anionic complexes with sulphate ions in aqueous solutions (it was presumed that the rare earths did not form such complexes). They tested this possibility experimentally<sup>(1)\*</sup>, and obtained 90% of the uranium and 65-70% of the thorium almost free of rare earths, using a solution which was apparently about 0.5M in sulphate ions (no information was given as to the pH of this solution). Retention of 30% of the thorium by the resin was tentatively attributed to absorption of cationic sulphate complexes. Unfortunately, pressure of other work prevented Herbst and Shaheen from following up these observations.

The purification of thorium, particularly the removal of small amounts of the rare earths, is not without technical difficulty. In general, most of the methods available (oxalate, double sulphate) involve precipitation of a thorium compound. The difficulty of washing these compounds, together with the problems of co-precipitation, makes the ion-exchange method appear quite attractive, particularly since, with a suitable elution procedure, it might also offer a simplified method for obtaining a rare earth concentrate.

---

\*See Reference on page 39.

The test work described in this report was therefore undertaken in an attempt to evaluate in a systematic way some of the important variables involved, and to establish the possibilities and limitations of the separation.

It was also desired to establish whether the system was amenable to theoretical interpretation, in view of the appearance over the past few years of considerable fundamental data on ion exchange separations and on the sulphuric acid-sulphate system, as well as on the complexity constants of the various metal sulphates (6-14).

The variables of interest were investigated principally in terms of a parameter to which we give the name "separation factor", and which we define as

$$S_{\text{Th, La}} = \frac{\frac{\text{Amount of La sorption, g La/g resin}}{\text{concentration of La in solution, g/l}}}{\frac{\text{Amount of Th sorption, g Th/g resin}}{\text{concentration of Th in solution, g/l}}}$$

The practical utility of this parameter is that it permits an approximate calculation of the amount of thorium that can be recovered free of lanthanum, using the expression

$$\text{Recovery \% Th} = \left(1 - \frac{1}{S_{\text{Th, La}}}\right) \times 100$$

## EXPERIMENTAL

### Outline of Tests Performed

#### Absorption of Cations Separately

Preliminary test work was carried out on thorium and on typical rare earth elements, separately, with a view to bracketing the conditions of sulphate ion concentrations which would provide the best separation, for use as a guide in the subsequent experiments with thorium and a rare earth present simultaneously in the solution.

#### Absorption of Cations from Common Solutions

This background having been established, the tests with thorium and the rare earths in the same solution were then carried out covering the range of sulphate concentrations indicated in the previous tests. Radiotracers for the rare earth were used in this work. The use of a radiotracer for thorium would also have been a convenience, but the instrumentation was not available to permit differentiating the two, hence thorium was determined colorimetrically. The variables investigated were: 1) the concentration of sulphate ion in solution, 2) the nature of the counter-ion (that is, the third cation, whose sulphate salt provides the sulphate ion for the complexing reaction), and 3) the type of cation exchange resin employed. Counter-ions investigated were hydrogen, sodium, and magnesium. Resins used were Rohm and Haas resins IR 120-H and IR 100-H.

## Elution of Cations

Elution tests were carried out to establish whether lanthanum and thorium were absorbed as the ions or as the complex metal sulphates. A few tests were also performed to establish what strengths of sulphuric acid would elute lanthanum from the resin.

## Materials and Apparatus

Thorium feed stock solutions were prepared by dissolving Fisher Chemical Co. C. P. thorium oxide in concentrated nitric acid containing a few drops of 2% hydrofluoric acid. The nitrate thus obtained was converted to chloride or sulphate as required, by repeated evaporation with hydrochloric or sulphuric acid, and made up to standard volume with distilled water.

Solutions were prepared which contained about 1 g/l thorium oxide, (a) in decinormal hydrochloric acid, and (b) in 10, 25, 50 and 100 g/l excess sulphuric acid. These solutions were standardized using the procedure described by Carron et al (2), the hydroxide being ignited and thorium weighed as the oxide. Lanthanum feed stock solutions were prepared from Lindsay Chemical Co., Code 529 lanthanum oxide, by the procedure employed for the thorium solutions. Solutions were prepared which contained about 1 g/l lanthanum oxide in hydrochloric and sulphuric acid as in (a) and (b) above. These solutions were also standardized by precipitation with ammonia, lanthanum being weighed as the oxide. The samarium and yttrium used were also from Lindsay Chemical Co.



and the solutions were prepared and standardized in the same manner as for lanthanum.

Feed stock solutions containing about 1 g/l each of thorium and lanthanum together were similarly prepared. The levels of concentration of sulphate and bisulphate ions and the nature and concentration of the exchange counter-ion in these solutions were obtained by the addition of sulphuric acid and sodium or magnesium sulphate (see Table 3). The lanthanum content of the solutions was labelled by the addition of radio-lanthanum or radio-europium. In these solutions, thorium was determined by sebacate separation followed by a Thorin reagent colorimetric finish, lanthanum was estimated by a gravimetric determination in a blank preparation, and sulphuric acid was determined by potentiometric titration against standard base using potassium oxalate as a complexing agent for thorium and lanthanum (3).

Rohm and Haas Co., Amberlite IR 120 (16-50 mesh) and IR 100 (16-50 mesh) cation exchange resins were received in the hydrogen form. The moisture contents of these materials, determined by drying to constant weight at 110°C, were as shown in Table 1.

TABLE 1

Moisture Contents of Amberlite Cation Exchange Resins

Resin	% Moisture Content		Bed Volume, ml/g "As Rec'd" Resin
	As Received	Equilibrium <sup>(3)</sup>	
IR 120-H	57.7	51.0	1.52
IR 100-H	45.4	40.8	1.09

Ion exchange columns were prepared from these materials by standard procedures. Before use in exchange experiments, these columns were treated with a large excess of molar sulphuric acid and then washed with distilled water until the effluent was acid free.

Radio-lanthanum ( $\text{La}^{140}$ , half life 40.22 hr) and radio-europium (unseparated  $\text{Eu}^{152}$  and  $\text{Eu}^{154}$ , half life 13-16 yr), obtained by neutron irradiation of spectrographically pure lanthanum and europium oxide, were supplied by Atomic Energy of Canada, Ltd. Sulphate solutions of the active oxides were prepared by the procedure already described and aliquots of these solutions were employed in the preparation of labelled feed stock solutions as required. The appropriate aliquots for optimum count rates in the cation exchange column effluents of this study were determined in preliminary experiments.

Radiometric determinations were made, using a 20th Century Electronics Co., Ltd., Type F.10, G.M. flow counter with a liquid capacity of 0.5 ml. The counter was connected in turn to a Tracerlab Model SC-34 ratemeter and an Esterline Angus Model AW recording ammeter. Colorimetric determinations were made using a Beckman Model B spectrophotometer with 1 cm cells. pH determinations were made using a Cambridge Instrument Co., Ltd., portable pH meter, standardized at pH 0.915 against 0.098 M sulphuric acid.

Except where otherwise stated, all reagents were of analytical reagent grade.

## Procedure

### Analytical Method for Rare Earths and Thorium

It was first necessary to establish an analytical method for determining rare earths in the presence of magnesium and sulphate ions. Dilute solutions containing thorium and lanthanum oxide were prepared from the thorium and lanthanum, chloride and sulphate feed stock solutions (a) and (b) above. Alizarin Red S colours were developed in these dilutions, using the procedure described by Rinehart<sup>(4)</sup> for the determination of rare earths in chloride solutions. The absorbancies of these colours were measured at 550 m $\mu$  and at other wavelengths in the range 475 to 650 m $\mu$ . The thorium colours in sulphate solutions exhibited an absorption maximum at 535 m $\mu$ , approximately coincident with that observed by Rinehart for the rare earths in chloride solutions. Working curves were constructed at 550 m $\mu$ . The curves obtained for thorium and lanthanum were linear and not significantly different in sulphate solution than in chloride solution. Rinehart's procedure was employed for subsequent determinations of thorium and lanthanum in the preliminary tests described in the following section.

## Test Work

### Absorption of Cations Separately

In these tests on the exchange characteristics of thorium, lanthanum, samarium and yttrium in sulphate solution, columns 0.45 x 32 cm, containing about 5 ml of Amberlite IR 120-H, were loaded until equilibrium was established, by downward percolation of thorium or lanthanum feed stock solution (b) above, at a flow rate

of 0.5 ml/min. The effluents were collected in 50-ml fractions and the concentration of thorium or rare earths in each fraction was determined colorimetrically. When equilibrium was reached, as indicated by equality of the metal concentrations in the influent and effluent solutions, the resin beds were washed free of acid, extruded, and their metal content determined colorimetrically after a wet oxidation procedure to destroy the resin. The results of these tests are reported in Table 2 (page 11).

#### Absorption of Cations from Common Solutions

In these tests, columns 0.45 x 32 cm and 0.45 x 13.5 cm Amberlite IR 120-H and 0.45 x 35 cm Amberlite IR 100-H<sup>+</sup> were employed. The particular column size for a given series of experiments was selected to give an eluate fraction of convenient volume for analysis.

These columns were loaded to lanthanum breakthrough (8.6 mg La<sub>2</sub>O<sub>3</sub>/l) by downward percolation of the several thorium-lanthanum feed stock solutions of this study, the flow rate again being maintained at 0.5 ml/min. The effluents from the columns were passed through the helix of the G. M. tube and collected in a graduated cylinder, the throughput volume and effluent count rate being observed at 15-min intervals. Breakthrough was indicated, and loading was stopped when the effluent count rate reached one hundredth of that of the loading solution, which had been determined in a preliminary experiment. On completion of the loading cycle, the columns were washed with distilled water until acid free. Their thorium and lanthanum contents were then eluted with molar sulphuric acid. Thorium in these eluates was deter-

mined by sebacate precipitation followed by a Thorin colorimetric finish (3). The regenerated columns were then employed for the next following experiments; thus generally only one resin bed, successively loaded and regenerated, was employed in each series of experiments. Background corrections were applied to all observed count rates, paralysis time corrections were negligible throughout, and decay corrections were necessary only in those few experiments where radio-lanthanum was employed as a tracer. Observed throughput volumes at lanthanum breakthrough were corrected for solution holdup between the column and G. M. tube effluent outlets (2 ml). Results obtained from these experiments are reported in Table 3' (page 12).

#### Elution of Cations

##### Investigation of Non-adsorption of Complex Metal Sulphate Cations by the Resin

A column containing one gram Amberlite IR 120 was loaded to saturation with 100 ml of a solution containing 1 g  $\text{La}_2\text{O}_3$ /l in 0.51M sulphuric acid. After washing free of sulphate ions, the column was eluted with 2M sodium chloride solution and the eluate was analyzed for sulphate. A similar test was carried out using the corresponding thorium solution.

##### Elution of Lanthanum by Sulphuric Acid of Various Strengths

A few tests were carried out in which the lanthanum-loaded resin (containing the radiotracer) was eluted with 5 bed volumes of sulphuric acid of successively increasing concentration covering the

range 0.01 to 0.50M. This was continued until complete elution was obtained to establish a) the highest concentration of sulphuric acid which would not elute lanthanum and b) the lowest concentration which would cause it to elute completely.

## RESULTS

The results of the tests on the adsorption of thorium, lanthanum, samarium, and yttrium on Rohm and Haas resin IR 120-H, from individual sulphuric acid solutions, are given in Table 2. Both saturation loadings and loadings until breakthrough (at a flow rate of 0.1 ml of solution per ml of resin, or 3.15 ml per sq cm of resin bed) are given.

Table 3 gives the same data for thorium and lanthanum loadings from common solutions containing sulphate in the form of various salts and for both IR 100 and IR 120 resins, at the same flow rate.

Following the tables, there is a résumé of the elution tests.

TABLE 2

Adsorption of Thorium, Lanthanum, Samarium  
and Yttrium on IR 120-H from Separate  
Sulphuric Acid Solutions

Feed Stock Composition		Resin Adsorption			
Element (conc'n 1 g/l)	H <sub>2</sub> SO <sub>4</sub> conc'n M	to Breakthrough, per dry gram		to Saturation per dry gram	
		mg	meq	mg	meq
ThO <sub>2</sub>	0.10	250	3.79	282.7	4.28
	0.25	122	1.89	172.8	2.62
	0.50	70	1.06	82.1	1.24
	1.00	<12	<0.2	19.8	0.30
La <sub>2</sub> O <sub>3</sub>	0.10	228	4.20	291.8	5.39
	0.25	190	3.50	248.0	4.58
	0.50	<12	<0.2	173.4	3.20
	1.00	<12	<0.2	82.9	1.53
Sm <sub>2</sub> O <sub>3</sub>	0.10	258	4.44	276.6	4.76
	0.25	25.4	0.43	237.0	4.08
	0.50	18.8	0.32	169.5	2.91
	1.00	5.0	0.09	76.1	1.31
Y <sub>2</sub> O <sub>3</sub>	0.10	157	4.17	183.7	4.88
	0.25	123	3.26	163.0	4.33
	0.50	35	0.93	111.7	3.11
	1.00	24	0.64	54.7	1.45

Resin column, 5 ml; flow rate, 0.5 ml/min.

Resin capacity (by extrapolation to zero acidity), 6.36 meq/dry gram.

TABLE 3

## Lanthanum and Thorium Loadings at Lanthanum

## Breakthrough, from a Common Solution Containing Sulphate

Resin and Counter-ion Sulphate Used	Solution Composition			Volume to Break-through, ml	Resin Loadings	
	H <sub>2</sub> SO <sub>4</sub> conc'n M	Counter-ion Sulphate conc'n, M	pH		mg/ gram dry resin	
					ThO <sub>2</sub>	La <sub>2</sub> O <sub>3</sub>
0.846-g, IR 120-H, H <sub>2</sub> SO <sub>4</sub>	0.052	-	1.13	101.2	111.5	102.9
	0.108	-	0.86	96.7	109.3	98.3
	0.249	-	0.56	89.0	82.5	90.5
	0.378	-	0.39	69.5	47.3	70.7
	0.505	-	0.29	50.5	40.7	51.3
	0.577	-	0.20	36.0	22.6	36.6
	0.684	-	0.14	23.0	16.0	23.4
0.846-g, IR 120-H, Na <sub>2</sub> SO <sub>4</sub>	0.019	0.000	1.46	101.2	116.4	102.9
	0.019	0.040	1.62	92.2	105.6	93.7
	0.019	0.080	1.76	83.0	61.5	84.4
	0.019	0.100	1.81	78.2	38.8	79.5
	0.019	0.140	1.88	53.0	17.6	53.9
	0.019	0.170	1.97	24.3	8.9	24.9
	0.019	0.250	2.01	7.2	4.3	7.3
	0.019	0.400	2.09	2.2	2.5	2.5
1.967 g, IR 120-H, Mg SO <sub>4</sub>	0.034	0.065	1.44	169.0	17.4	73.8
	0.034	0.091	1.46	94.0	15.5	41.1
	0.034	0.120	1.50	60.0	14.9	26.2
	0.034	0.140	1.52	36.0	10.7	15.7
	0.034	0.160	1.55	27.6	8.9	12.1
2.000 g, IR 100-H, Na <sub>2</sub> SO <sub>4</sub>	0.034	0.100	1.57	75.0	7.5	32.3
	0.034	0.140	1.65	33.0	2.7	14.2
	0.034	0.160	1.68	20.0	2.5	8.6

Feed stock composition: 0.970 g ThO<sub>2</sub>/l  
0.860 g La<sub>2</sub>O<sub>3</sub>/l



### Elution Tests

The elution tests established that no sulphate was associated with the ionic species adsorbed by the resin.

It was also found that lanthanum was not eluted by sulphuric acid solutions up to a concentration of 0.15M  $H_2SO_4$ . There was appreciable lanthanum leakage with solutions containing 0.20M  $H_2SO_4$ , and substantially all the lanthanum was eluted by a solution containing 0.50M sulphuric acid.

## DISCUSSION

### Preliminary Testwork

The results of the tests on thorium and the rare earths separately are given in Table 2. These results are illustrated graphically in Figure 1 and also in Figure 2, where the results for column capacity have been plotted against sulphate concentration. These results were used as a guide in establishing the sulphate concentration range of interest for testwork with the other counter ions.

### Separation of Lanthanum and Thorium from a Common Solution Containing Sulphate Ions

To illustrate that sulphate complexing is indeed the principal factor in controlling free metal-ion concentration, the results of Table 3 for the thorium-lanthanum separation on IR 120, sodium and hydrogen as counter-ions, are shown in Figures 3 and 4. Figure 3 gives the loadings of each metal on the resin, as a function of the total sulphate concentration and there appears to be little correlation. In Figure 4,

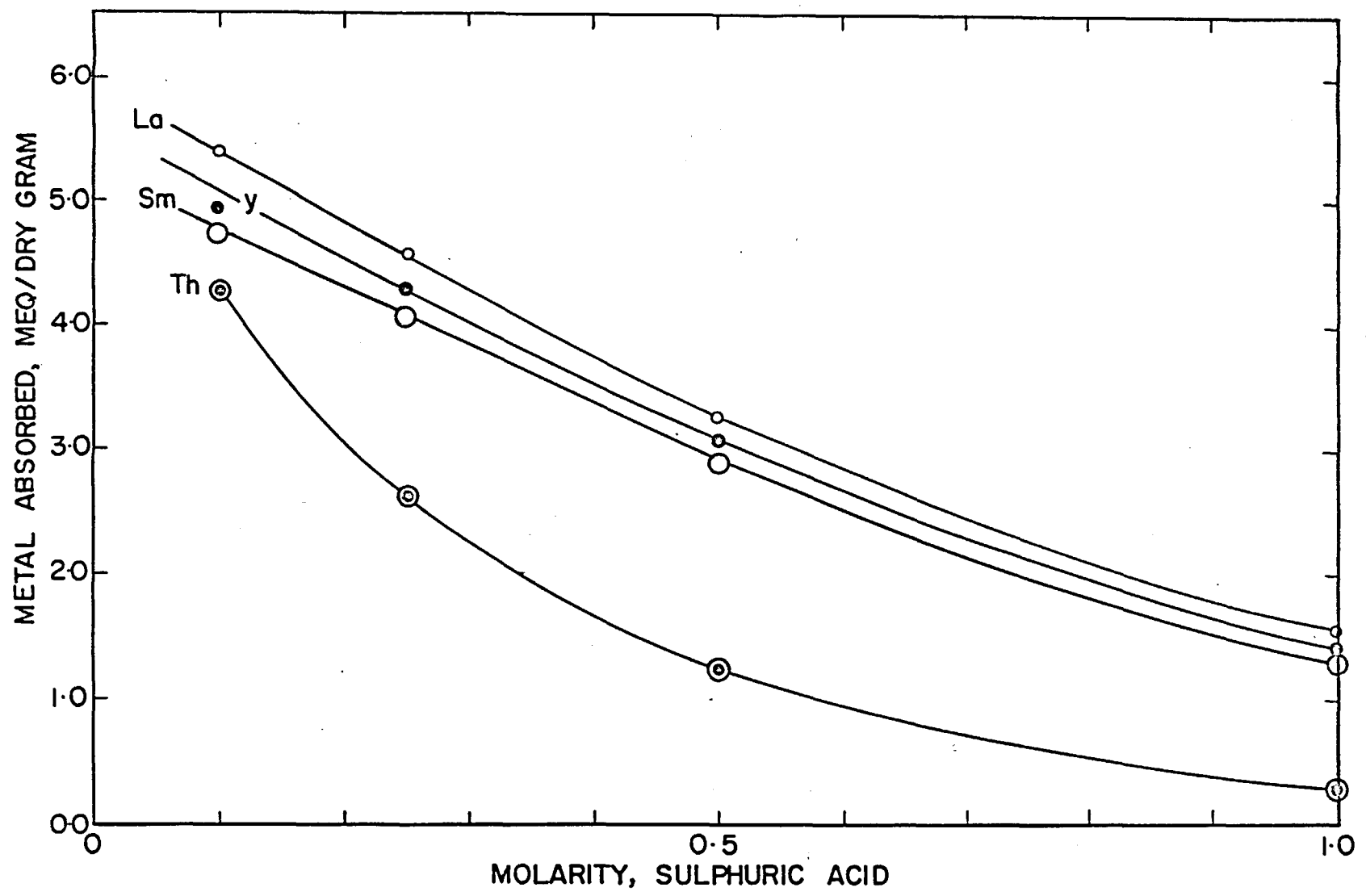


FIGURE I  
RESIN SATURATION ABSORPTION OF RARE EARTHS AND THORIUM  
FROM SEPARATE SULPHURIC ACID SOLUTIONS

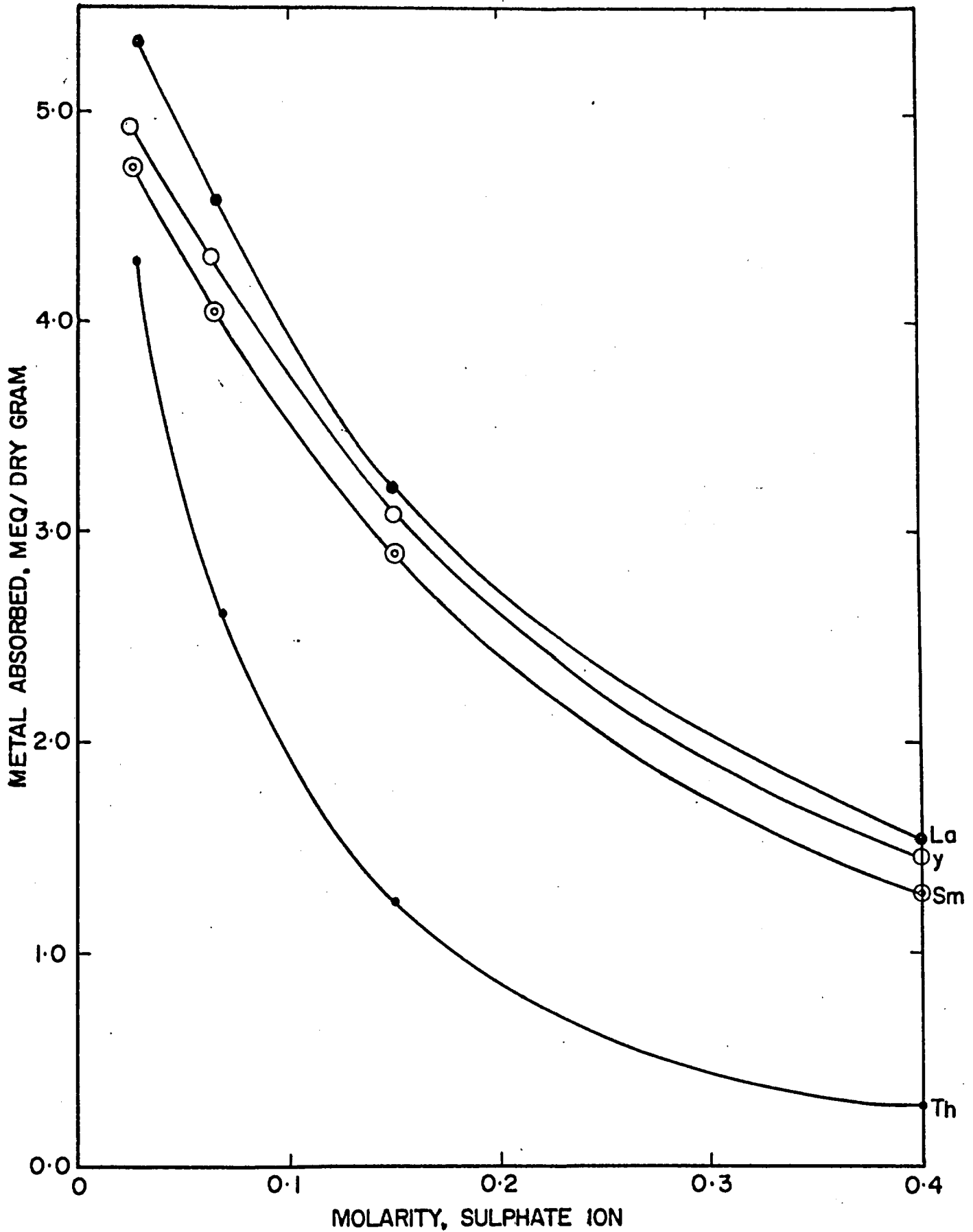


FIGURE 2  
SATURATION ABSORPTION OF RARE EARTHS  
AND THORIUM AS A FUNCTION OF SULPHATE ION CONCENTRATION

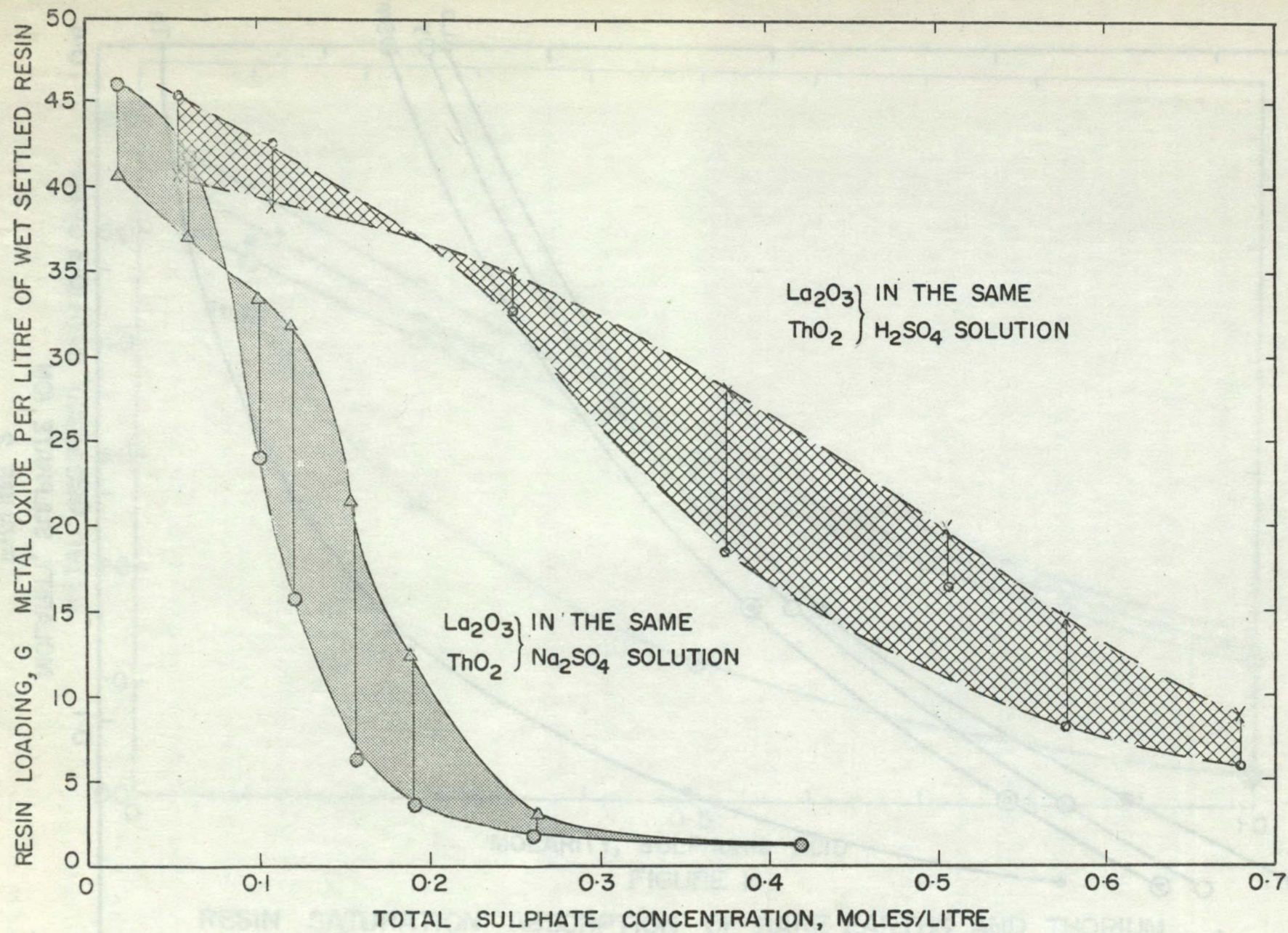


FIGURE 3  
 ABSORPTION OF THE METAL IONS AS  
 A FUNCTION OF TOTAL SULPHATE CONCENTRATION

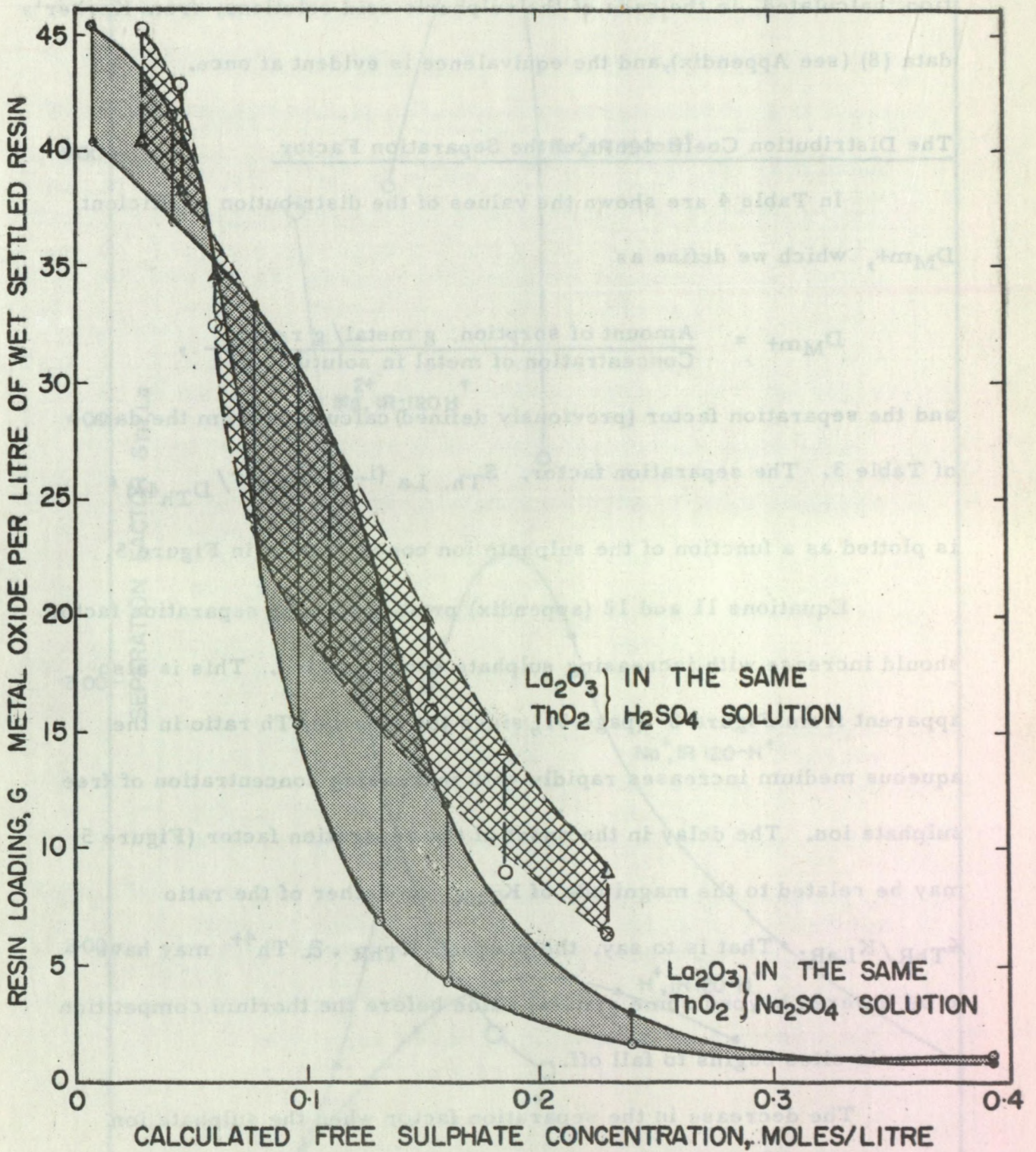


FIGURE 4  
ABSORPTION OF THORIUM AND LANTHANUM  
AS A FUNCTION OF FREE SULPHATE CONCENTRATION

A FUNCTION OF TOTAL SULPHATE CONCENTRATION

however, the same results are plotted against actual sulphate concentration calculated, in the case of the sulphuric acid solutions, from Kerker's data (8) (see Appendix), and the equivalence is evident at once.

### The Distribution Coefficient and the Separation Factor

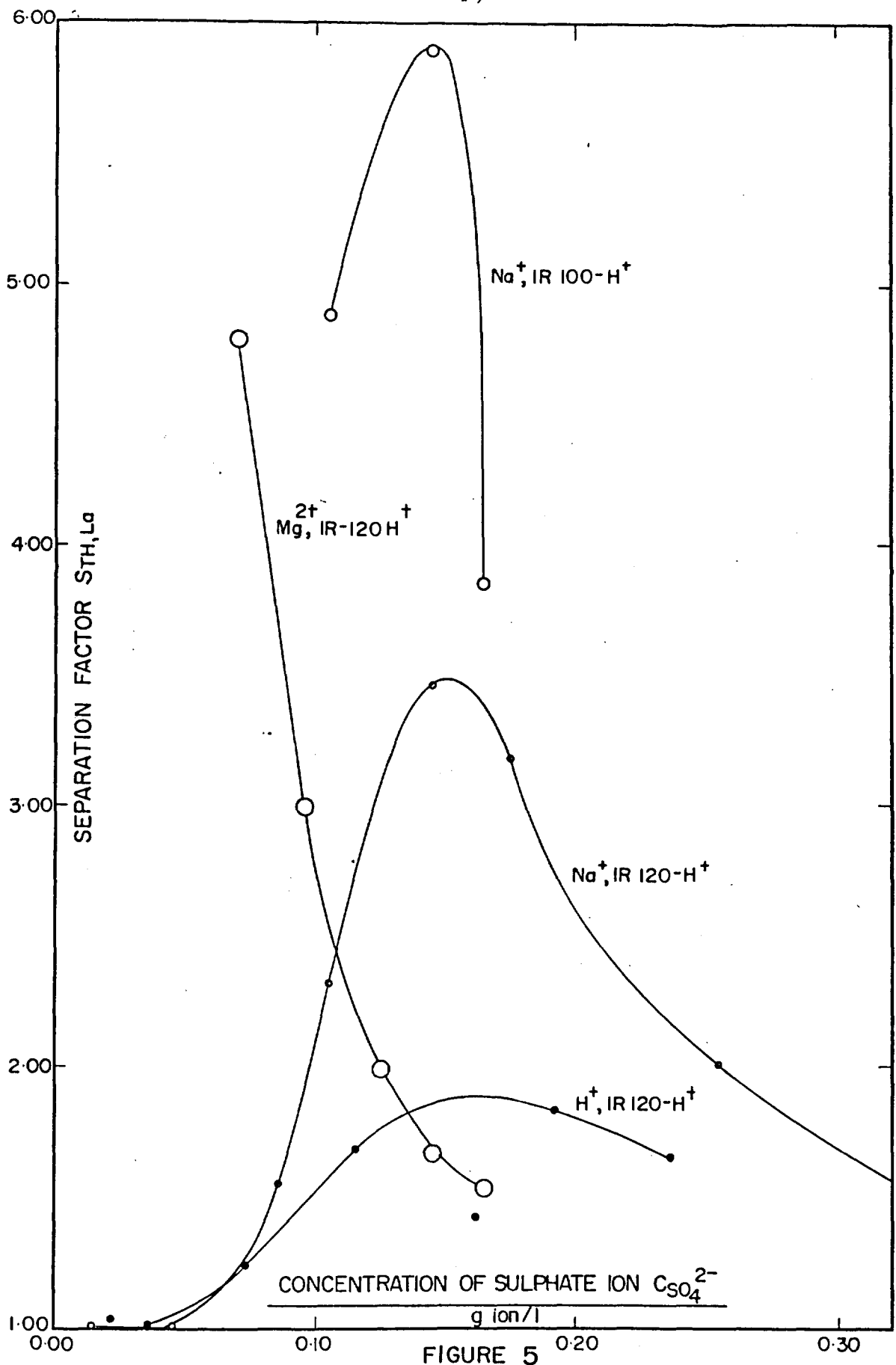
In Table 4 are shown the values of the distribution coefficient,  $D_{M^{m+}}$ , which we define as

$$D_{M^{m+}} = \frac{\text{Amount of sorption, g metal/g resin}}{\text{Concentration of metal in solution, g/l}},$$

and the separation factor (previously defined) calculated from the data of Table 3. The separation factor,  $S_{Th, La}$  (i. e.  $D_{La^{++}}/D_{Th^{4+}}$ ), is plotted as a function of the sulphate ion concentration in Figure 5.

Equations 11 and 12 (appendix) predict that the separation factor should increase with increasing sulphate concentration. This is also apparent from Figure 8 (page 31), since the free La/Th ratio in the aqueous medium increases rapidly with increasing concentration of free sulphate ion. The delay in the onset of the separation factor (Figure 5) may be related to the magnitude of  $K_{ThR}$ , or rather of the ratio  $K_{ThR}/K_{LaR}$ . That is to say, the product  $K_{ThR} \cdot a_{Th^{4+}}$  may have to be lowered beyond some critical value before the thorium competition for resin sites begins to fall off.

The decrease in the separation factor when the sulphate ion (and the counter-ion) concentration increases beyond 0.15M is not predicted by the mass action expression derived in the Appendix and indicates a basic flaw in the theoretical treatment. The deviation from theory is particularly evident in the case of magnesium (Table 3



SEPARATION FACTOR FOR THORIUM AND LANTHANUM, SHOWN AS A FUNCTION OF THE CONCENTRATION OF SULPHATE ION

TABLE 4 .

Distribution Coefficients and Separation Factors for  
Thorium and Lanthanum in Experiments on Separation  
by Exchange Sorption from Sulphate Solutions

Resin and Counter-ion, B <sup>b+</sup>	C <sub>B<sup>b+</sup></sub>	C <sub>SO<sub>4</sub><sup>2-</sup></sub> *	D <sub>La<sup>3+</sup></sub>	D <sub>Th<sup>4+</sup></sub>	S <sub>Th, La</sub>
IR 120-H, and H <sup>+</sup>	0.074	0.021	0.1197	0.1149	1.04
	0.140	0.036	0.1143	0.1126	1.02
	0.279	0.073	0.1052	0.0851	1.24
	0.412	0.115	0.0822	0.0488	1.68
	0.513	0.161	0.0597	0.0420	1.42
	0.630	0.191	0.0426	0.0233	1.82
	0.725	0.236	0.0272	0.0164	1.65
IR 120-H, and Na <sup>+</sup>	0.000	0.015	0.1197	0.1200	1.00
	0.080	0.045	0.1090	0.1089	1.00
	0.160	0.085	0.0981	0.0634	1.55
	0.200	0.105	0.0924	0.0400	2.31
	0.280	0.145	0.0627	0.0181	3.46
	0.340	0.175	0.0343	0.0108	3.18
	0.500	0.255	0.0084	0.0042	2.00
0.800	0.405	0.0029	0.0026	1.12	
IR 120-H, and Mg <sup>2+</sup>	0.065	0.070	0.0858	0.0179	4.79
	0.091	0.096	0.0480	0.0160	3.00
	0.120	0.125	0.0305	0.0154	1.98
	0.140	0.145	0.0183	0.0110	1.66
	0.160	0.165	0.0141	0.0092	1.53
IR 100-H, and Na <sup>+</sup>	0.200	0.105	0.0376	0.0077	4.88
	0.280	0.145	0.0165	0.0028	5.90
	0.320	0.165	0.0100	0.0026	3.85

\* Not corrected for sulphate in the metal complexes.



and Figure 5). In Figure 6, the separation factor has been plotted against  $(C_B^{b+})^{1/b}$  (the concentration of the counter-ion raised to the reciprocal power of its valence), and it will be seen that this correlates the magnesium data with data for the other counter-ions. It is apparent, therefore, that, at values for  $C_B^{b+}$  above 0.15M, the separation factor is no longer a direct function of the concentration of the counter-ion, and hence the expression derived in the Appendix is not valid at these higher counter-ion concentrations.

A point which has not been considered up to now, but which is of great practical importance, is the lanthanum loading of the resin. A good separation of lanthanum from thorium is not of much value unless accompanied by a reasonable retention of lanthanum by the resin. For comparative purposes the relevant data from Tables 3 and 4 are listed in Table 5.

Satisfactory loadings and separations were obtained with IR 120-H, using sodium as a counter-ion at a sulphate concentration of 0.140M, and with magnesium as a counter-ion at a sulphate concentration of 0.070. From Figure 5 it will be seen that an even better loading and separation should be possible with magnesium, at lower concentrations, as a counter-ion.

### Elution

Elution studies, though incomplete, showed that lanthanum was not eluted by 0.15M sulphuric acid, but was completely eluted by 0.50M sulphuric acid. Similar studies on thorium were not carried out.

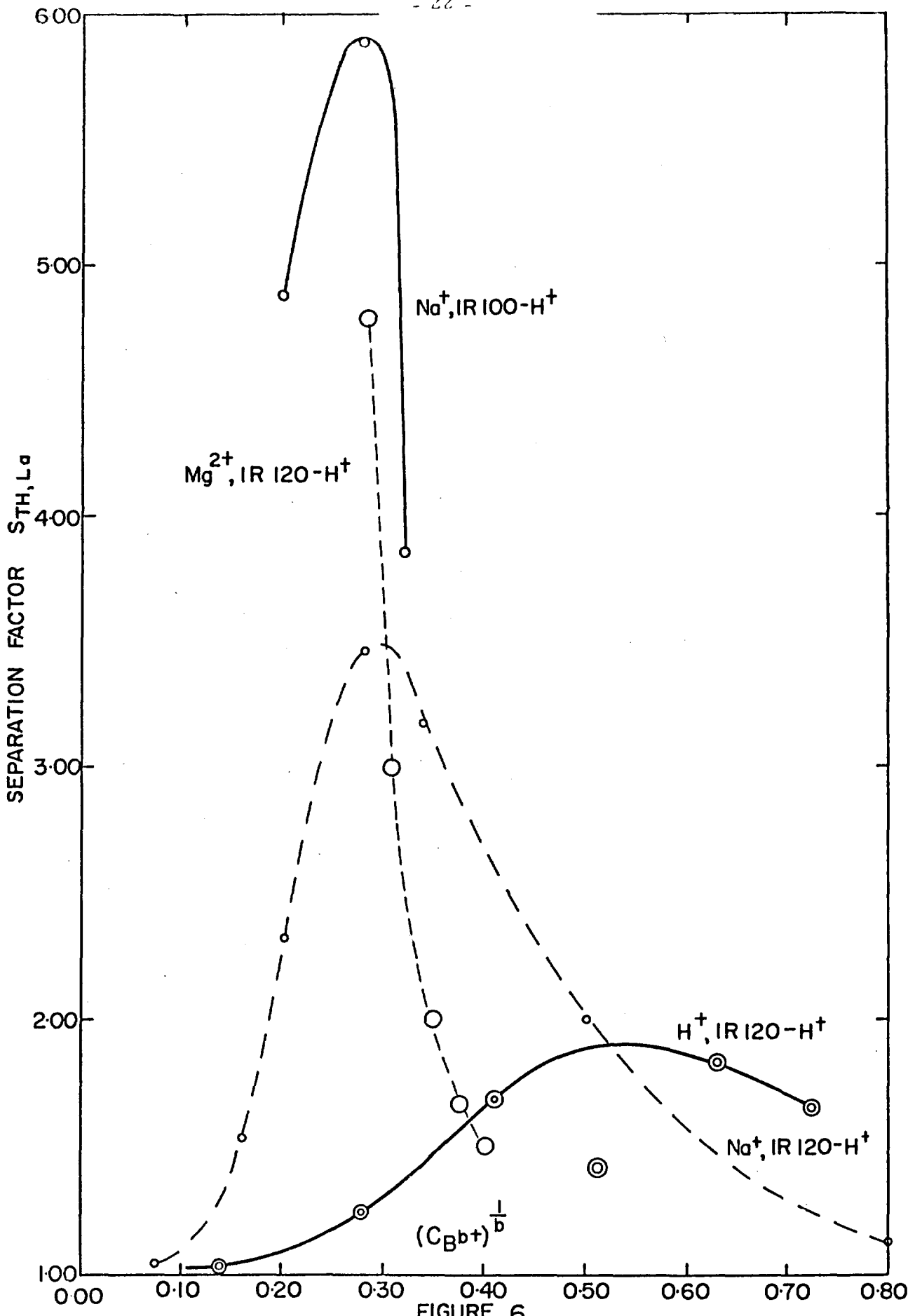


FIGURE 6  
SEPARATION FACTOR AND  
ITS RELATION TO THE FUNCTION OF COUNTERION CONCENTRATION  $(C_{B^{b+}})^{1/b}$

TABLE 5

Comparison of Lanthanum Loading  
and Separation Factors Obtained

Counter-ion	Resin	Sulphate Concentration M	Separation Factor	Loading MgLa <sub>2</sub> O <sub>3</sub> per gram dry resin
H <sup>+</sup>	IR 120-H	0.021	1.04	102.9
		0.036	1.02	98.3
		0.073	1.24	90.5
		0.115	1.68	70.7
		0.161	1.42	51.3
		0.191	1.82	36.6
		0.236	1.65	23.4
Na <sup>+</sup>	IR 120-H	0.015	1.00	102.9
		0.045	1.00	93.7
		0.085	1.55	84.4
		0.105	2.31	79.5
		0.145	3.46	53.9
		0.175	3.18	24.9
		0.255	2.00	7.3
Mg <sup>2+</sup>	IR 120-H	0.070	4.80	73.8
		0.096	3.00	41.1
		0.125	1.98	26.2
		0.145	1.66	15.7
		0.165	1.53	12.1
Na <sup>+</sup>	IR 100-H	0.105	4.88	32.3
		0.145	5.90	14.2
		0.165	3.85	8.6

However, Nietzel, Wessling and DeSesa<sup>(16)</sup> have examined the elution of thorium from IR 120, IR 105 and IR 100, using HCl and H<sub>2</sub>SO<sub>4</sub> over the concentration range 0 to 6M, and it appears to be possible to elute lanthanum free of thorium using 2M hydrochloric acid, and then elute the thorium with 3M sulphuric acid. In any case, further work on the elution step appears to be warranted.

#### SUMMARY OF RESULTS, AND CONCLUSIONS

1. As the concentration of sulphate in the feed stock increased, the magnitude of the separation factor increased to a maximum and then decreased. In the case of the monovalent counter-ions Na<sup>+</sup> and H<sup>+</sup> the maximum fell in a narrow range of sulphate concentrations, viz. 0.14 to 0.16 g ion/l.

Exchange was anomalous in the case of Mg<sup>2+</sup> as counter-ion and appeared to be related inversely to the square root of the concentration of this ion.

2. The maximum value of the separation factor was a function of the nature of the counter-ion, increasing with the affinity of the counter-ion for the resin, i. e. Mg > Na > H.

3. The maximum value of the separation factor was greater for the sulphonated phenolic resin IR 100 than for the sulphonated polystyrene resin IR 120, in the case of the sodium counter-ions systems examined. The two maxima occurred at about the same concentration of sulphate and counter-ion. The resin IR 100 has a lower total exchange capacity than IR 120 and this was reflected in the lanthanum loadings obtained.

Thorium and lanthanum exist in sulphate solutions in the form of the free ions, and as the complexes  $\text{Th}(\text{SO}_4)^{++}$ ,  $\text{Th}(\text{SO}_4)_2$ ,  $\text{Th}(\text{SO}_4 \cdot \text{HSO}_4)^+$  and  $\text{La}(\text{SO}_4)^+$ . Only the free ions are absorbed by the cation exchanger Amberlite IR 120. Partial separation of the metals, in which a thorium solution is produced free of lanthanum (but at the expense of some decrease in thorium concentration), has been obtained by exchange between solutions of their sulphates (approximately 1 g/l each of  $\text{La}_2\text{O}_3$  and  $\text{ThO}_2$ ) containing added sulphate, and columns of Amberlite IR 120 and IR 100. Improvement in the separation was obtained as the counter-ion (the cation whose sulphate salt provides the added sulphate for complexing) was varied from  $\text{H}^+$  through  $\text{Na}^+$  to  $\text{Mg}^{2+}$ . The separation was again improved (at the expense of lower lanthanum loading) when the sulphonated phenolic resin Amberlite IR 100 was employed instead of the sulphonated polystyrene resin Amberlite IR 120. Optimum results were obtained for a total sulphate concentration of 0.14 - 0.16 g ion/l in the case of  $\text{Na}^+$  and 0.065 or lower in the case of  $\text{Mg}^{2+}$ . An equation which partially describes these observations has been developed by the application of the law of mass action to the complexing and exchange equilibria.

## APPENDIX

### APPLICATION OF THE LAW OF MASS ACTION TO THE THORIUM-LANTHANUM DATA

It is known that the law of mass action (in modified form, it is true) can be applied to the reactions of cation exchange resins with cations, and indeed many "equilibrium constants" (or selectivity

coefficients) are available for these reactions (5). Moreover, stability constants have recently become readily available for many metal sulphate complexes. With this in mind, the data of the preliminary experiments for thorium and for lanthanum (Table 6) have been examined theoretically by the method of Boyd et al, (7), for the application of the law of mass action to ion exchange equilibria.

As has already been noted, the elution experiments established that we are dealing only with the free cation and not with positively charged metal complex cations. Figure 7 gives an idea of the relative free metal-ion concentrations involved.

The exchange reaction between a metal cation  $M^{m+}$  and the hydrogen form HR of a cation exchange resin R, may be written as:



The thermodynamic equilibrium constant  $K_{MR}$  for this reaction is defined by

$$K_{MR} = \frac{a_{MR} \cdot a_{H^+}^m}{a_{M^{m+}} \cdot a_{HR}^m},$$

where  $a_{MR}$  and  $a_{HR}$  represent respectively the activities of the metal and hydrogen ions in the resin phase, and  $a_{M^{m+}}$  and  $a_{H^+}$  their activities in the aqueous phase.

According to Boyd et al, if the resin phase is regarded as an ideal solid solution, then the activities of ions in this phase, which cannot otherwise be readily evaluated, may be equated with their mole fractions,

and

$$K_{MR} = \frac{a_{H^+}^m \cdot N_{MR}}{a_{M^{m+}} \cdot N_{HR}^m} = \frac{a_{H^+}^m}{a_{M^{m+}}} \cdot \frac{n_{MR}}{n_{HR}} (n_{MR} + n_{HR})^{m-1}$$

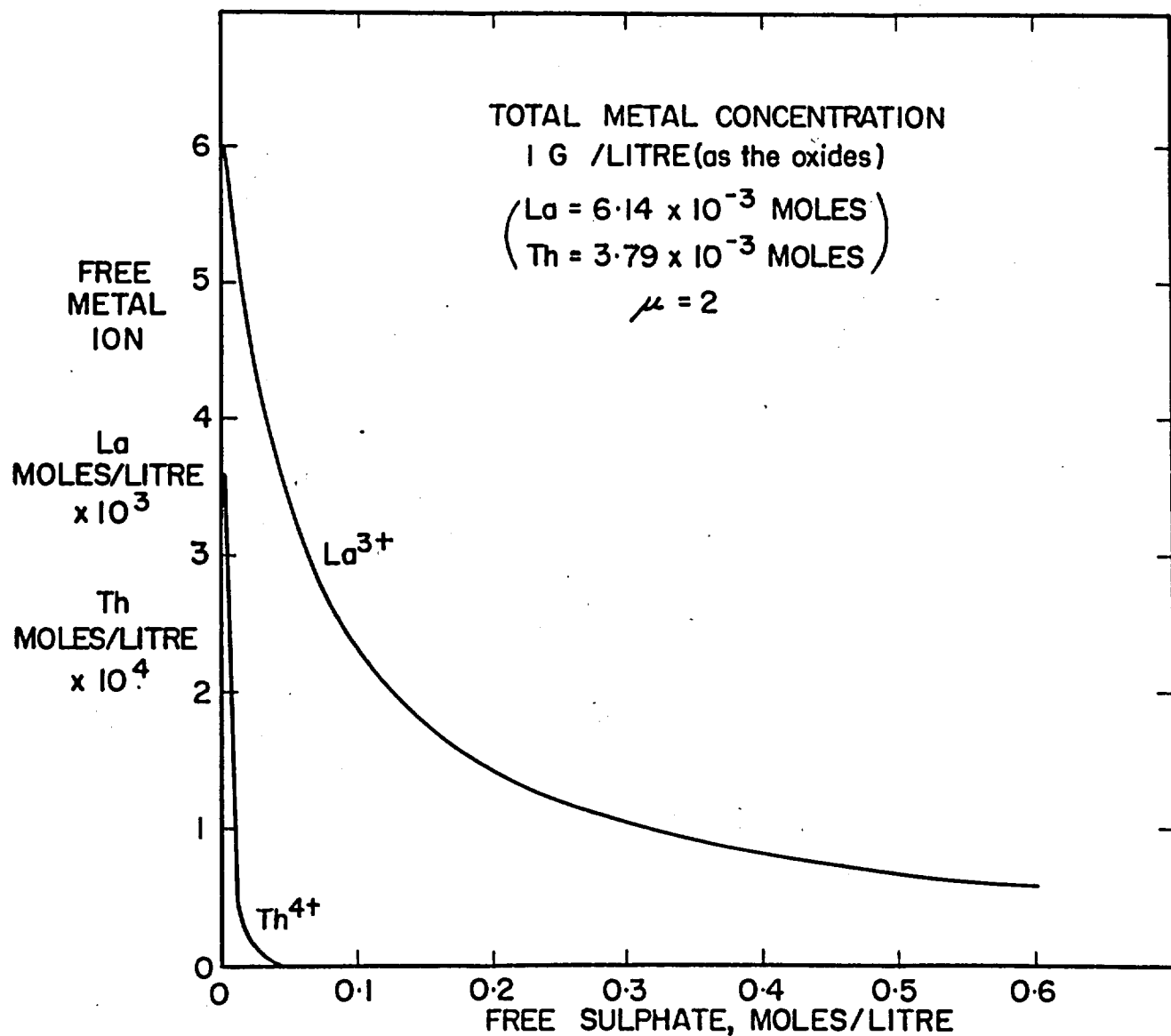


FIGURE 7

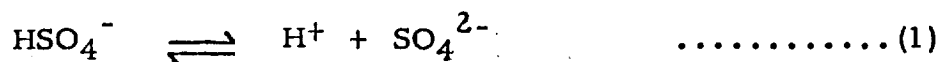
CONCENTRATION OF FREE  
METAL IONS IN SULPHATE SOLUTION

where  $N_{MR}$  and  $N_{HR}$  represent the mole fractions and  $n_{MR}$  and  $n_{HR}$  represent the number of moles of metal and hydrogen ions, respectively, in the resin phase.

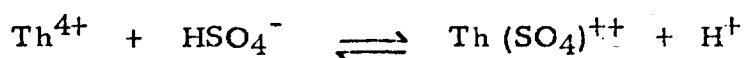
Deviations from ideal solid solution behaviour in the resin phase, and hence from equality between activity and mole fraction in that phase, would be revealed by a deviation from linearity with unit gradient in a graph of  $\log \frac{a_{Mm+}}{a_{H+}^m}$  versus  $\log \frac{N_{MR}}{N_{HR}^m}$ , for a variety of compositions of the exchanging system. Non-ideal behaviour is probable in the exchange for hydrogen ions of polyvalent ions widely different in size from hydrogen ions.

The reactions occurring in sulphuric acid have been investigated by Kerker (8) and Baes (9), those in sulphate solutions of thorium by Zebroski et al (10), and those in sulphate solutions of lanthanum by Spedding and Jaffe (11), Mattern (12) and Davies (13).

The most important of the equilibria characterized by the authors for the present purpose were:

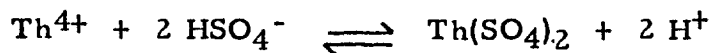


$$K_a = \frac{a_{\text{H}^+} \cdot a_{\text{SO}_4^{2-}}}{a_{\text{HSO}_4^-}} = 1.02 \times 10^{-2} \dots\dots (2)$$

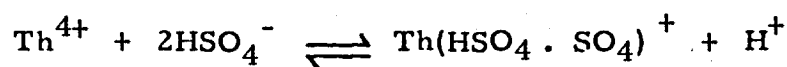


$$k^*_{\text{Th SO}_4^{++}} = \frac{C_{\text{Th SO}_4^{++}} \cdot C_{\text{H}^+}}{C_{\text{Th}^{4+}} \cdot C_{\text{HSO}_4^-}} = 1.59 \times 10^2, \mu=2 \dots (3)$$

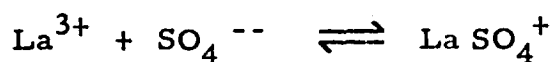




$$k^*_{\text{Th}(\text{SO}_4)_2} = \frac{C_{\text{Th}(\text{SO}_4)_2} \cdot C_{\text{H}^+}^2}{C_{\text{Th}^{4+}} \cdot C_{\text{HSO}_4^-}^2} = 2.85 \times 10^3, \mu = 2 \dots (4)$$



$$k^*_{\text{Th}(\text{HSO}_4 \cdot \text{SO}_4)^+} = \frac{C_{\text{Th}(\text{HSO}_4 \cdot \text{SO}_4)^+} \cdot C_{\text{H}^+}}{C_{\text{Th}^{4+}} \cdot C_{\text{HSO}_4^-}^2} = 8.00 \times 10^2, \mu = 2 \dots (5)$$



$$k_{\text{LaSO}_4^+} = \frac{C_{\text{LaSO}_4^+}}{C_{\text{La}^{3+}} \cdot C_{\text{SO}_4^{--}}} \dots (6)$$

$$= 4.16 \times 10^3, \mu = 0$$

$$= 25, \mu = 1$$

$$\approx 15 \text{ (estimated)}, \mu = 2,$$

where  $K$  and  $a$  represent thermodynamic equilibrium constant and ionic activity, as before, and  $k$ ,  $C$  and  $\mu$  represent respectively concentration equilibrium constant, ionic concentration, and ionic strength ( $k^*$  represents the constant for the reaction with the protonated liquid). The value for  $k_{\text{LaSO}_4^+}$  at  $\mu = 2$  has been extrapolated by comparison of the data of Davies (13) and Mattern (12) with the values for  $k_{\text{CeSO}_4^+}$  which were reported over the same range of ionic strengths by Newton and Arcand (14). By using these results and

approximating activities with concentrations, estimates may be obtained for the concentrations of  $\text{Th}^{4+}$  and  $\text{La}^{3+}$  ion in sulphate solutions of thorium and lanthanum, viz.

$$C_{\text{Th}^{4+}} \approx \frac{\tau C_{\text{Th}}}{1 + \frac{k_{\text{ThSO}_4^{2+}} \cdot C_{\text{SO}_4}}{K_a} + \frac{k_{\text{ThSO}_4} \cdot C_{\text{SO}_4}^2}{K_a^2} + \frac{k_{\text{Th}(\text{HSO}_4\text{SO}_4)^+} \cdot C_{\text{SO}_4}^2 \cdot C_{\text{H}^+}}{K_a^2}} \dots\dots\dots (7)$$

and

$$C_{\text{La}^{3+}} \approx \frac{\tau C_{\text{La}}}{1 + k_{\text{LaSO}_4^+} \cdot C_{\text{SO}_4}^{2-}} \dots\dots (8)$$

where  $\tau C_{\text{Th}}$  and  $\tau C_{\text{La}}$  represent respectively the total concentration of thorium and lanthanum in solution, and other symbols have the meanings previously assigned.

In Figure 7, the free metal concentrations have been plotted as a function of the free sulphate concentration, calculated using equations (7) and (8) and the constants for  $\mu = 2$ . In Figure 3 the La/Th ratio has been plotted on the same basis. The graphs of  $\log \frac{C_{\text{M}^{m+}}}{C_{\text{H}^+{}^m}}$  versus  $\log \frac{C_{\text{M}^{m+}}}{C_{\text{H}^+{}^m}}$  for thorium, based on constants for  $\mu = 2$ , and for lanthanum, based on the constant for  $\mu = 0$  (Figure 10), are highly linear, but have gradients less than unity (0.53 and 0.63 respectively). This deviation derives from non-ideal behaviour in both resin and solution phases. Thus, in the case of the aqueous medium, no account has been taken of the effect of the change in the ionic strength as the sulphuric acid con-

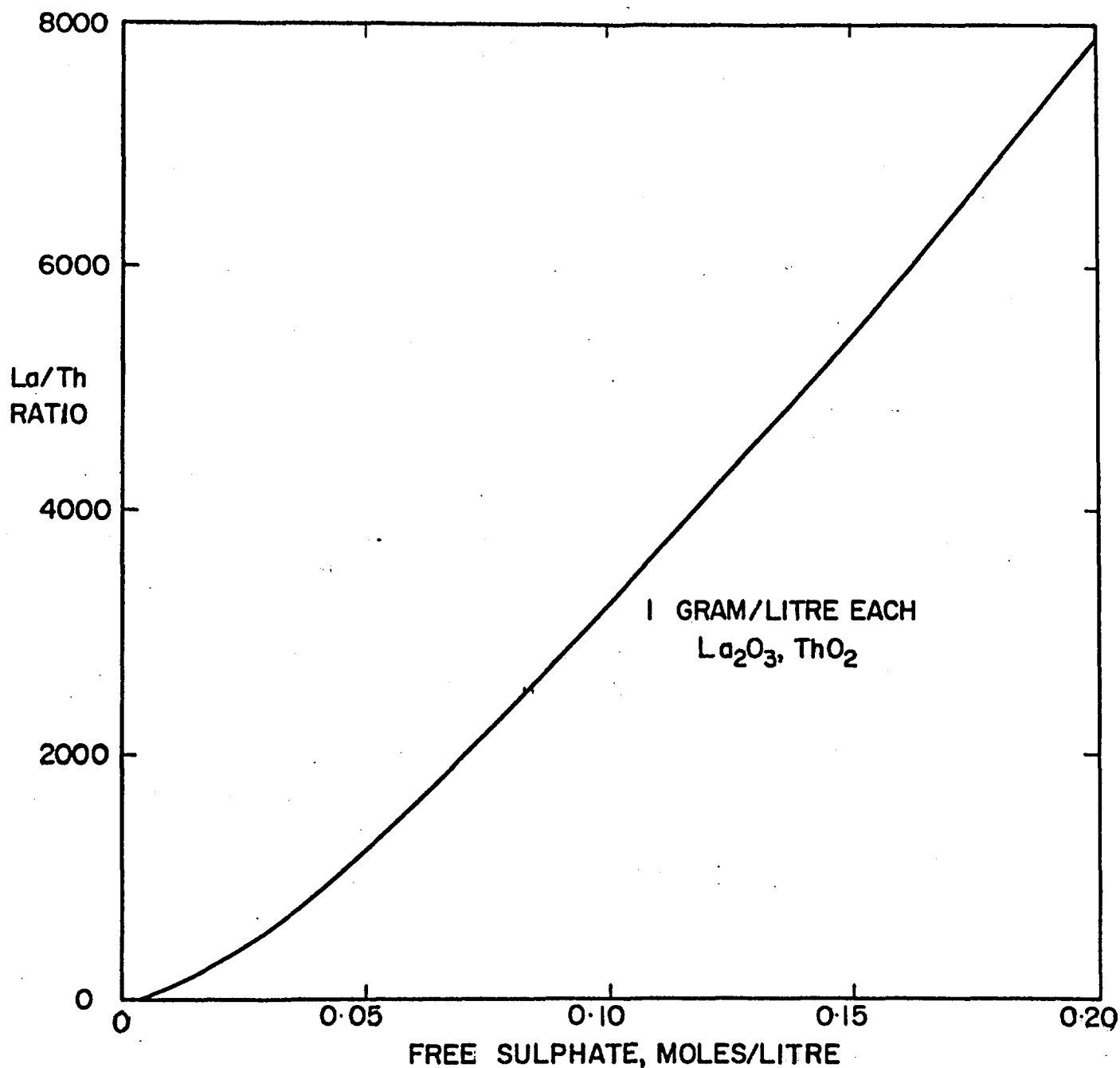


FIGURE 8  
EFFECT OF FREE SULPHATE  
CONCENTRATION ON La/Th RATIO

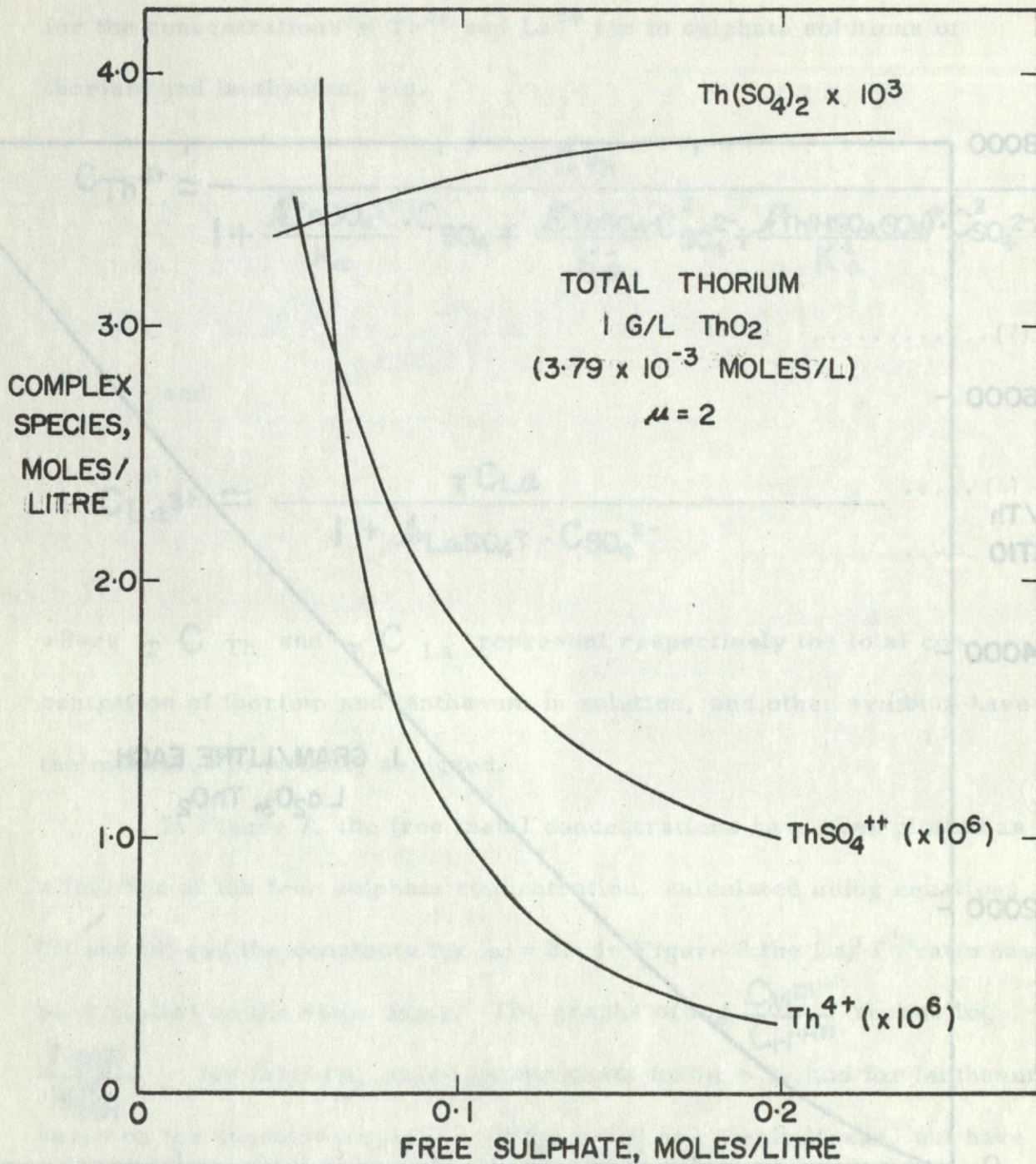


FIGURE 9  
COMPLEX THORIUM  
SPECIES IN SULPHATE SOLUTION

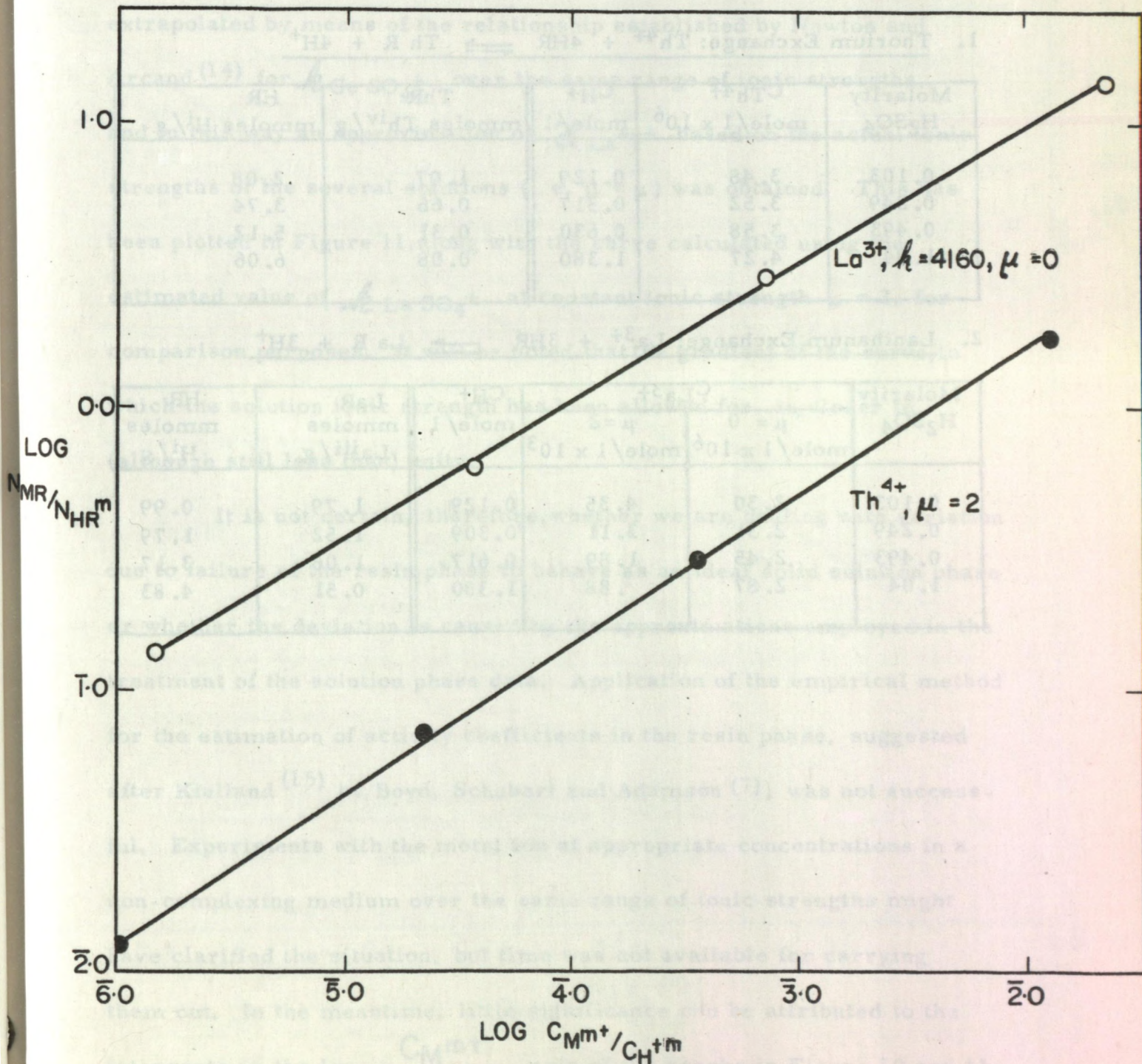


FIGURE 10  
GRAPH OF DATA OF  
TABLE 2 ACCORDING TO EQUATION (1)

TABLE 6

Exchange Sorption of Thorium and Lanthanum fromSulphate Solutions onto Amberlite IR 120Metal Concentrations in Solution and Resin Phase for Mass Law Plots1. Thorium Exchange:  $\text{Th}^{4+} + 4\text{HR} \rightleftharpoons \text{Th R} + 4\text{H}^+$ 

Molarity $\text{H}_2\text{SO}_4$	$C_{\text{Th}^{4+}}$ mole/l $\times 10^6$	$C_{\text{H}^+}$ mole/l	ThR mmoles $\text{Th}^{\text{iv}}/\text{g}$	HR mmoles $\text{H}^{\text{i}}/\text{g}$
0.103	3.48	0.129	1.07	2.08
0.249	3.52	0.317	0.66	3.74
0.493	3.58	0.630	0.31	5.12
1.04	4.27	1.380	0.08	6.06

2. Lanthanum Exchange:  $\text{La}^{3+} + 3\text{HR} \rightleftharpoons \text{La R} + 3\text{H}^+$ 

Molarity $\text{H}_2\text{SO}_4$	$C_{\text{La}^{3+}}$		$C_{\text{H}^+}$ mole/l	LaR mmoles $\text{La}^{\text{iii}}/\text{g}$	HR mmoles $\text{H}^{\text{i}}/\text{g}$
	$\mu = 0$ mole/l $\times 10^6$	$\mu = 2$ mole/l $\times 10^3$			
0.103	2.30	4.35	0.129	1.79	0.99
0.249	2.31	3.71	0.309	1.52	1.79
0.493	2.45	1.89	0.617	1.06	3.17
1.04	2.87	.88	1.380	0.51	4.83

centration is increased. To illustrate the magnitude of this effect, the activities of lanthanum in the solutions have been calculated approximately from the data of Table 2. The values of  $k_{\text{La SO}_4^+}$  at  $\mu = 0$  and  $\mu = 1$  given by Davies (13) and Mattern (12) were interpolated, and extrapolated by means of the relationship established by Newton and Arcand (14) for  $k_{\text{Ce SO}_4^+}$  over the same range of ionic strengths, and in this way an approximation of  $a_{\text{La}^{+++}}$  based on the actual ionic strengths of the several solutions (i. e.  $\mu = \mu$ ) was obtained. This has been plotted in Figure 11, along with the curve calculated using the estimated value of  $k_{\text{La SO}_4^+}$  at constant ionic strength  $\mu = 2$ , for comparison purposes. It will be noted that the gradient of the curve, in which the solution ionic strength has been allowed for, is closer to (although still less than) unity.

It is not certain, therefore, whether we are dealing with variation due to failure of the resin phase to behave as an ideal solid solution phase or whether the deviation is caused by the approximations employed in the treatment of the solution phase data. Application of the empirical method for the estimation of activity coefficients in the resin phase, suggested after Kielland (15) by Boyd, Schubert and Adamson (7), was not successful. Experiments with the metal ion at appropriate concentrations in a non-complexing medium over the same range of ionic strengths might have clarified the situation, but time was not available for carrying them out. In the meantime, little significance can be attributed to the intercepts on the log  $\frac{C_{\text{M}^{m+}}}{C_{\text{H}^+}}$  axis of the graphs in Figure 10 and 11,

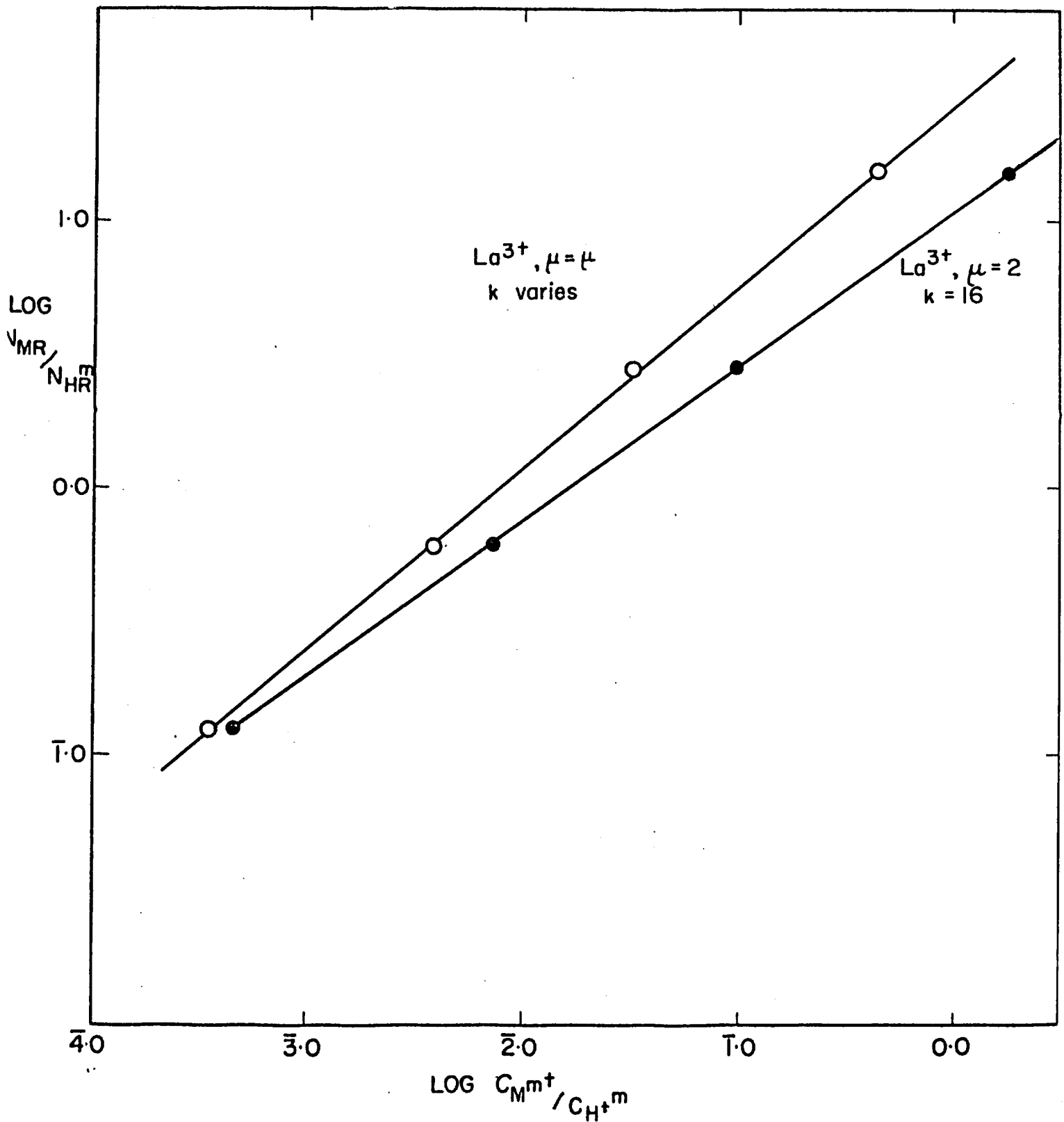


FIGURE 11

GRAPH OF DATA OF TABLE 2  
 ACCORDING TO EQUATION (1) USING REVISED CONSTANTS



which are related to  $-\log K_{MR}$ , since the use of concentration equilibrium constants displaces the graph along this axis. However, use of the extrapolated data for  $k_{LaSO_4}$  gives more realistic relative values to the the two intercepts.

Although it cannot be rigorously demonstrated that the complexing and exchange reactions occurring in the systems treated in this report are as formulated in equations 1 to 6, limited success obtained by the above treatment suggests that this is indeed the case. By an extension of the same reasoning one can obtain an expression for the separation factor in terms of solution concentrations and the various constants for the reactions involved. Thus, the thermodynamic equilibrium constants for the exchange reactions of  $Th^{4+}$  ion and  $La^{3+}$  ion with the hydrogen form of a resin, as formulated above, are respectively:

$$K_{ThR} = \frac{a_{ThR} \cdot a_{H^+}^4}{a_{Th^{4+}} \cdot a_{HR}^4} \quad \text{and} \quad K_{LaR} = \frac{a_{LaR} \cdot a_{H^+}^3}{a_{La^{3+}} \cdot a_{HR}^3}$$

Assuming that the affinity of one of these ions for the resin is unaffected by the presence of the other, then for exchange sorption from a common solution

$$\frac{a_{LaR}}{a_{ThR}} = \frac{K_{LaR}}{K_{ThR}} \cdot \frac{a_{La^{3+}}}{a_{Th^{4+}}} \cdot \frac{a_{H^+}}{a_{HR}}$$

If a counter-ion  $B^{b+}$  is employed in place of hydrogen, the more general expression is obtained

$$\frac{a_{LaR}}{a_{ThR}} = \frac{K_{LaR}^{1/b}}{K_{ThR}^{1/b}} \cdot \frac{a_{B^{b+}}^{1/b}}{a_{BR}^{1/b}} \cdot \frac{a_{La^{3+}}}{a_{Th^{4+}}} \dots\dots\dots (9)$$

By again equating activities in the aqueous phase with the corresponding concentrations terms from equations (6) and (7), and equating activity in the resin phase with mole fraction, equation (9)

$$\text{may be reduced to the form } \frac{N_{LaR} K_{LaR}^{1/2} C_B^{bt}}{N_{ThR} K_{ThR}^{1/2} N_{BR}^{1/2}} \cdot \frac{_{T}C_{La}}{(1+k_{LaSO_4} \cdot C_{SO_4})} \cdot \frac{(1+k_{ThSO_4}^{2+} \cdot C_{SO_4} + k_{Th(SO_4)_2} \cdot (C_{SO_4})^2 + k_{Th(SO_4} \cdot HSO_4)^+ (C_{SO_4})^2 C_{H^+})}{_{T}C_{Th}} \dots\dots (10)$$

It can be readily demonstrated (Fig. 9) that over the range 0 to 0.50M in sulphate and 0 to 0.30M in  $H_2SO_4$ , most of the thorium can be accounted for by the complex  $Th(SO_4)_2$  and, therefore, for practical purpose the free thorium content is given by

$$\frac{_{T}C_{Th}}{k_{Th(SO_4)_2} \cdot (C_{SO_4})^2}$$

Equation (10) thus simplifies to

$$\frac{N_{LaR}/_{T}C_{La}}{N_{ThR}/_{T}C_{Th}} = \frac{K_{LaR}^{1/2} (C_B^{bt})^{1/2} k_{Th(SO_4)_2} \cdot (C_{SO_4})^2}{K_{ThR}^{1/2} N_{BR}^{1/2} (1+k_{LaSO_4} \cdot C_{SO_4})} \dots\dots (11)$$

Moreover, for all except hydrogen-ion, the counter-ion concentration is given by  $2/b (C_{SO_4})$ , and we have

$$\frac{N_{LaR}/_{T}C_{La}}{N_{ThR}/_{T}C_{Th}} = \frac{K_{LaR}^{1/2} k_{Th(SO_4)_2} \cdot (2/b C_{SO_4})^{1/2} \cdot (C_{SO_4})^2}{K_{ThR}^{1/2} N_{BR}^{1/2} (1+k_{LaSO_4} \cdot C_{SO_4})} \dots\dots (12)$$

Since, as we have seen, the actual constants involved in this expression are unknown, and since the magnitude of the error introduced by approximating activities with concentration is also unknown, equation (11) cannot be employed quantitatively. Moreover, as has been seen,

this equation does not account even qualitatively for the behaviour of the system as the counter-ion sulphate concentration is increased beyond a value for the counter-ion concentration which gives a value for  $C_{Bb+}^{1/b}$  over 0.15 moles. It is therefore presented here solely to demonstrate where reasoning based on the law of mass action leads, and as a point of departure for further experimental work and theoretical treatment.

#### REFERENCES

1. Herbst, H.J., and Shaheen, L.E., Radioactivity Division Internal Report IR 233/57, Mines Branch, Dept. of Mines and Technical Surveys, Ottawa (1957)
2. Carron, M.K., Skinner, D.L., and Stevens, R.E., *Anal. Chem.* 27, 1058 (1955)
3. Ingles, J.C. ed., "A Manual of Analytical Methods for the Uranium Concentrating Plant", Mines Branch Monograph No. 1, The Queen's Printer, Ottawa. (In Press)
4. Rinehart, R.W., *Anal. Chem.* 26, 1820 (1954)
5. Bonner, O.D., and Smith, L.L., *J. Phys. Chem.* 61, 326 (1957)
6. Bjerrum, J., Schwarzenbach, G., and Sillen, L.G., "Stability Constants of Metal-Ion Complexes" (Part II: Inorganic Liquids, pp.78-86), The Chemical Society, London (1958)
7. Boyd, G.E., Schubert, J., and Adamson, A.W., *J. Am. Chem. Soc.*, 69, 2818 (1947)
8. Kerker, M., *J. Am. Chem. Soc.* 79, 3664 (1957)
9. Baes, C.F., Jr., *J. Am. Chem. Soc.* 79, 5611 (1957)
10. Zebroski, E.L., Alter, H.W., and Neuman, F.K., *J. Am. Chem. Soc.*, 73, 5643 (1951)
11. Spedding, F.H., and Jaffe, S., *J. Am. Chem. Soc.*, 76, 882 (1954)
12. Mattern, K.L., University of California, Report UCRL 1407 (1951)

13. Davies, C. W., J. Chem. Soc., 1930, 2421
14. Newton, T. W., and Arcand, G. M.,  
J. Am. Chem. Soc. 75, 2449 (1953)
15. Kielland, J., J. Soc. Chem. Ind., 54, 232 T (1935)
16. Nietzel, O. A., Wessling, B. W., and DeSesa, M. A., Anal.  
Chem. 30, 1182. (1958)

= = =

DCL/JCI/ew

QUEEN'S PRINTER AND CONTROLLER OF STATIONERY  
OTTAWA, 1968