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Data of Inorganic Solvent Extraction (2)

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Data of Inorganic Solvent Extraction (2)

SUMMARY

Solvent extraction behavior of more than sixty chemical elements was studied in the following solvent extraction systems:

(1) 5% TIOA xylene - H_2SO_4,
(2) 0.1% TIOA xylene - H_2SO_4,
(3) 10% Amberlite LA-1 xylene - H_2SO_4,
(4) 0.1% Amberlite LA-1 xylene - H_2SO_4,
(5) 10% Primene JM-T xylene - H_2SO_4,
(6) 0.1% Primene JM-T xylene - H_2SO_4,
(7) TIOA xylene - 0.1N H_2SO_4,
(8) Amberlite LA-1 xylene - 0.1N H_2SO_4,
(9) Primene JM-T xylene - 0.1N H_2SO_4,

The results obtained are arranged according to the sequence of the periodic system.

The alkali and alkaline earth metal ions are not extractable. The tervalent ions are generally extractable into Primene JM-T, but not into Amberlite LA-1 and tri-iso-octylamine. In most cases, the actinide elements are highly extracted with the high molecular alkylamines used.

The extractability of amines studied increases in the order tertiary < secondary < primary in a sulfuric acid system.

Feb. 1964

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無機溶媒抽出データ集(2)

要　　旨

無機溶媒抽出データ集(1)につづいて，次にあげるような9種の溶媒抽出系における，約60種の化学元素の抽出行動をしらべた。

(1)　5％トリイソオクチルアミン　$-H_2SO_4$

(2)　0.1％トリイソオクチルアミン　$-H_2SO_4$

(3)　10％アンバーライトLA−1　$-H_2SO_4$

(4)　0.1％アンバーライトLA−1　$-H_2SO_4$

(5)　10％プライメンJM−T　$-H_2SO_4$

(6)　0.1％プライメンJM−T　$-H_2SO_4$

(7)　トリイソオクチルアミン　$-0.1N\ H_2SO_4$

(8)　アンバーライトLA−1　$-0.1N\ H_2SO_4$

(9)　プライメンJM−T　$-0.1N\ H_2SO_4$

(1)〜(6)の抽出系については，いわゆる acid dependence (7)〜(9)については solvent dependence をしらべた。希釈剤はすべてキシレンを用いた。

結果は，周期律表の形の図にまとめた。アルカリ，アルカリ土類金属イオンは抽出されない。3価陽イオンは，プライメンJM−T によく抽出されるが，アンバーライトLA−1，およびトリイソオクチルアミンには，あまり抽出されない。アクチニド元素は，一般によく抽出される。ここでしらべた3種の高分子アミン抽出は，1級，2級，3級の順ですなわちプライメンJM−T，アンバーライトLA−1，トリイソオクチルアミンの順に抽出率が低くなる傾向がある。

1964年2月

東海研究所化学部放射化学研究室

石森富太郎，吾勝永子，鄭　文彬，

卓地邦子，小坂部富子

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1. INTRODUCTION

Since the acid-binding property of high-molecular-weight amines was reported in 1948[1], the long chain alkylamines have been widely studied and reported in numerous papers[2]. The extraction of uranium in particular has been minutely studied using a number of alkyl and aromatic amines diluted with various diluents. Most of these published studies were carried out holding in view such practical purposes as processing of uranium ore sulfate liquors or the decladding fuel solutions, and while the published reports usually give the extraction isotherm, data on acid and solvent dependence are rarely reported. To fill this gap, this work covers the inorganic solvent extraction behavior of about sixty chemical elements, systematically investigated with the aid of radioactive tracer techniques in order to obtain a series of acid and solvent dependence curves.

As organic extractant, Primene JM-T, Amberlite LA-1 and tri-iso-octylamine were selected from the primary, secondary and tertiary amines in this study. The same alkylamines have already been studied in nitric and hydrochloric acid systems by the same authors[3].

The data obtained are assembled together in periodic table arrangement (Figs. 1-6).

2. EXPERIMENTAL

2.1 Radioisotopes Used

The radioactive tracers used are listed in Table 1 together with target materials and methods of preparation[4)-8)]. Some radioisotopes were imported from ORNL (USA) and the Radiochemical Centre, Amersham (UK), and others were prepared by irradiating high purity target material in the Institute's reactors JRR-1 (neutron flux 10^{11} n/sec/cm^2), JRR-2 (neutron flux 10^{12} n/sec/cm^2) or linear electron acceralator, followed by chemical separation or purification where necessary.

Most of the tracers were used after converting to sulfate, though in some cases, as indicated in Fig. 1, chloride and chlorocomplex were added into the sulfuric acid media of the extraction system. For instance, with iron and calcium, their specific activities were very low, as also the solubility of their sulfates, and chloride solutions were therefore used without converting to sulfate. Osmium and iridium tracers supplied in the form of sodium hexachloroosmate and ammonium hexachloro iridate respectively, were also used as received.

Usually, the tracers studied were in their most stable states of oxidation. In some cases, definite oxidation states were attained by the use of the oxidizing or reducing reagents, as given in Table 2.

2.2 Reagents

The high molecular weight alkylamines used are Primene JM-T of primary amine, Amberlite LA-1 of secondary amine and tri-iso-octylamine

of tertiary amine. The sources of the amines are shown in Table 3 together with details of the extraction systems studied.

The xylene and sulfuric acid used were of analytical grade.

2.3 Determination of Distribution Ratios

The method of determining the distribution ratio Kd was the same as that described in previous papers[9),10)]. The organic and aqueous solutions of equal volume were shaken together for about one minute in contactor. After separation of both phases with centrifuge, an aliquot of each phase was subjected to measurement of radioactivity. Beta and alpha activities were measured with gas-flow counter by mounting the aliquot of samples on a stainless steel or platinum plate. The plates carrying sulfur-35 and technetium-99 were not ignited, since these elements are volatilized by ignition. The counting rates of tin-113 and lead-212 were measured after radioactive equilibrium was attained. Gamma assay was carried out in 1 ml glass bottle with a conventional scintillation counter equipped with 1½"ϕ NaI cristal.

In determining the acid dependence, the organic phase was pre-equilibrated with the corresponding aqueous phase of 0.01, 0.02, 0.05, 0.1, 0.2, 0.5, 1.0, 2.0, 5.0 and 10.0N sulfuric acid. The solvent dependence curves were obtained with sulfuric acid, maintained at constant normality (0.1N), changing the amine concentration in xylene solution in steps of 0.01, 0.02, 0.05, 0.1, 0.2, 0.5, 1.0, 2.0, 5.0 and 10.0% (v/o), which was pre-equilibrated with 0.1N sulfuric acid.

3. RESULTS AND DISCUSSION

Results obtained are summarized in Figs. 1-6 as a series of graphs of log Kd vs. N H_2SO_4 or %(v/o) alkylamine, where Kd is the distribution ratio determined and N the normality of acid.

3.1 Acid Dependence

Figs. 1-3 show the acid dependence curves of chemical elements in 5% and 0.1%(v/o) TIOA xylene-sulfuric acid systems, 10% and 0.1%(v/o) Amberlite LA-1 - sulfuric acid systems, and 10% and 0.1%(v/o) Primene JM-T - sulfuric acid systems, respectively. The curves drawn in dotted lines are not very accurate because of insufficient radioactivity or distribution ratio obtained. The Kd values determined by using tracers in chlorocomplex or chloride solution are also indicated in dotted lines.

It is seen from Figs. 1-3 that univalent species of the alkali metals and bivalent species of the alkaline earths as well as of copper, nickel, cobalt and cadmium ions are generally non-extractable in the whole range of acidity studied. The Kd values for the tervalent species of scandium and yttrium (both Group IIIB), aluminum, gallium and indium (Group IIIA), as well as lanthanum and the lanthanide elements, are very low in TIOA-sulfuric acid system, but very high in Primene JM-T - sulfuric acid system, and intermediate in the system of Amberlite LA-1. Therefore, the extractability for tervalent ions increases in the order

of tertiary, secondary and primary amine.

Anionic species such as molybdate, technetate, tantalate, and tungstate are more or less extractable into the organic phase.

The actinide elements show usually high extractability. Americium and quinquivalent neptunium in TIOA and Amberlite LA-1 systems are not extractable. On the other hand, uranium and thorium are found to show a strong affinity to Primene JM-T of the primary amine.

Generally speaking, measured Kd values of an element are independent of the sulfuric acid concentration except in the case of tervalent ions and some of the actinide elements. In these cases of varying Kd values, the distribution ratio usually increases with increasing acidity from 0.01N to 0.1N sulfuric acid, and then decreases rapidly with further increase in acidity from 0.1N to 10N. This situation suggests that extraction might be carried out at 0.1N and scrubbing performed with sulfuric acid of higher acidity. From this standpoint, alkylamine is not practical, since the resulting solution has a fairly high sulfuric acid concentration.

The extractability of the alkylamines studied increases in the order primary > secondary > tertiary, as revealed from Figs. 1-6. This general tendency of extractability is in reverse order to that observed in the system of the same alkylamines with hydrochloric acid[11].

3.2 Solvent Dependence

Figs. 4-6 represent the solvent dependence curves of the elements in the systems of 0.1N H_2SO_4-TIOA xylene, 0.1N H_2SO_4-Amberlite LA-1 xylene and 0.1N H_2SO_4-Primene JM-T xylene.

3.3 The exact Kd values

Figs. 7-15 show the exact Kd values measured for each element in nine extraction systems studied. The figures given in this form have the advantage of indicating directly the difference of Kd values between two elements.

4. APPLICATION

4.1 Preparation of Carrier-free ^{113m}In Tracer

Indium-113m, having a half-life of 105 minutes, is produced through the decay of tin-113.

$$^{113}Sn \xrightarrow[112d]{EC} {}^{113m}In \xrightarrow[105m]{IT} {}^{113}In \text{ (stable)}$$

Therefore, indium separated from its mother nuclide, tin-113, is carrier-free indium-113m tracer. The results with Primene JM-T-H_2SO_4 system were tried on the separation of tin and indium, as presented in Fig. 16. The indium solution prepared was examined by means of decay measurement (Fig. 17) and gamma ray spectrometry (Fig. 18).

4.2 Preparation of Carrier-free ^{234}Th Tracer

Thorium-234 is well-known as UXI of the daughter nuclide of uranium-238.

$$^{238}U \xrightarrow[10^9\ y]{alpha} {}^{234}Th \xrightarrow[24.1d]{beta} {}^{234m}Pa \xrightarrow[1.18m]{beta}$$

Thorium-234 solution was prepared using the tri-iso-octylamine - H_2SO_4 system shown in Fig. 19. Radiochemical purity was verified by means of beta ray absorption with aluminum foil, and decay measurement. The results are shown in Figs. 20 and 21.

4.3 Preparation of Carrier-free ^{140}La Tracer

In the fission products of irradiated uranium, the amount of ^{140}Ba-La reached a maximum around 20 days after irradiation, when other fission products are ^{143}Pr, ^{141}Ce, ^{133}Xe, ^{131}I, ^{147}Nd, ^{95}Zr-Nb, ^{91}Y, ^{89}Sr, ^{103}Ru-Rh, ^{99}Mo, ^{132}Te-I. Using 10% Primene JM-T xylene solution, most of these elements can be extracted from 0.1N sulfuric acid solution together with uranium and neptunium, leaving barium and strontium in the aqueous phase. Lanthanum-140 can be separated from the obtained aqueous phase after barium-140 decays into lanthanum-140. Thus, the separation process was planned as shown in Fig. 22. The results of decay measurement and gamma ray spectrometry of lanthanum-140 thus prepared are shown in Figs. 23 and 24.

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Table 1 Radioisotopes used

Nuclide	Target	irradiated in	Remarks
^{24}Na	Na_2CO_3	JRR-1[a]	
^{27}Mg	Mg metal	JRR-1	
^{28}Al	Al metal	JRR-1	
^{32}P			JAERI, RI[b]
^{35}S			JAERI, RI
^{38}Cl	NH_4Cl	JRR-1	
^{42}K	KNO_3	JRR-1	
^{45}Ca			imported; used as chloride
^{46}Sc	Sc_2O_3	JRR-2[c]	
^{52}V	NH_4VO_3	JRR-1	
^{51}Cr			JAERI, RI or imported; Na_2CrO_4
^{56}Mn	MnO_2	JRR-1	
$^{55,59}Fe$			imported; $FeCl_3$ soln.
^{60}Co			imported
^{65}Ni	Ni sponge	JRR-1	separated from Co by amine[4]
^{64}Cu	Cu metal	JRR-1	
^{65}Zn			imported
^{72}Ga	Ga_2O_3	JRR-1	
^{76}As	As_2O_3	JRR-1	
^{75}Se			imported; used as chloride
$^{80,80m}Br$	NH_4Br	JRR-1	
^{86}Rb			imported
^{85}Sr			imported
^{88}Y	Y_2O_3	LINAC[d]	
^{95}Zr			imported; used after eliminating ^{95}Nb
^{95}Nb			milked from ^{95}Zr-^{95}Nb by anion exchange
^{99}Mo	ammonium molybdate	JRR-1	
^{99}Tc			imported
^{106}Ru			imported
^{110m}Ag	$AgNO_3$	JRR-1	

(a) neutron flux 10^{11} n/sec/cm^2
(b) Interim Facilities of Radioisotope Production
(c) neutron flux 10^{12} n/sec/cm^2
(d) Linear Electron Accelarator

Table 1 Radioisotopes used

(continued)

Nuclide	Target	irradiated in	Remarks
^{115m}Cd			imported
^{114m}In			imported
^{113}Sn			imported
^{124}Sb			imported
^{131}I			JAERI, RI
^{137}Cs			imported
^{139}Ba	Ba hydroxide	JRR-1	
^{140}La	La_2O_3	JRR-1	
^{144}Ce			imported
^{147}Pm			imported
$^{152,154}Eu$			imported
^{160}Tb	Tb_4O_7	JRR-2	
^{177}Lu	Lu_2O_3	JRR-1	
$^{175,181}Hf$			imported
^{182}Ta			imported; potassium tantalate
^{185}W			imported; Na_2WO_4 soln.
$^{186,188}Re$	Re sponge	JRR-1	
$^{191,193}Os$			imported; sodium hexachloroosmate soln.
^{192}Ir			imported; ammonium hexachloroiridate
$^{193,197}Pt$	Pt sponge	JRR-1	separated from Au by TBP extn.
^{198}Au	Au metal	JRR-1	used as chlorocomplex.
^{203}Hg			imported
^{204}Tl			imported
^{212}Pb			radioactive deposit of thorium
^{210}Bi			milked from RaDEF by TBP extn.
^{231}Th	ThO_2	LINAC	purified by TBP extn.[5]
^{233}Pa	$Th(NO_3)_4$	JRR-1	separated by TBP extn.[6]
^{237}U	UO_2	LINAC	purified by TBP extn.[7]
^{239}Np	$UO_2(NO_3)_2$	JRR-1	separated by TBP extn.[8]
^{241}Am			imported

Table 2 Oxidation states and chemical treatments

element	oxidation state	oxidizing and reducing agent; chemical treatment
As	3+	ascorbic acid; aqueous phase was scrubbed twice.
As	5+	$K_2Cr_2O_7$, organic phase was scrubbed once.
Sn	2+	ascorbic acid;
Sn	4+	$KClO_4$; warmed; organic phase was scrubbed three times.
Ce	3+	hydroxylamine hydrochloride.
Ce	4+	ceric ammonium nitrate.
Hg	2+	warmed with conc. HNO_3.
Np	4+	ferrous sulfamate; organic phase was scrubbed 4 times.
Np	5+	warmed in 1N $HClO_4$. Np^{4+} and Np^{6+} were removed by TBP extraction.
Se	4+	warmed in 2N HCl.

Table 3 The inorganic solvent extraction systems studied

Amines	received from	org. and aq. phase		
Primene JM-T	Rhom & Haas	Acid dependence	10.0% xylene.	0.01N ~ 10.0N H_2SO_4
			0.1% xylene.	0.01N ~ 10.0N H_2SO_4
		Solvent dependence	0.1N H_2SO_4.	0.01% ~ 10.0% amine xylene soln.
Amberlite LA-1	Rhom & Haas	Acid dependence	10.0% xylene	0.01N ~ 10.0N H_2SO_4
			0.1% xylene	0.01N ~ 10.0N H_2SO_4
		Solvent dependence	0.1N H_2SO_4	0.01% ~ 10.0% amine xylene soln.
tri-iso-octylamine	Union Carbide and Chemicals	Acid dependence	5.0% xylene	0.01N ~ 10.0N H_2SO_4
			0.1% xylene	0.01N ~ 10.0N H_2SO_4
		Solvent dependence	0.1N H_2SO_4	0.01% ~ 10.0% amine xylene soln.

Fig. 1 0.1%* 5 % TIOA xylene - H_2SO_4 acid dependence

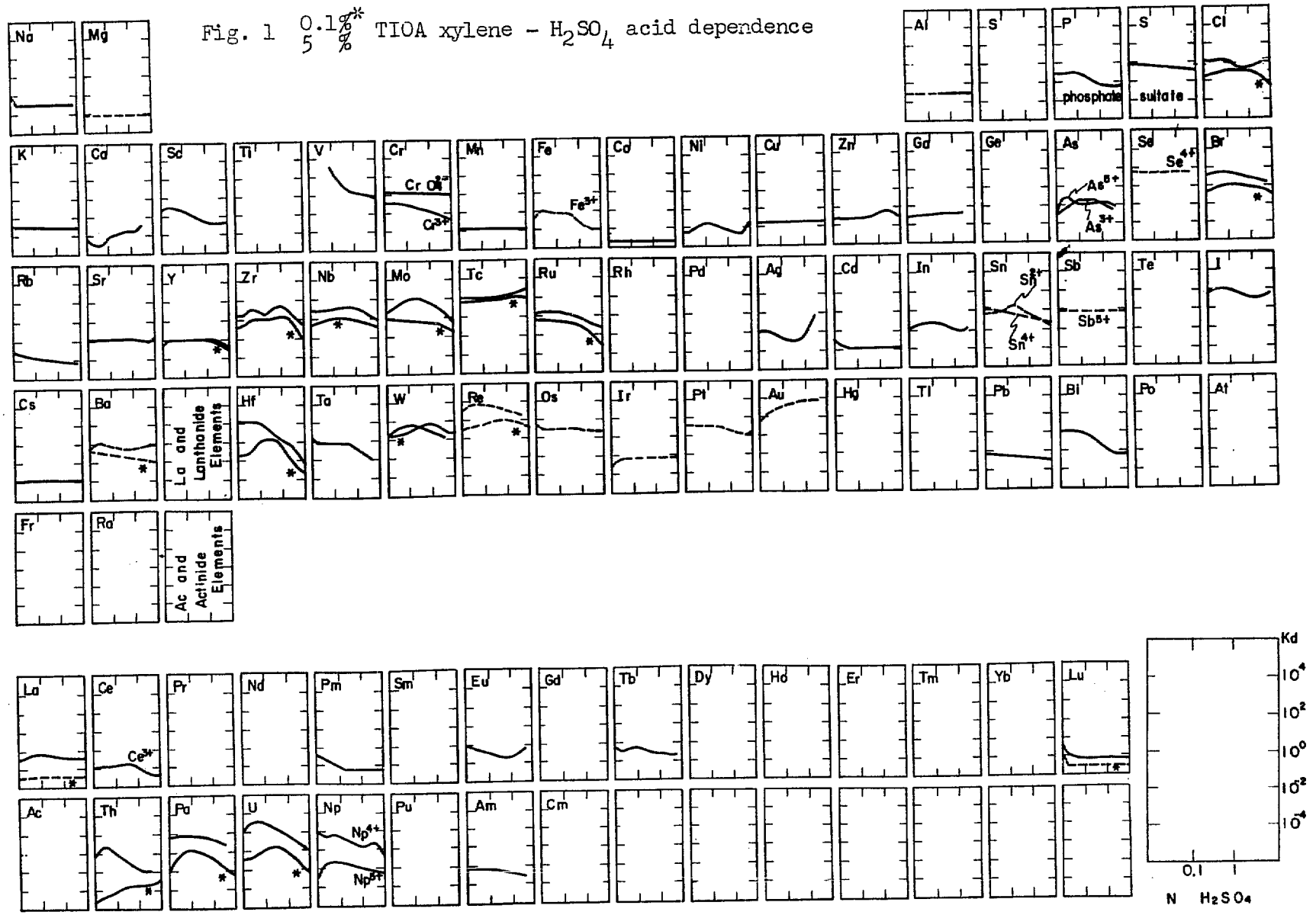


Fig. 2 0.1%* 10 % Amberlite LA-1 xylene - H_2SO_4 acid dependence

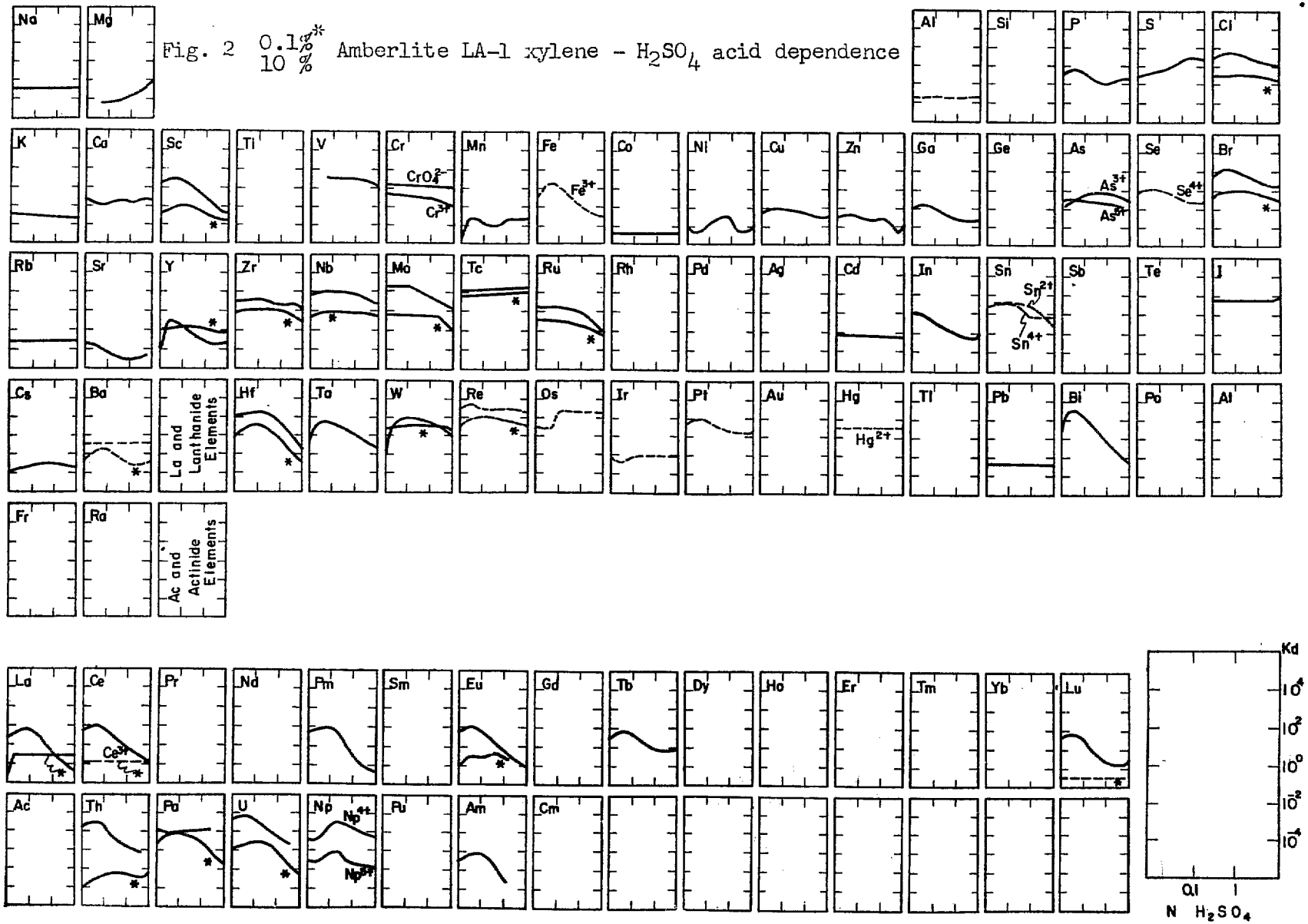


Fig. 3 0.1%* 10 % Primene JM-T xylene - H_2SO_4 acid dependence

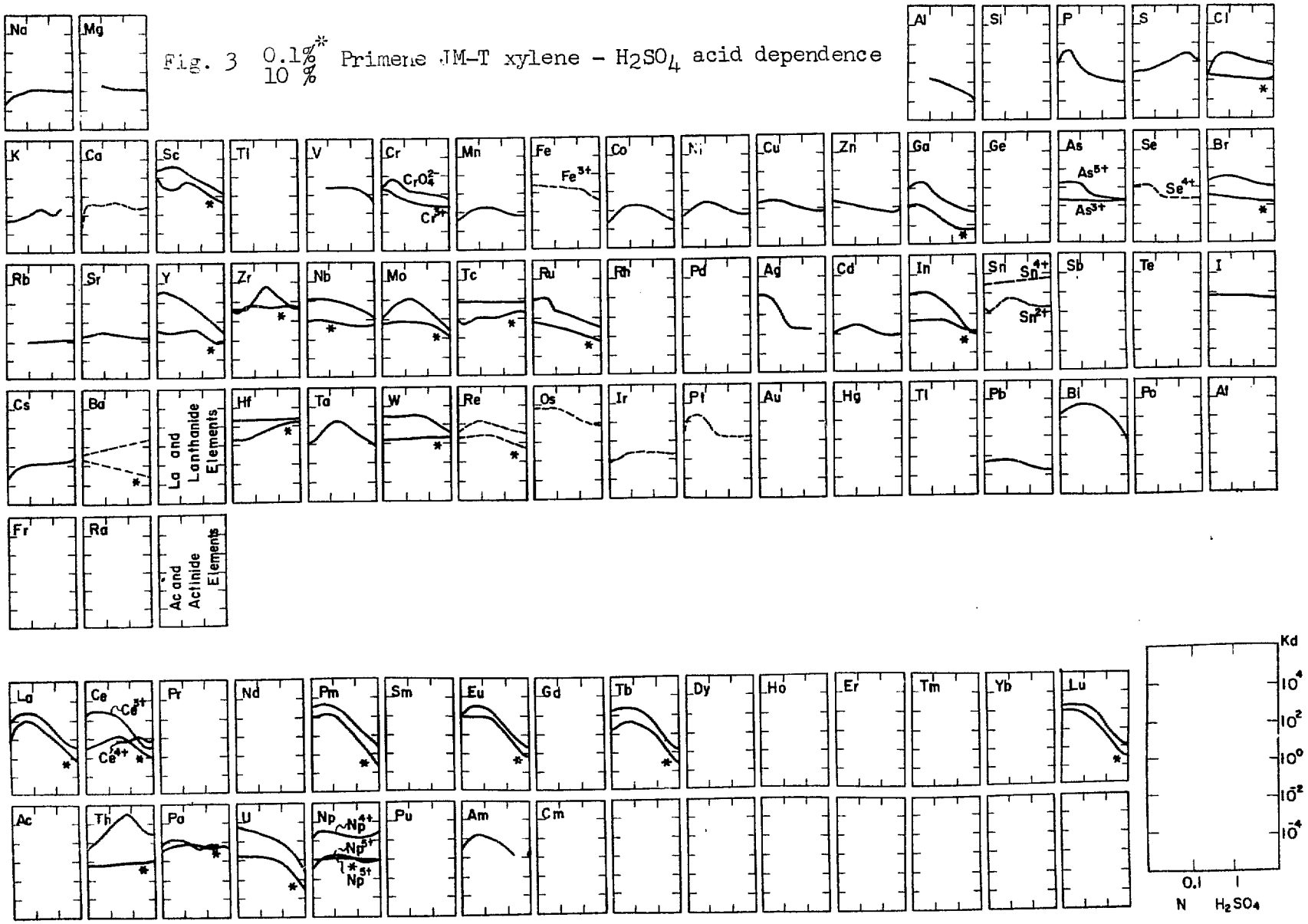


Fig. 4 TIOA xylene - 0.1N H_2SO_4 solvent dependence

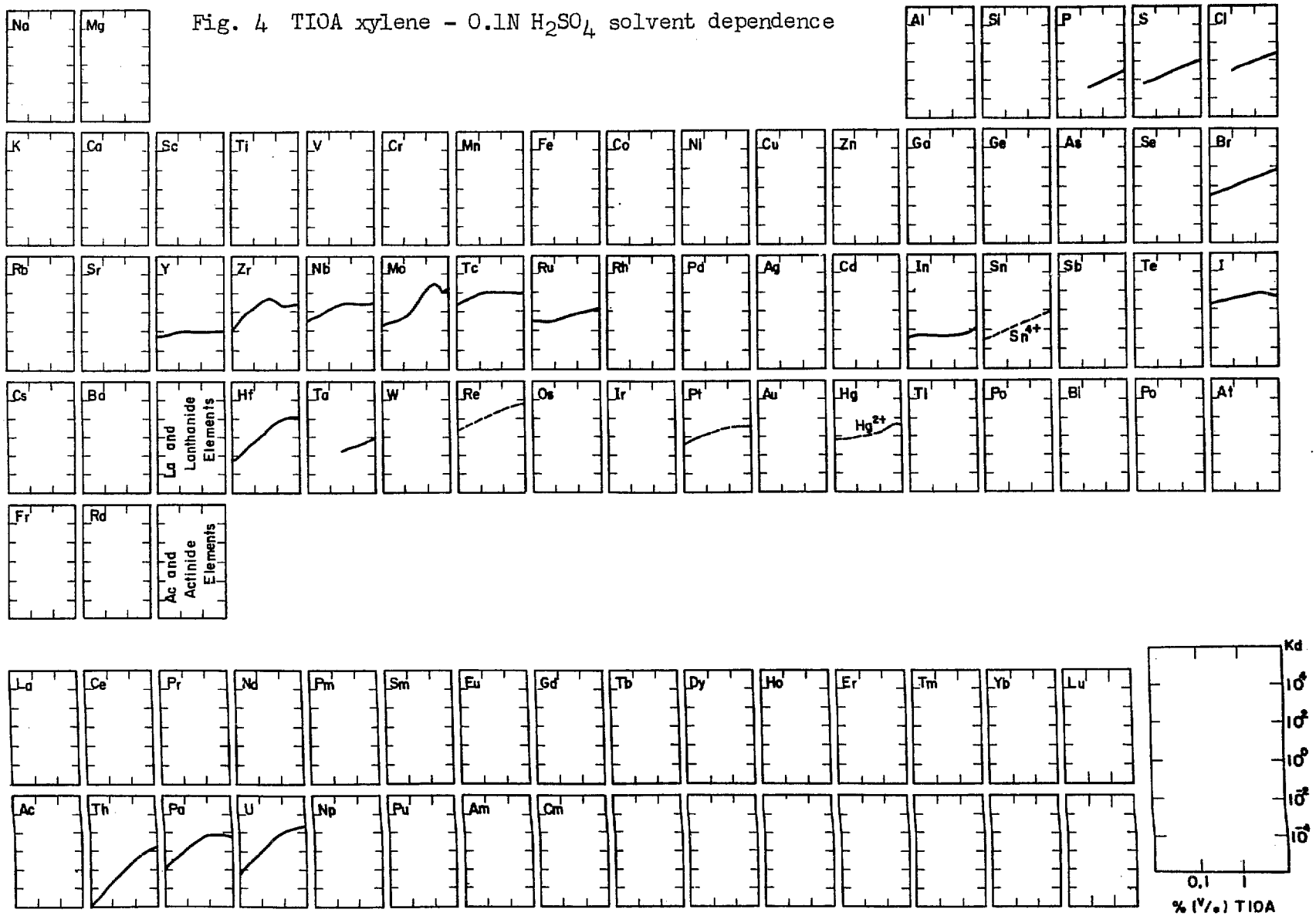
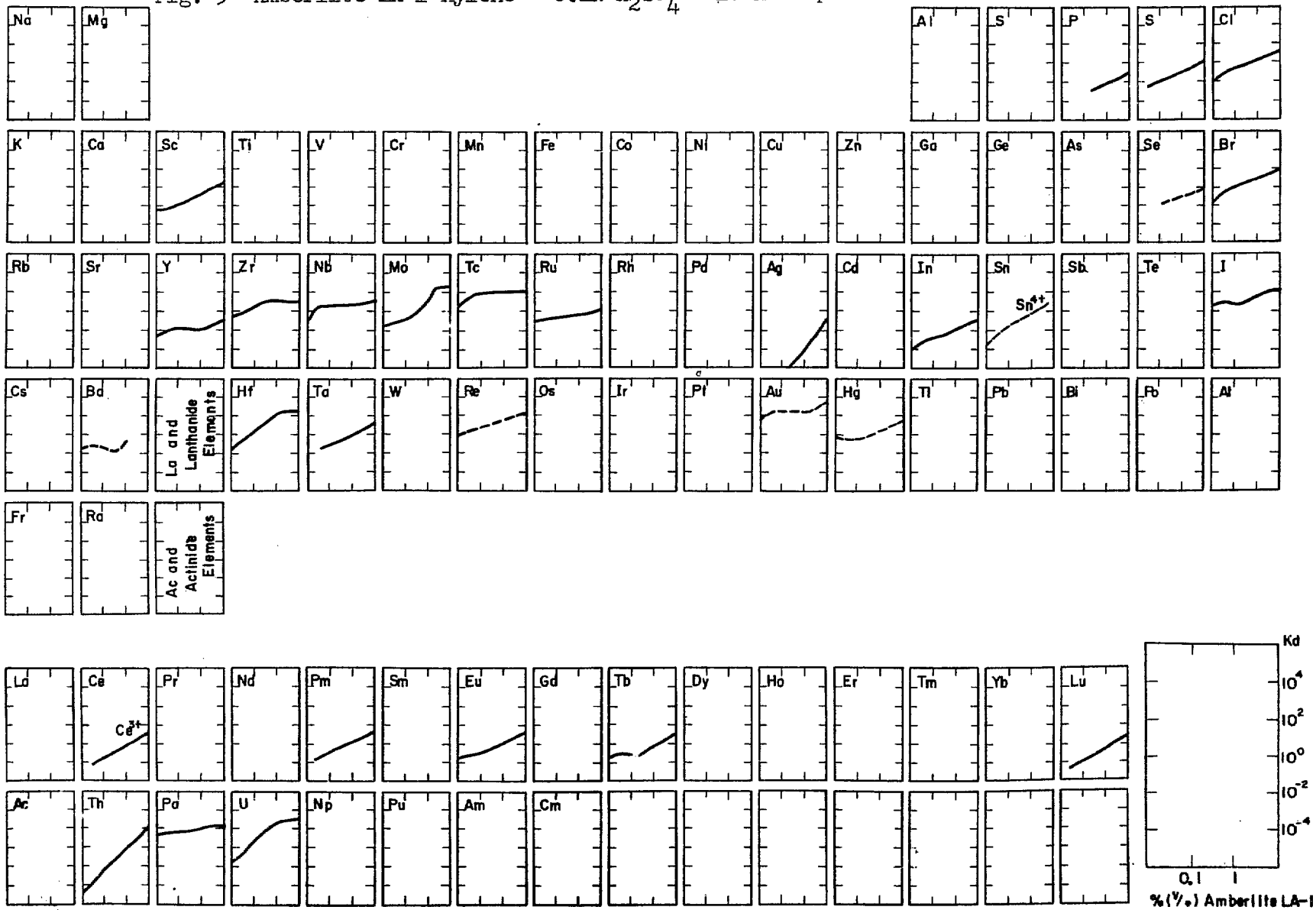


Fig. 5 Amberlite LA-1 xylene - 0.1N H_2SO_4 solvent dependenc-



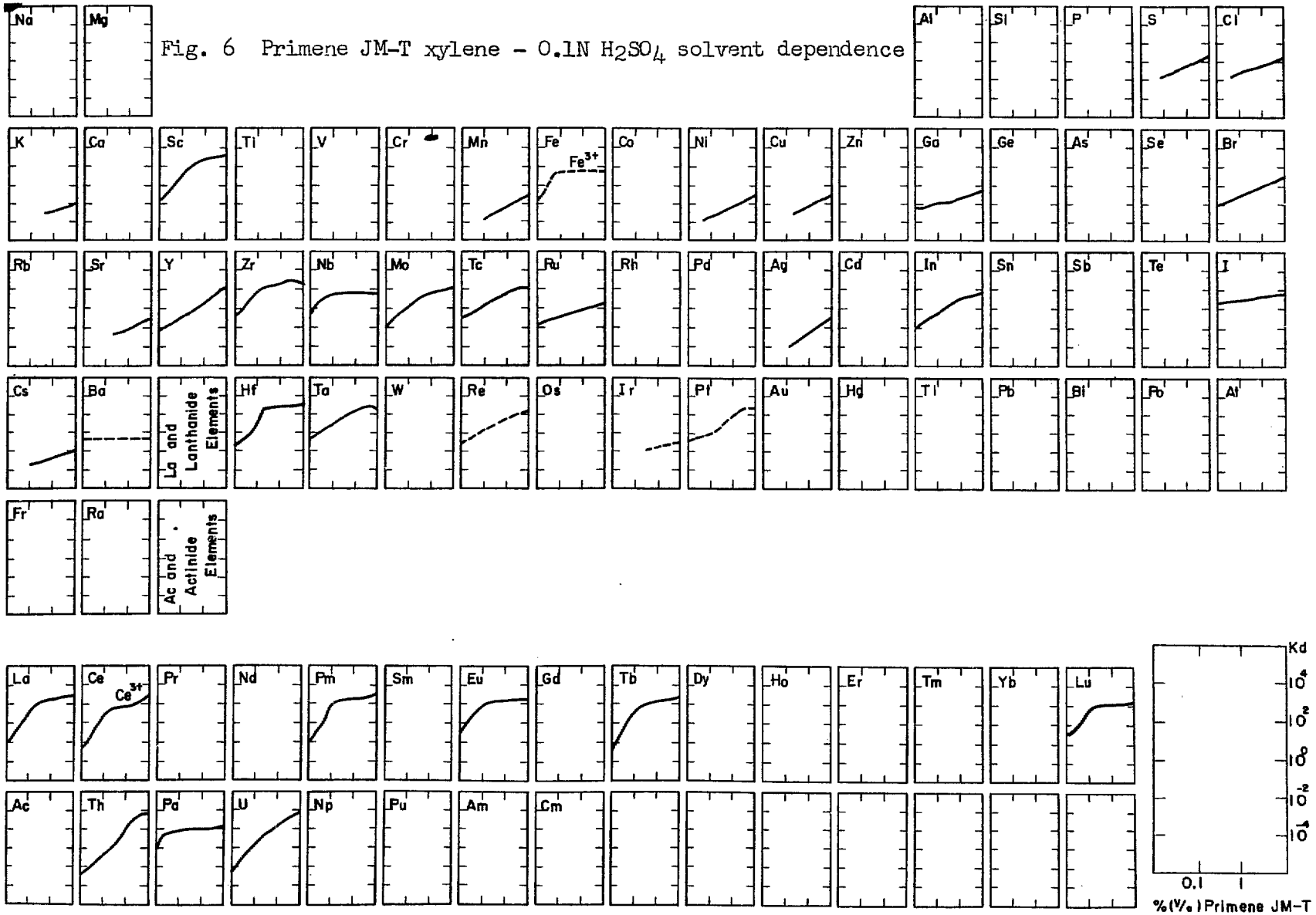


Fig. 6 Primene JM-T xylene - 0.1N H_2SO_4 solvent dependence

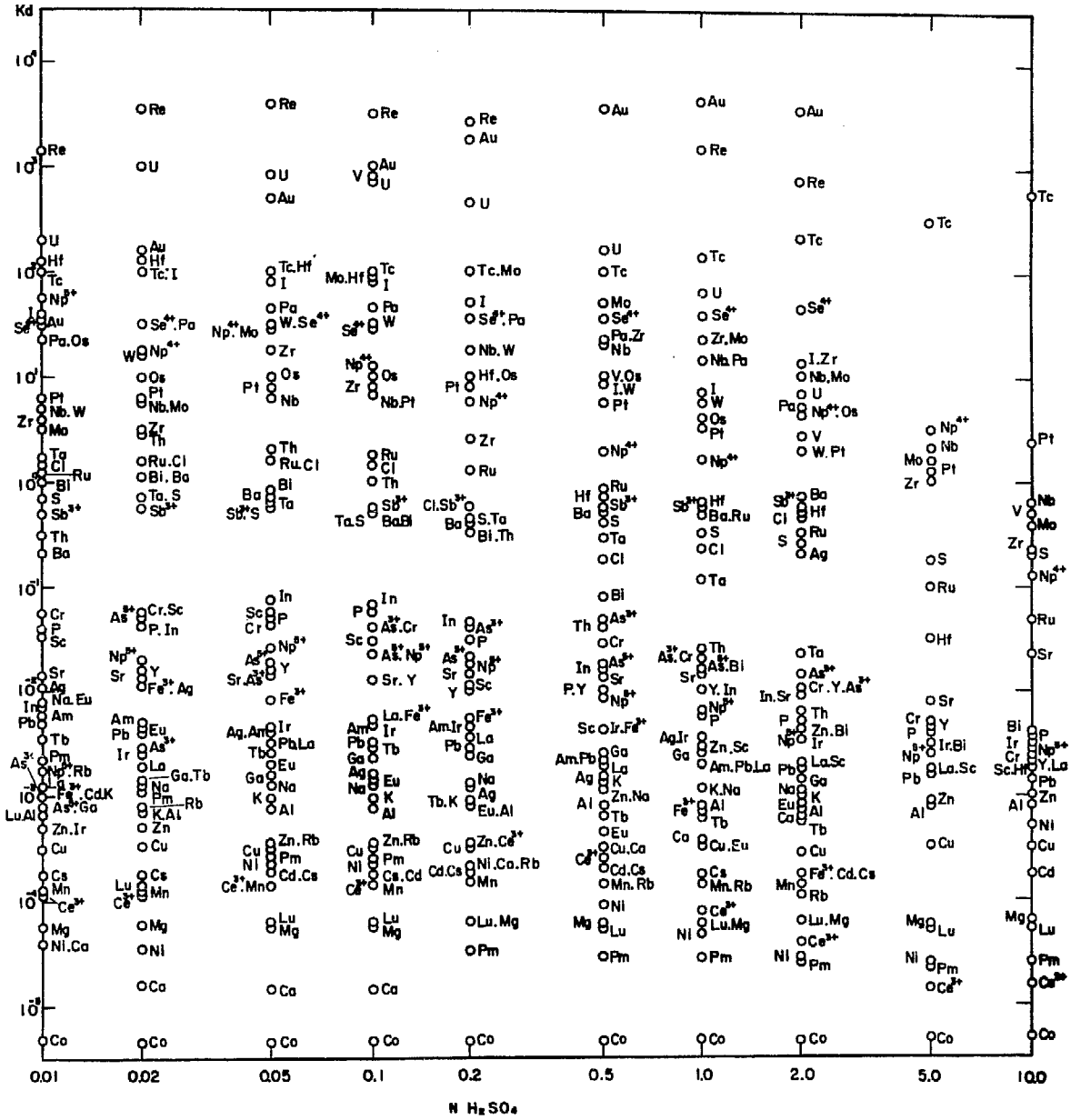


Fig. 7 Kd values in 5% TIOA xylene - H_2SO_4 system

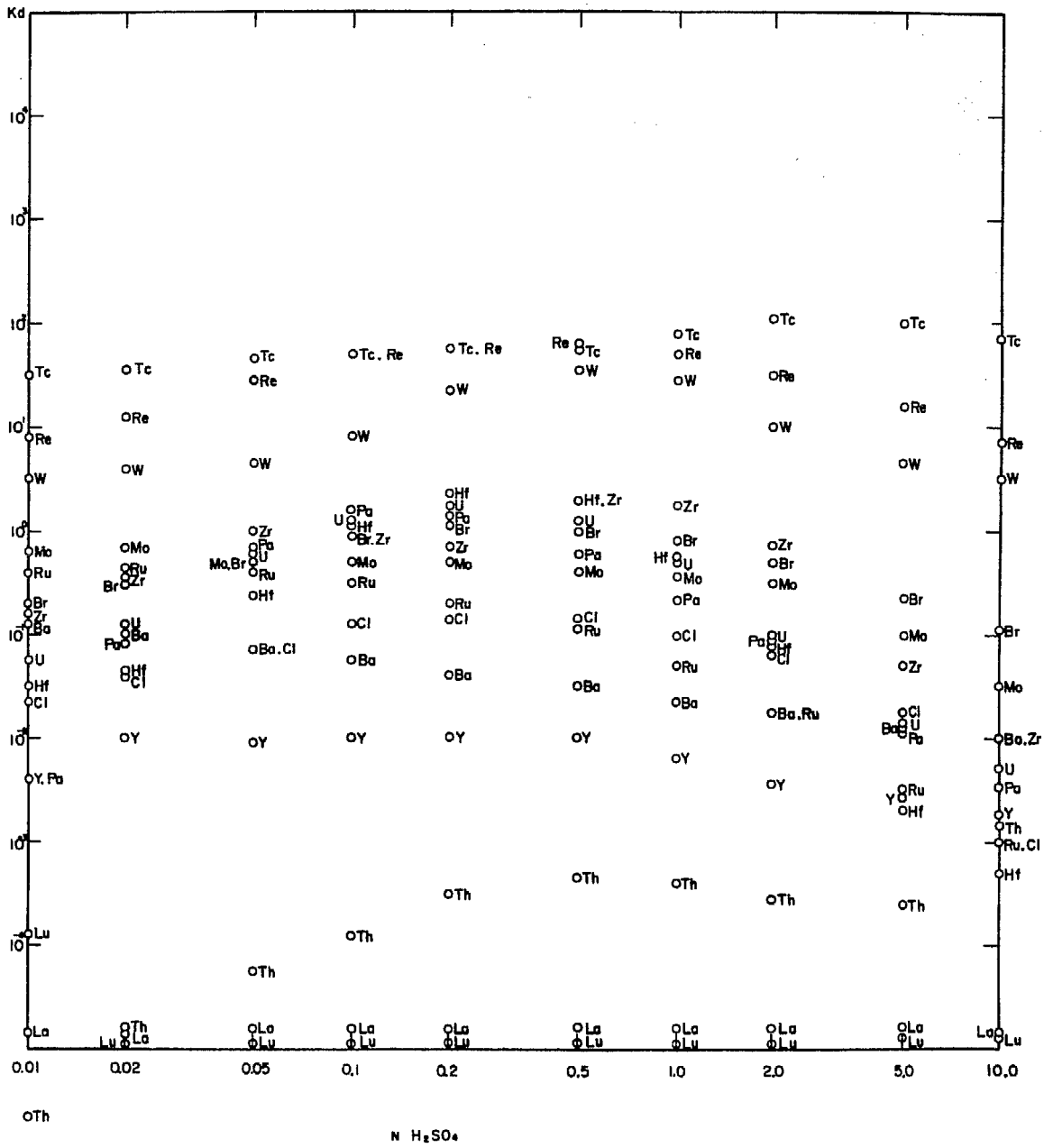


Fig. 8 Kd values in 0.1% TIOA xylene - H_2SO_4 system

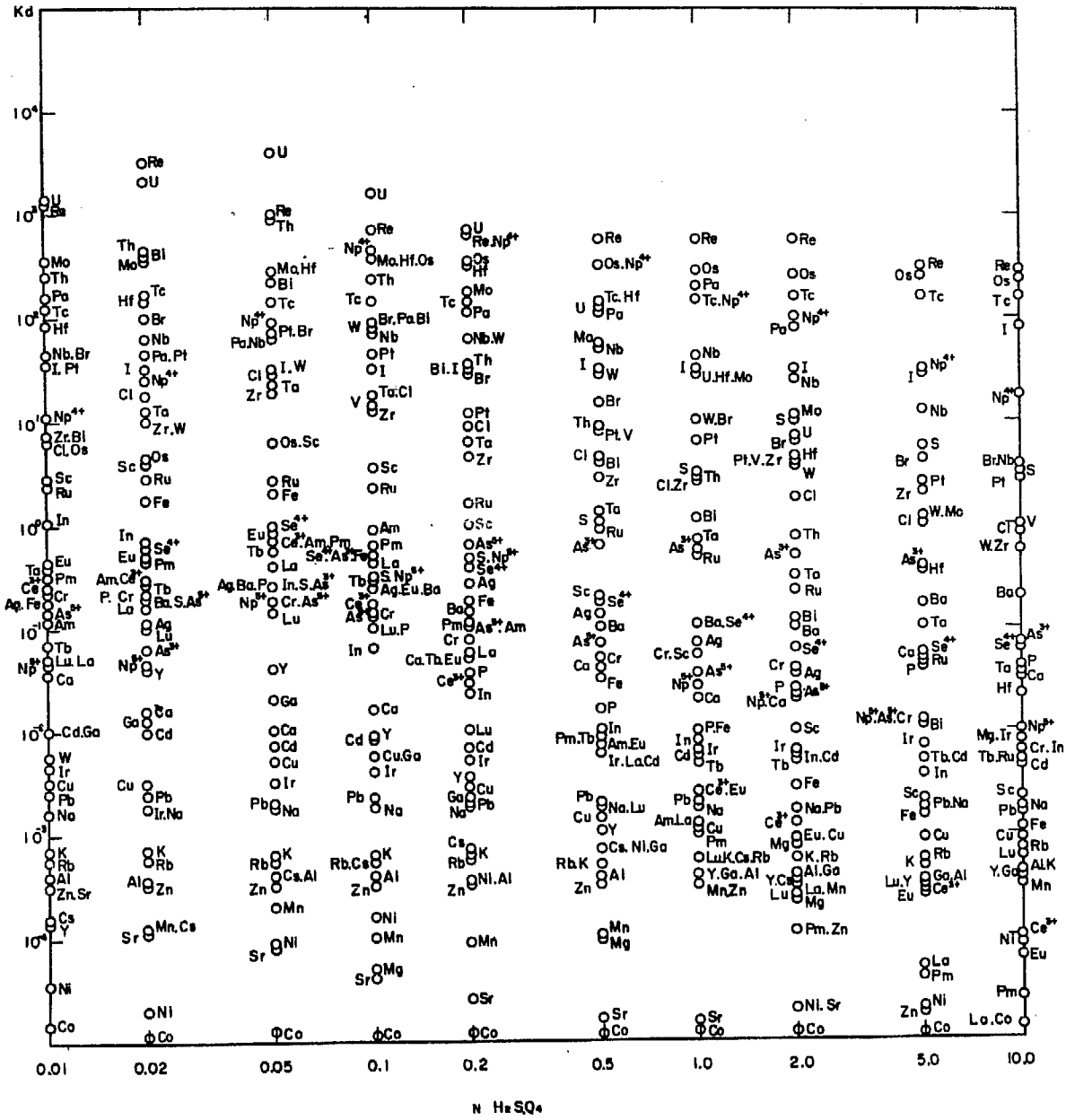


Fig. 9 Kd values in 10% Amberlite LA-1 xylene - H_2SO_4 system

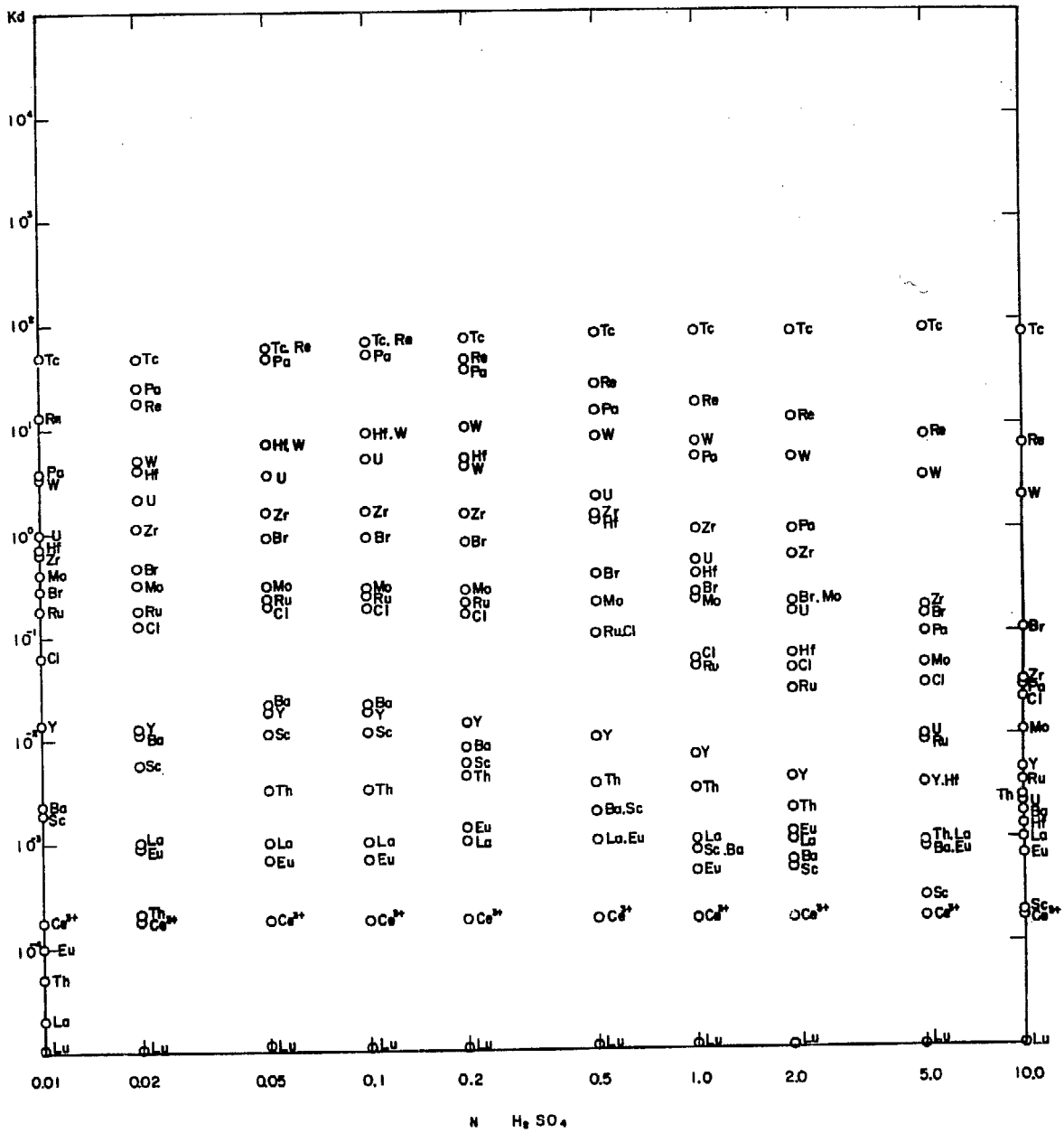


Fig. 10 Kd values in 0.1% Amberlite LA-1 xylene - H_2SO_4 system

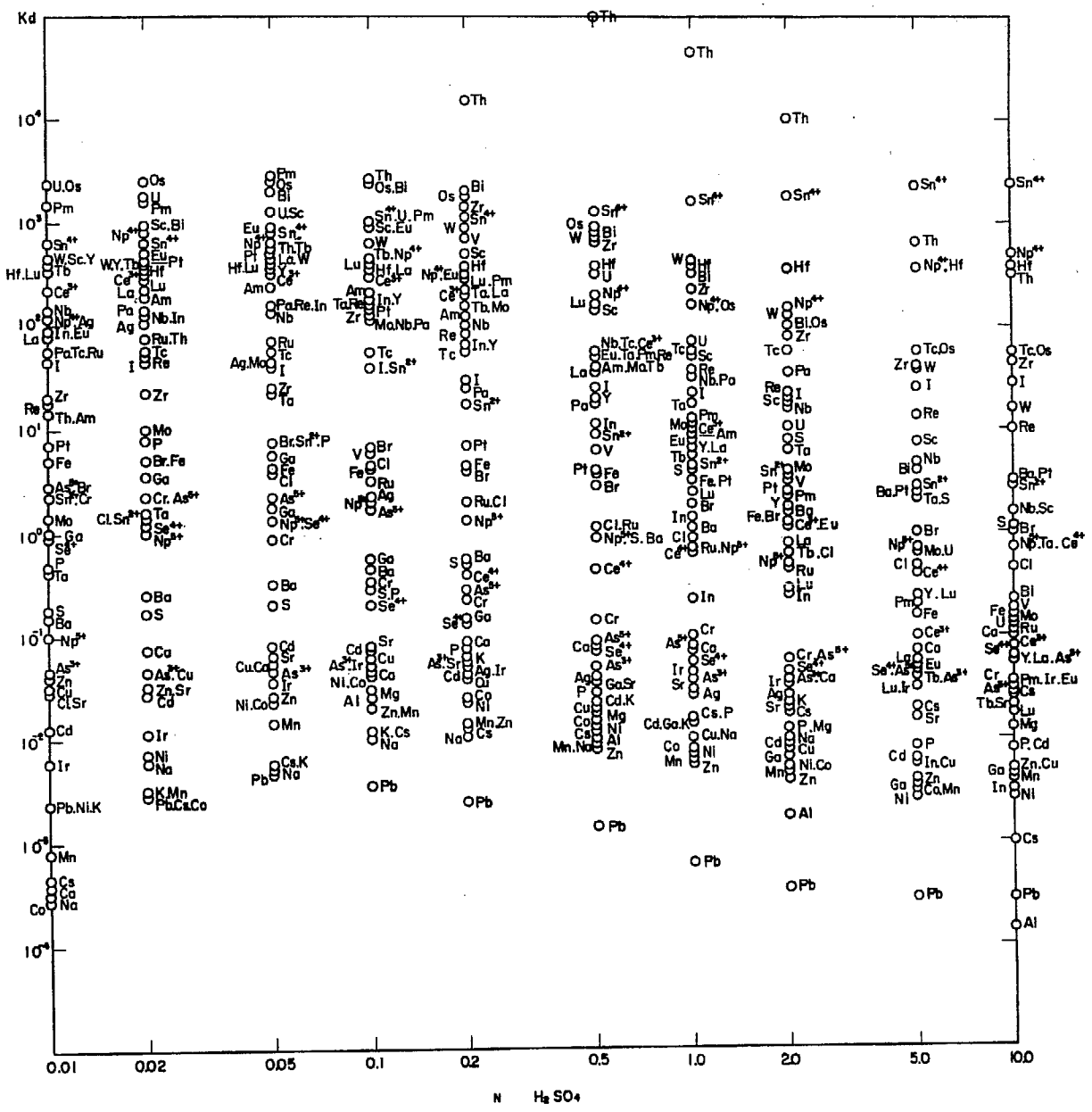


Fig. 11 Kd values in 10% Primene JM-T xylene - H_2SO_4 system

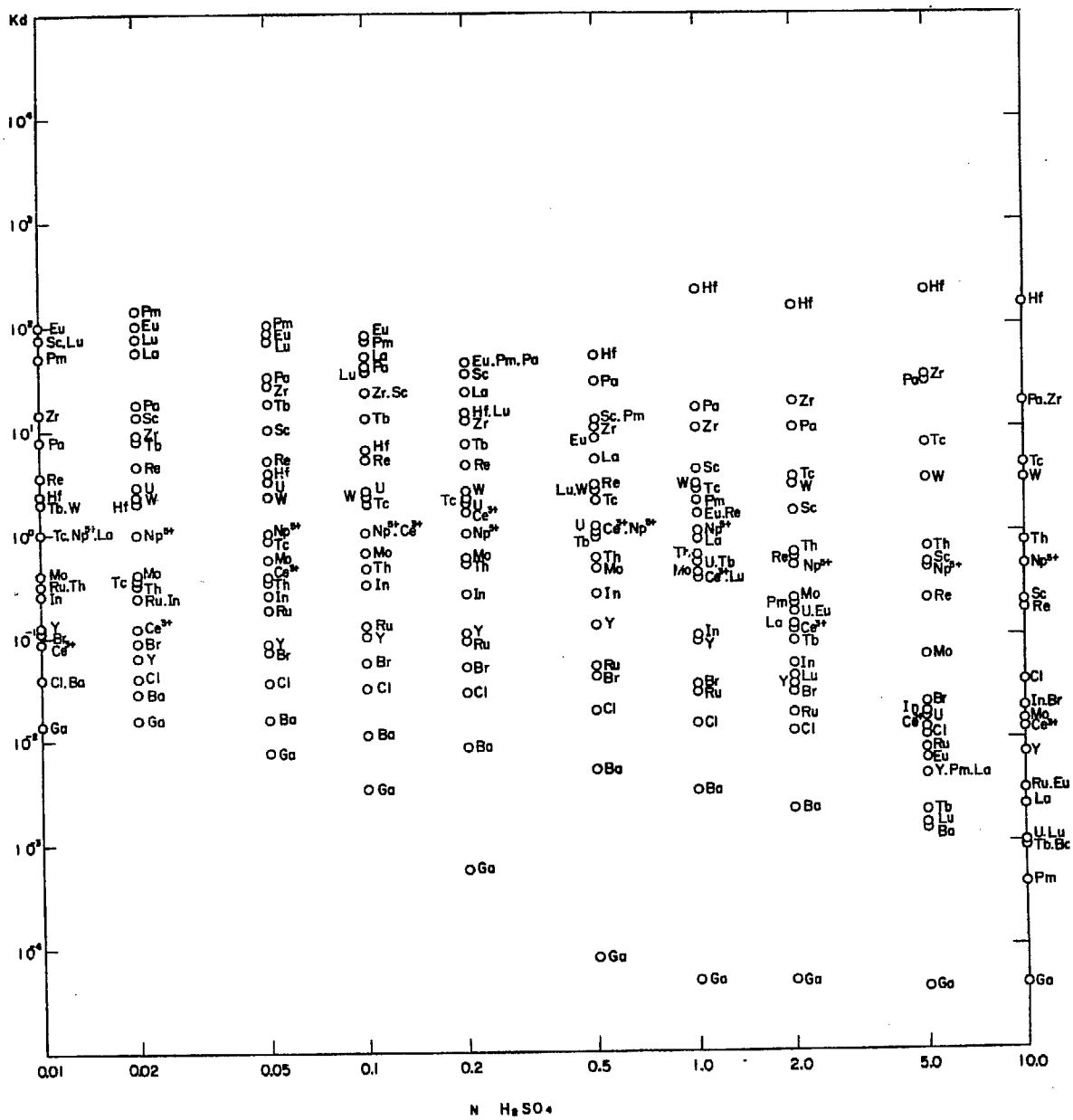


Fig. 12 Kd values in 0.1% Primene JM-T xylene - H_2SO_4 system

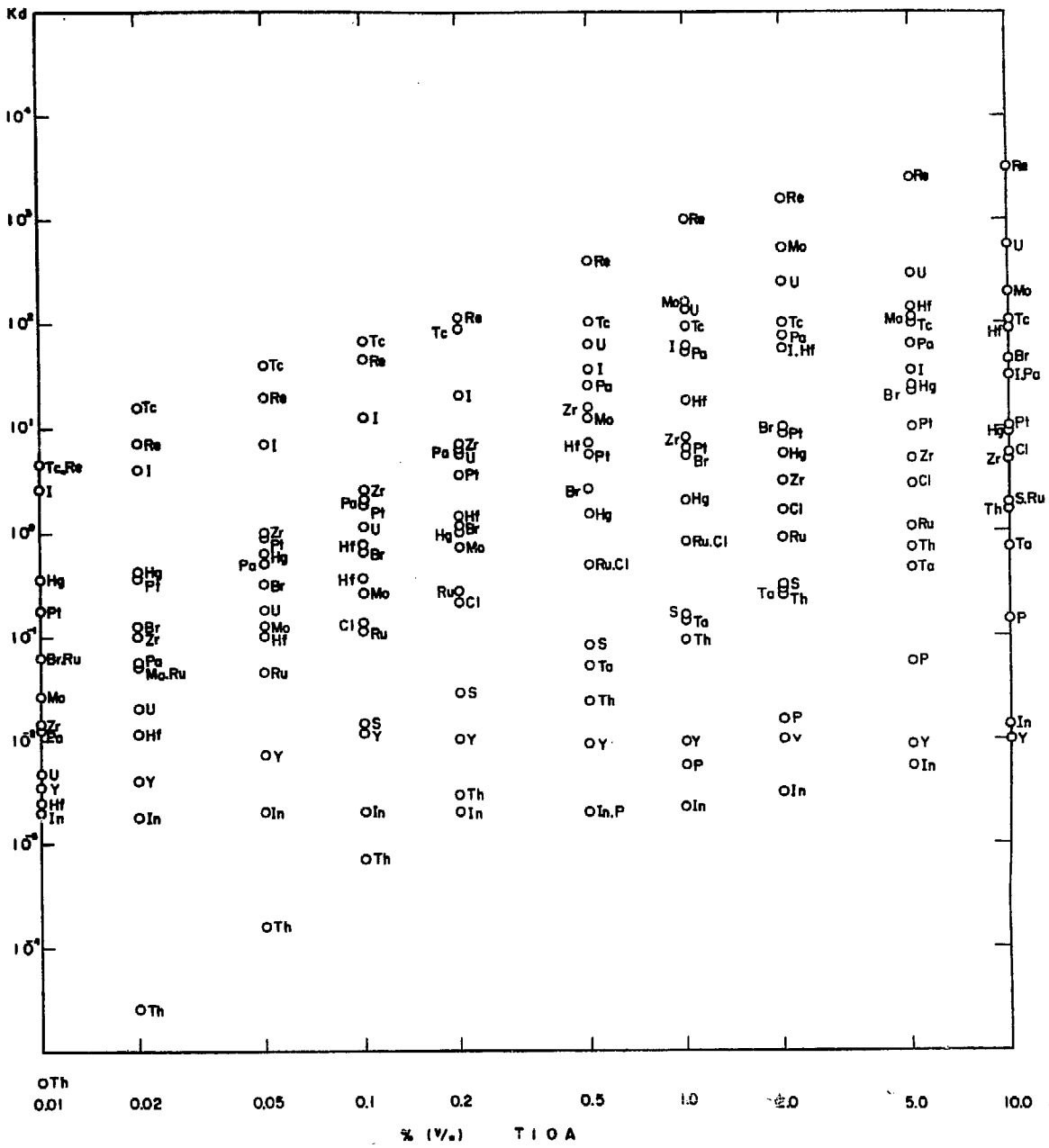


Fig. 13 Kd values in TIOA xylene - 0.1N H_2SO_4 system

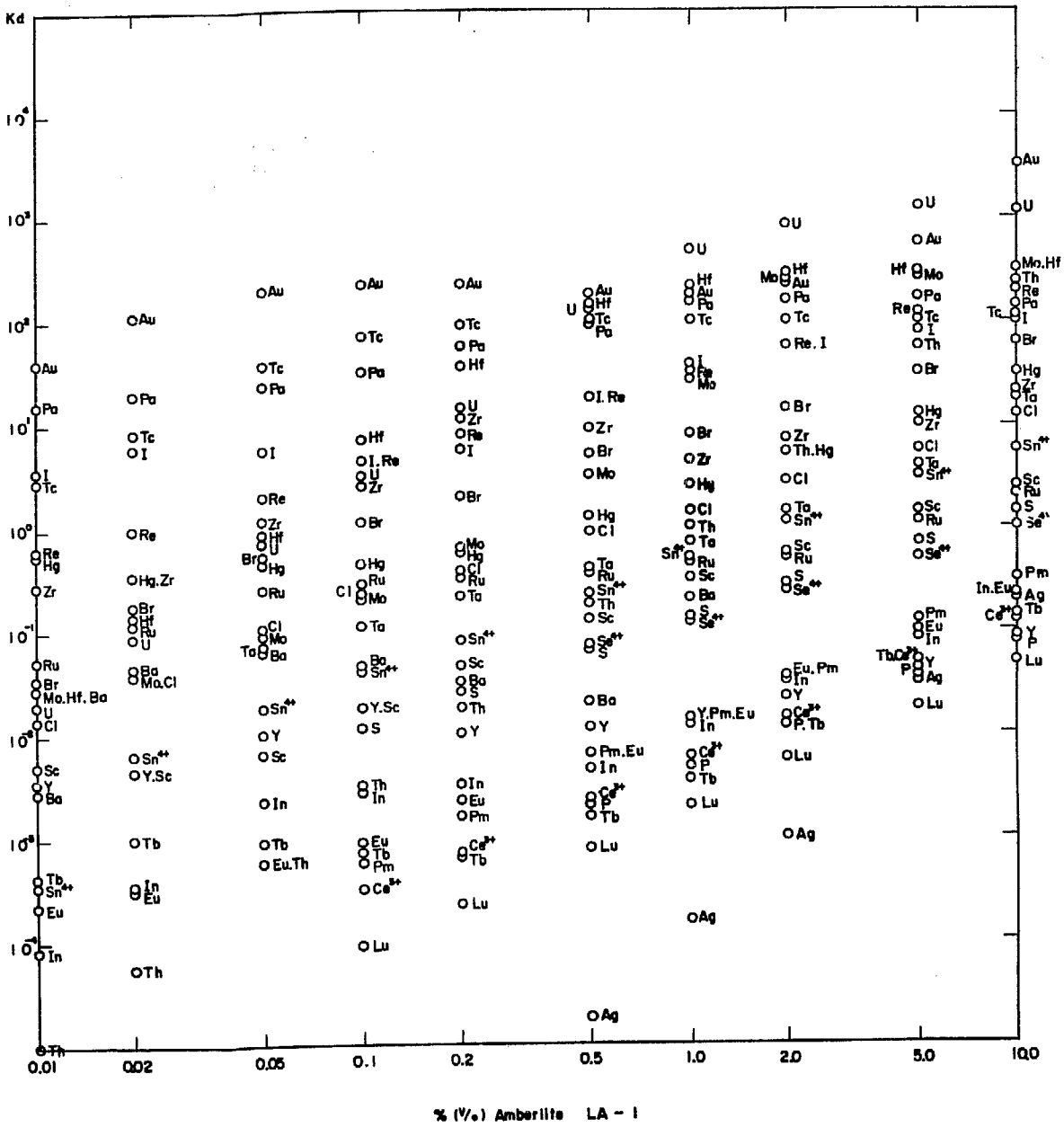


Fig. 14 Kd values in Amberlite LA-1 xylene - 0.1N H_2SO_4 system

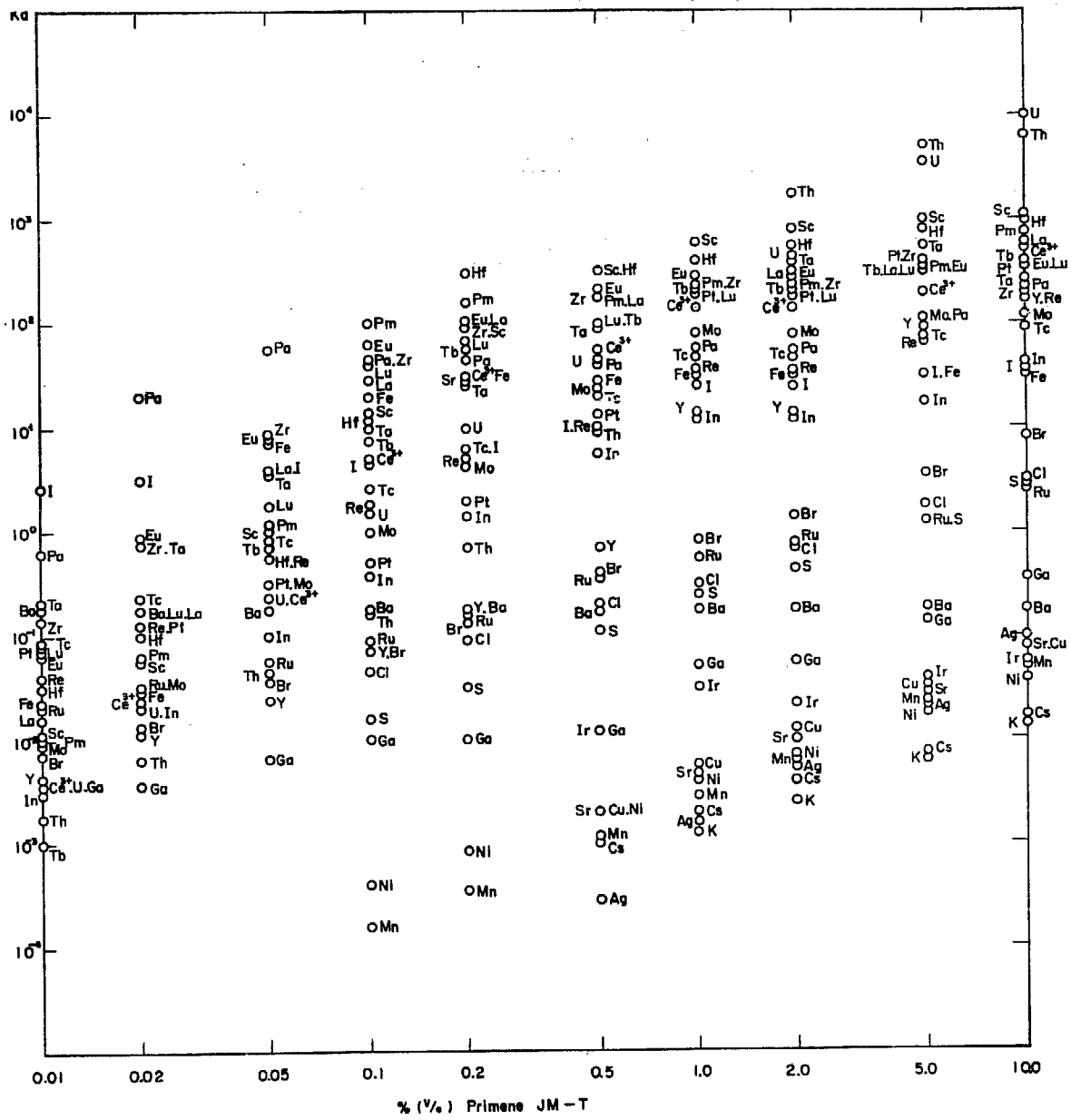


Fig. 15 Kd values in Primene JM-T xylene - 0.1N H_2SO_4 system

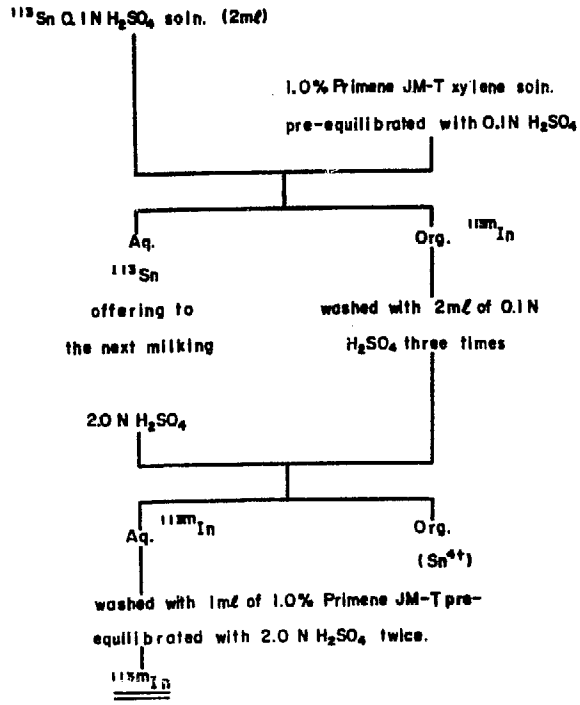


Fig. 16 The separation process of carrier-free ^{113m}In from ^{113}Sn

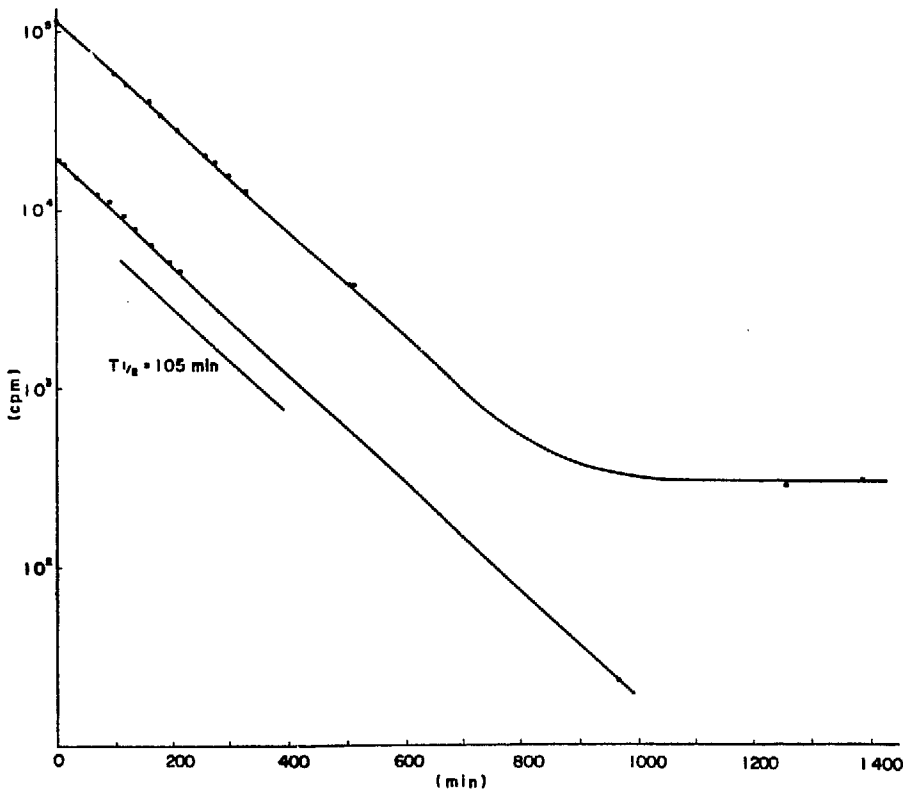


Fig. 17 The decay curve of ^{113m}In prepared

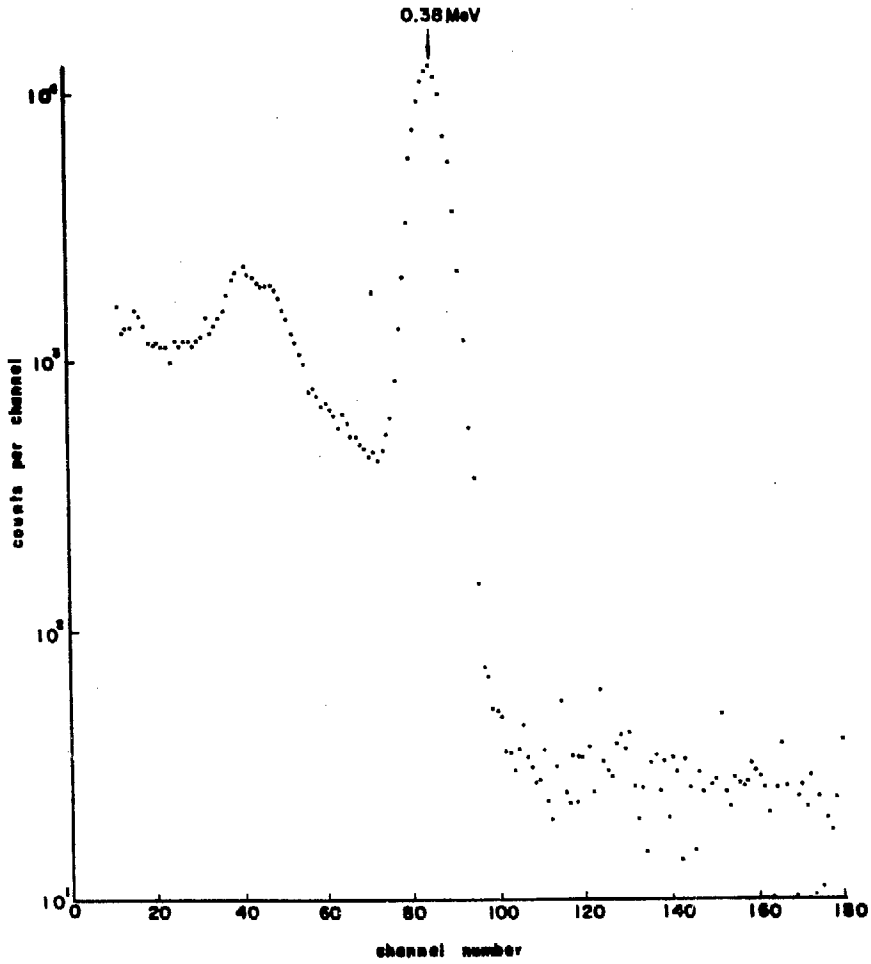


Fig. 18 The gamma ray spectrum of ^{113m}In prepared

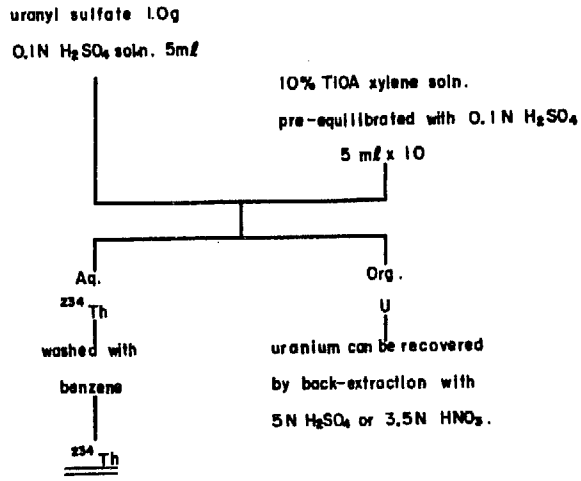


Fig. 19 The separation process of ^{234}Th(UXI) from natural uranium

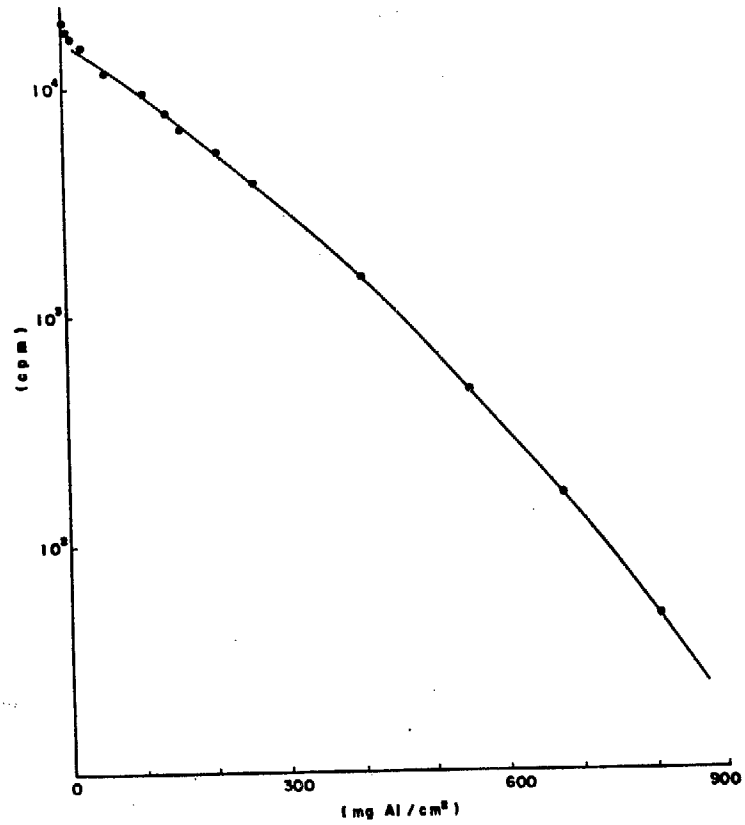


Fig. 20 The beta ray absorption with aluminum foil for ^{234}Th prepared; maximum β-energy was determined to be 2.5 Mev by Feather Analysis

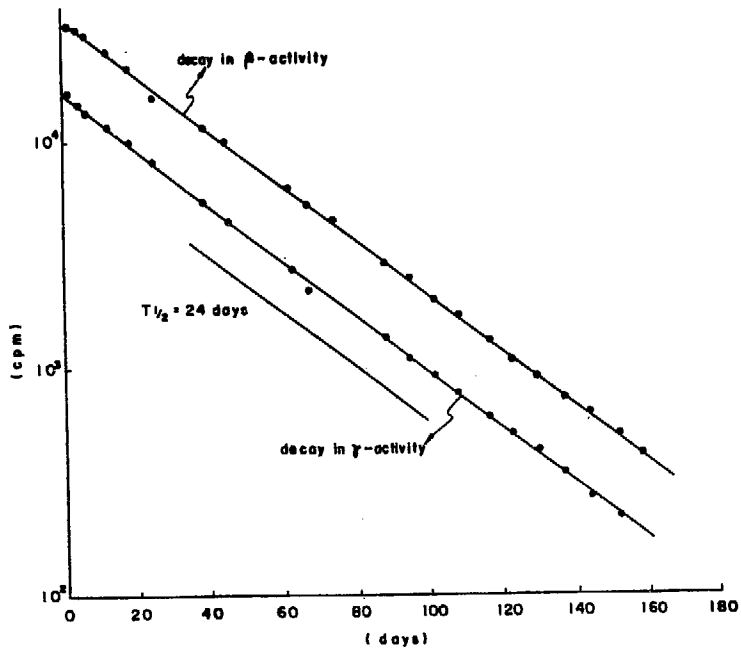


Fig. 21 The decay curve of ^{234}Th prepared

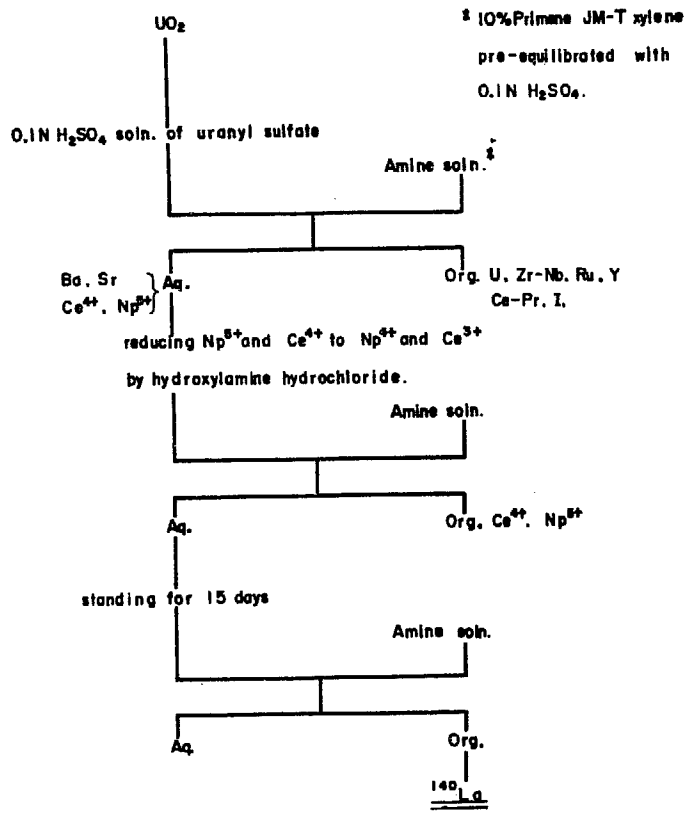


Fig. 22 The separation process of ^{140}La from irradiated uranium

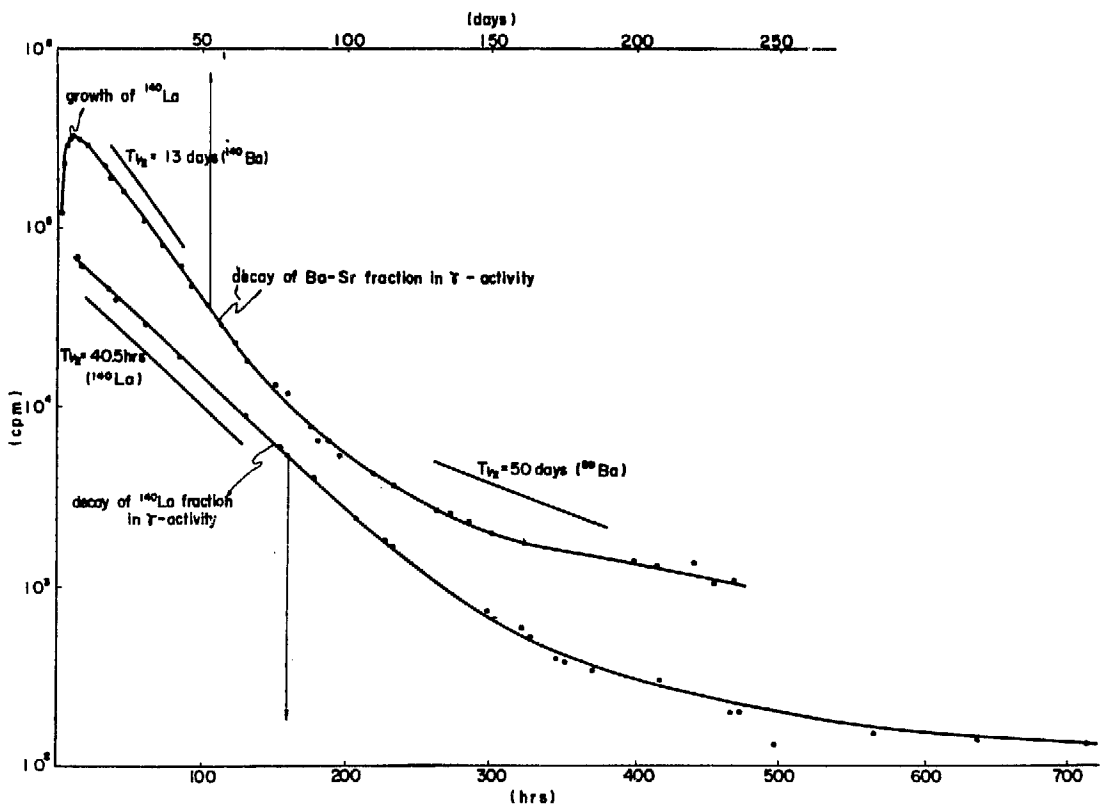


Fig. 23 The decay curve of ^{140}La prepared

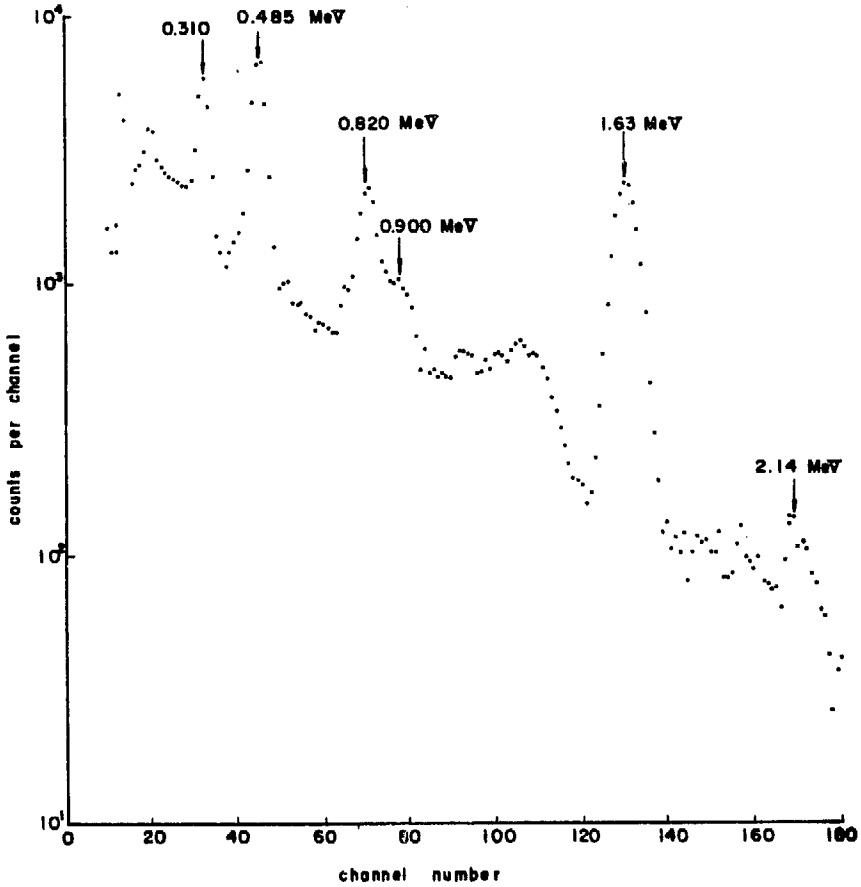


Fig. 24 The gamma ray spectrum of ^{140}La prepared