

Data of Inorganic Solvent Extraction (3)

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Summary

Solvent extraction behavior of about fifty chemical elements is studied in the following solvent extraction systems:

(1) Diethyl Cellosolve-NH₄NO₃, (2) Pentaether-NH₄NO₃, (3) Di-isopropyl ketone-HCl, (4) Hexone-HCl, (5) Hexone-HNO₃, (6) Isopropyl ether-HCl.

These systems are surveyed, since they are not covered in the previous publications of "Data of Inorganic Solvent Extraction (1) and (2)". The acidity dependence is radiochemically determined in the above systems. The additional results of "Data of Inorganic Solvent Extraction (1) and (2)" are also given.

(7) TBP-H₂SO₄ system, (8) 10% (v/o) Primene JM-T-HNO₃ system.

Jan. 1966

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無機溶媒抽出データ集 (3)

要　　旨

無機溶媒抽出データ集 (1) および (2) について、次にあげるような、6種の溶媒抽出系における約50種の化学元素の抽出行動をしらべた。

(1) ジエチルセロソルブ-NH₄NO₃, (2) ペンタエーテル-NH₄NO₃, (3) ジイソプロピルケトン-HCl, (4) ヘキソン-HCl, (5) ヘキソン-HNO₃, (6) イソプロピルエーテル-HCl

いずれも、いわゆる acidity dependence についてしらべた。このほか、データ集 (1) および (2) に関する追加および、補正のデータを加えた。

(7) リンサン酸トリプチル-H₂SO₄, (8) 10% プライメン JM-T-HNO₃.

1966年1月

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1. Introduction

Ethylether is well-known to extract uranium from nitrate solution¹⁾. The other ethers, which are useful for extracting uranium and plutonium, have also been reported, such as Pentaether and ethers of glycols^{2,3)}. However, the extractability of only several elements with ethers has been reported in nitrate system.

In this work, some ethers and ketones are studied radiochemically for the extraction of about fifty chemical elements from sodium to neptunium. The organic extractant used are Pentaether, Diethyl Cellosolve, isopropyl ether, di-isopropyl ketone and hexone.

Pentaether and Diethyl Cellosolve are the trivial name of dibutoxytetraethylene glycol and 1, 2-diethoxy ethan, respectively. These extractants are soluble in 3N nitric and hydrochloric acid, therefore, they have been used at low acidity together with a salting-out agent like calcium nitrate or aluminum nitrate³⁾.

Isopropyl ether is well-known to extract iron very well from chloride solution^{4,5)}. Extraction of indium (III)⁶⁾, antimony (III) and (V)⁷⁾ from chloride solution has been also studied.

Di-isopropyl ketone is known to extract protactinium¹⁾. The extraction of the other elements has not been reported.

Hexone is the trivial name of 4-methyl 2-pentanone. The substance has another trivial name, methyl isobutyl ketone. This has been studied for extraction of some of fission products, the salting agent being used⁸⁾. A separation of protactinium by hexone has been also reported⁹⁾.

In this work, the additional and comprehensive data are obtained in the systems given in TABLE 1.

TABLE 1 The solvent extraction systems studied

Organic extractant	Trivial name	Received from	Purification	Aqueous phase
4-Methyl 2-pentanone	Methyl isobutyl ketone or Hexone	Kanto Chemical Co., Inc., Tokyo	Distillation 114~116.5°C	1, 2, 4, 6, 8, 10 and 12N HNO ₃ 1M Al(NO ₃) ₃ soln. of 1, 2, 4, 6, 8 and 10N HNO ₃ 1, 2, 4, 6 and 8N HCl
2, 4-Dimethyl pentanone	Di-isopropyl ketone	K & K Laboratories, Inc., New York; Dr. Theodor Schuchardt GMBH & Co., München	Distillation 123~127°C	1, 2, 4, 6, 8 and 10N HCl
1, 2-Diethoxy ethan	Diethyl Cellosolve	Kanto Chemical Co., Inc., Tokyo	Distillation 120~121°C	1, 3, 6 and 9M NH ₄ NO ₃ 1N HNO ₃ soln. of 1, 3, 6 and 9M NH ₄ NO ₃
Dibutoxy tetra- ethylene glycol	Penta Ether	Roberts Chemicals Inc.	—	the same to those used in Diethyl Cellosolve
Isopropyl ether		Koso Chemical Co. Ltd., Tokyo	Washing with (1 : 1) H ₂ SO ₄ and H ₂ O successively	1, 2, 4, 6, 8, 10N HCl 0.01~10 N HNO ₃

2. Experimental

2.1 The radioisotopes used

The radioisotopes used were the same with those used in the previous work^{10,11}.

2.2 The reagents

The organic extractants used are listed in TABLE 1 together with the details of the extraction systems studied.

The hydrochloric and nitric acids used were of analytical grade.

2.3 Determination of distribution ratios

The method of determining distribution ratios, Kd , was the same with that described in the previous paper¹⁰.

The pre-equilibration was carried out for the organic phases.

3. Results

The results obtained are summarized in Figs. 1~6 as the series of graphs of $\log Kd$ vs. $N HNO_3$ or $N HCl$ or $M NH_4NO_3$, where Kd is the distribution ratio determined, N the normality of acid and M the molarity of ammonium nitrate.

3.1 Diethyl Cellosolve-NH₄NO₃ system

Fig. 1 shows the ammonium nitrate concentration dependence curves of chemical elements in Diethyl Cellosolve-NH₄NO₃ and -NH₄NO₃-1N HNO₃ systems. It can be seen from Fig. 1 that most elements are not extracted with Diethyl Cellosolve from ammonium nitrate solution. The Kd values near one are shown by sulfate, chromate, technetate, palladium and thorium. The Kd values above one are given by gold, mercury (II) and uranium (VI). However, gold and palladium seem to be chlorocomplex in solution, since chloride solution of the neutron irradiated metal was used.

On the other hand, METZ³ determined Kd values of plutonium (IV) and (VI) to be 32.36 and 24.03 respectively at the conditions of 10M NH₄NO₃-1N HNO₃. Therefore, Diethyl Cellosolve is said to be a extractant of mercury, uranium and plutonium from nitric acid solution.

3.2 Pentaether-NH₄NO₃ system

The results obtained are shown in Fig. 2. Most of the elements studied give low Kd value even at 9M NH₄NO₃-1N HNO₃. Kd values above one are measured for mercury (II), thorium, protactinium and uranium (VI) at high ammonium nitrate concentration.

3.3 DIPK (Di-isopropyl ketone)-HCl system

The results obtained are summarized in Fig. 3. Gallium, indium and protactinium show very high Kd value at high hydrochloric acid concentration, as shown in Fig.3. Kd values near one are given by iron (III), molybdenum and iodine. The other elements studied are not extracted with DIPK from hydrochloric acid.

The results of protactinium agree very well with the data reported by the other investigators^{12,13}.

3.4 Hexone-HCl system

Fig. 4 shows the hydrochloric acidity dependence of Kd values of chemical elements in

Hexone-HCl system. Behaving similar to DIPK-HCl system, gallium, indium and protactinium show very high K_d values. Iron (III), molybdenum, selenium (IV) and rhenium are more extracted with hexone than DIPK. But the extractability of hexone is quite similar to that of DIPK in hydrochloric acid media, and is similar to that of TBP-HCl system except for scandium, zirconium and niobium¹⁾.

3.5 Hexone-HNO₃ system

The results obtained are represented in Fig. 5. The salting-out agent used is 1M aluminum nitrate. Technetate, iodine, mercury (II), cerium (IV), protactinium, uranium (VI) and neptunium (VI) show K_d values near one. METZ reported a K_d value of plutonium (IV) at 10M NH₄NO₃-1M HNO₃ to be 4.57.

3.6 Isopropyl ether-HCl system

The acidity dependence curves determined are shown in Fig. 6. Iron (III) and gallium (III) show high K_d value at high acidity, as reported by NACHTRIEB *et al.*⁴⁻⁶⁾. The K_d values determined are somewhat lower than those reported, as Fig. 6 shows. This fact seems to be attributed to the prolonged shaking period of NACHTRIEB *et al.*⁴⁻⁶⁾.

3.7 Isopropyl ether-HNO₃ system

The results obtained are shown in TABLE 2. Most of the elements studied are not extracted with isopropyl ether from nitric acid solution.

TABLE 2 K_d values of elements in Iso-propyl ether-HNO₃ system

K_d value	Acidity		
	0.01~2N HNO ₃	2~5N HNO ₃	>5N HNO ₃
10 ⁰ ~10 ¹			I
10 ⁻¹ ~10 ⁰	Hg(II)	I, Hg(II)	Hg(II)
10 ⁻² ~10 ⁻¹	I		P, Ag, Re, Th, U
10 ⁻³ ~10 ⁻²	Zn, Y, U	P, Zn, Y, Ag, Re, U	Zn, Y, Mo, Np(V)
<10 ⁻³	P, K, Sc, Ni, Cd, Mo, Ag, Cs, Ba, La, Ce(III, IV), Eu, Hf, Re, Th, Np(V)	K, Sc, Ni, Cd, Mo, Cs, Ba, La, Ce(III, IV), Eu, Hf, Np(V)	K, Sc, Ni, Cd, Cs, Ba, La, Ce(III, IV), Eu, Hf

4. Exact K_d values

Exact K_d values are shown in Figs. 7~14.

5. Supplemental and corrected results of "Data of Inorganic Solvent Extraction (1) and (2)"

5.1 TBP-H₂SO₄ system

The results obtained in the system are shown in Figs. 15 and 16, being added to those in TBP-HCl and TBP-HNO₃ systems in the previous report¹⁰⁾.

In cases of iron, tin, platinum and gold, as indicated by dashed line in Fig. 15, the respective chloride tracer was added to the sulfuric acid media of the system.

Technetium and rhenium give fairly high Kd values. Octavalent osmium also shows high values, suggesting high values for octavalent ruthenium.

The Kd values for hafnium, thorium, protactinium and neptunium are taken from the previous publication¹⁹⁾.

5.2 10% (v/o) Primene JM-T in xylene-HNO₃ system

The results obtained are shown in Fig.17. The Kd values measured are low in every case of the chemical elements studied.

5.3 TBP-HCl system

Fig.18 shows the new results obtained. The data given in the previous publication¹⁰⁾ are corrected.

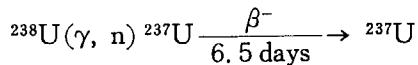
5.4 Kd values in alkylamine-HCl system

The exact Kd values reported in Fig. 4.1 and 4.3 of the previous publication¹⁰⁾ are plotted in Fig. 19 and 20.

6. Applications

6.1 Preparation of ^{237}U

^{237}U is formed through (γ , n) reaction



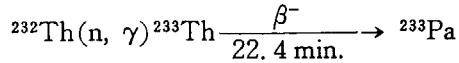
together with a large amount of fission products.

The isotope ^{237}U is useful as a convenient uranium radioisotope, since it is beta and gamma emitter. The formed ^{237}U in uranium target must be separated from fission products for the use of radioisotope of uranium.

The results of Fig. 1 shows that Diethyl Cellosolve is useful for the separation of uranium from fission products. The separation process tried is represented in Fig. 21. The gamma ray spectrum and decay curve of ^{237}U obtained are shown in Figs. 22 and 23.

6.2 Preparation of ^{233}Pa

^{233}Pa is produced through (n, γ) reaction of thorium



and prepared by separating protactinium from thorium.

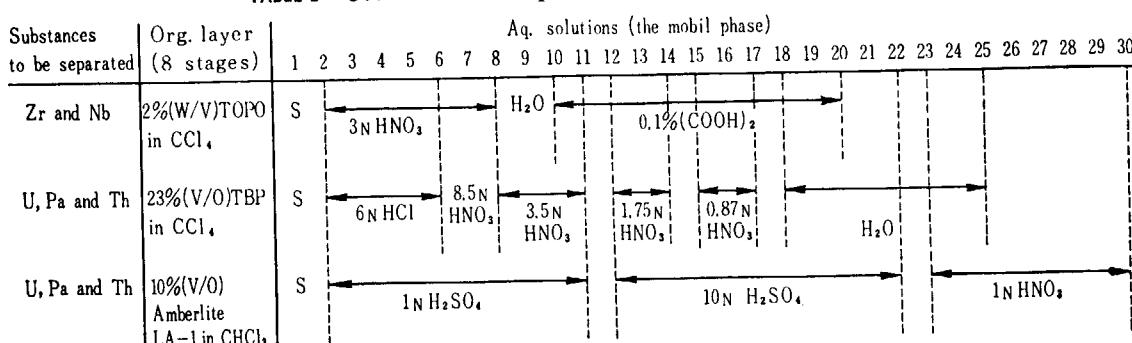
The results of DIPK offered a separation method of thorium and protactinium. The separation process used is shown in Fig. 24. The decay curve measured is given in Fig. 25.

6.3 Countercurrent separations

Three separations were performed on the basis of "Data of Inorganic Solvent Extraction (1) and (2)". The gradient multistage extraction method²⁰⁾ was applied here to separate zirconium-niobium and uranium-protactinium-thorium. The used apparatus was a Craig type countercurrent train with 8 mixing cells, and operated automatically. Five ml of aqueous solution was shaken in each equilibrium cell for the given period of time. The experimental conditions are shown in TABLE 3.

Zirconium and niobium were ascertained by beta ray absorption with aluminum foil. Thorium

TABLE 3 Countercurrent separations in the gradient method

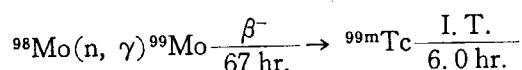


and uranium were determined by gravimetric and colorimetric analysis respectively.

The results are shown in Figs. 26~28.

6.4 Preparation of ^{99m}Tc

^{99m}Tc is produced through (n, γ) reaction of molybdenum



^{99m}Tc is separated from the irradiated ammonium molybdate by use of TBP-sulfuric acid system. The process, the decay curve and gamma ray spectrum of the ^{99m}Tc prepared are shown in Figs. 29~31.

6.5 Separation of Zr and Nb

^{95}Nb is separated from $^{95}\text{Zr-Nb}$ mixture by the method of Fig. 32. The beta ray absorption curve with aluminum foil (Fig. 33) and gamma ray spectrum (Fig. 34) of the obtained ^{95}Nb are given. The latter was measured by use of lithium-drifted germanium radiation counter in the Reactor Instrumentation Lab. of the JAERI, for that the authors wish to thank Dr. E. SAKAI and Mr. H. YOSHIDA.

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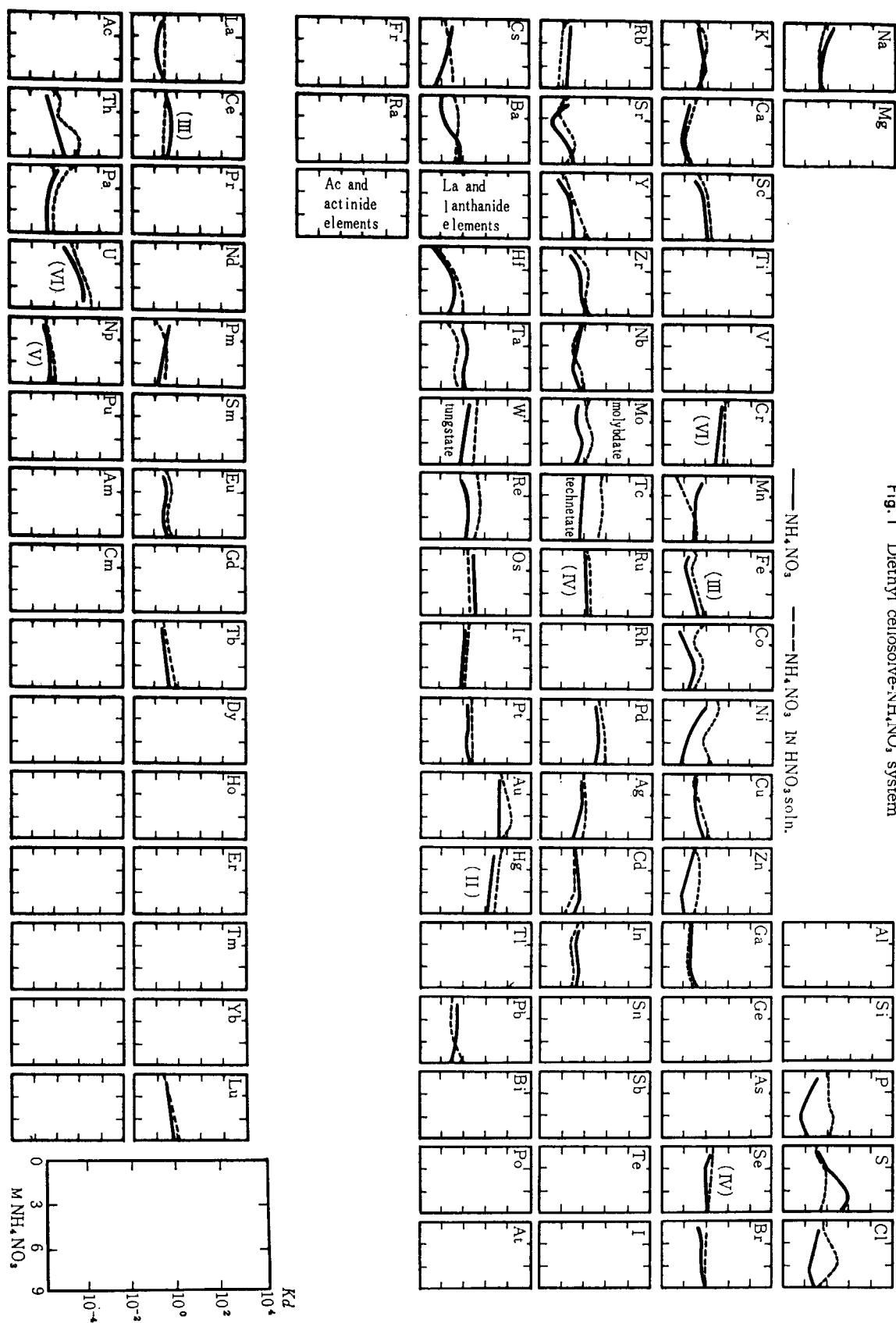
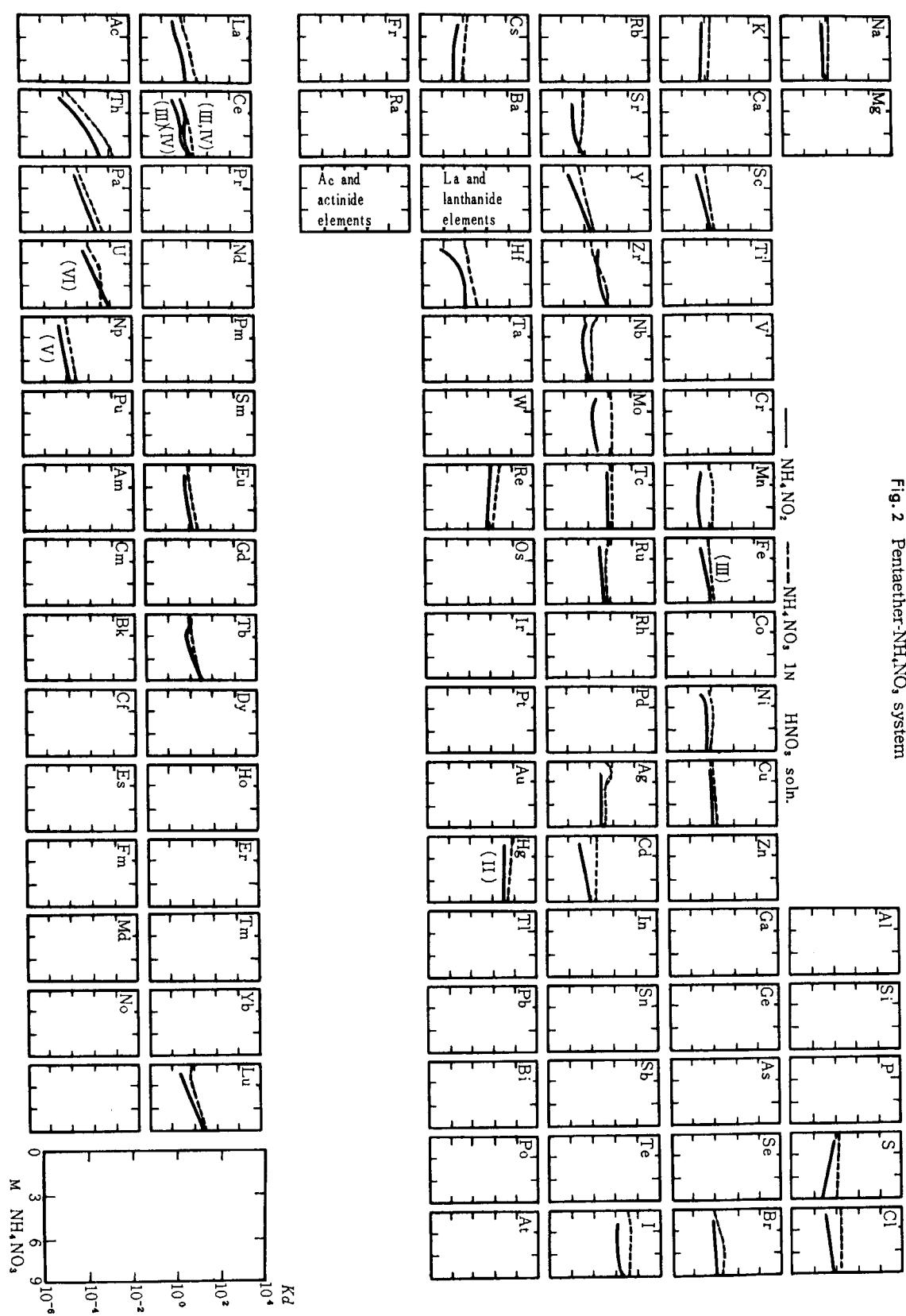
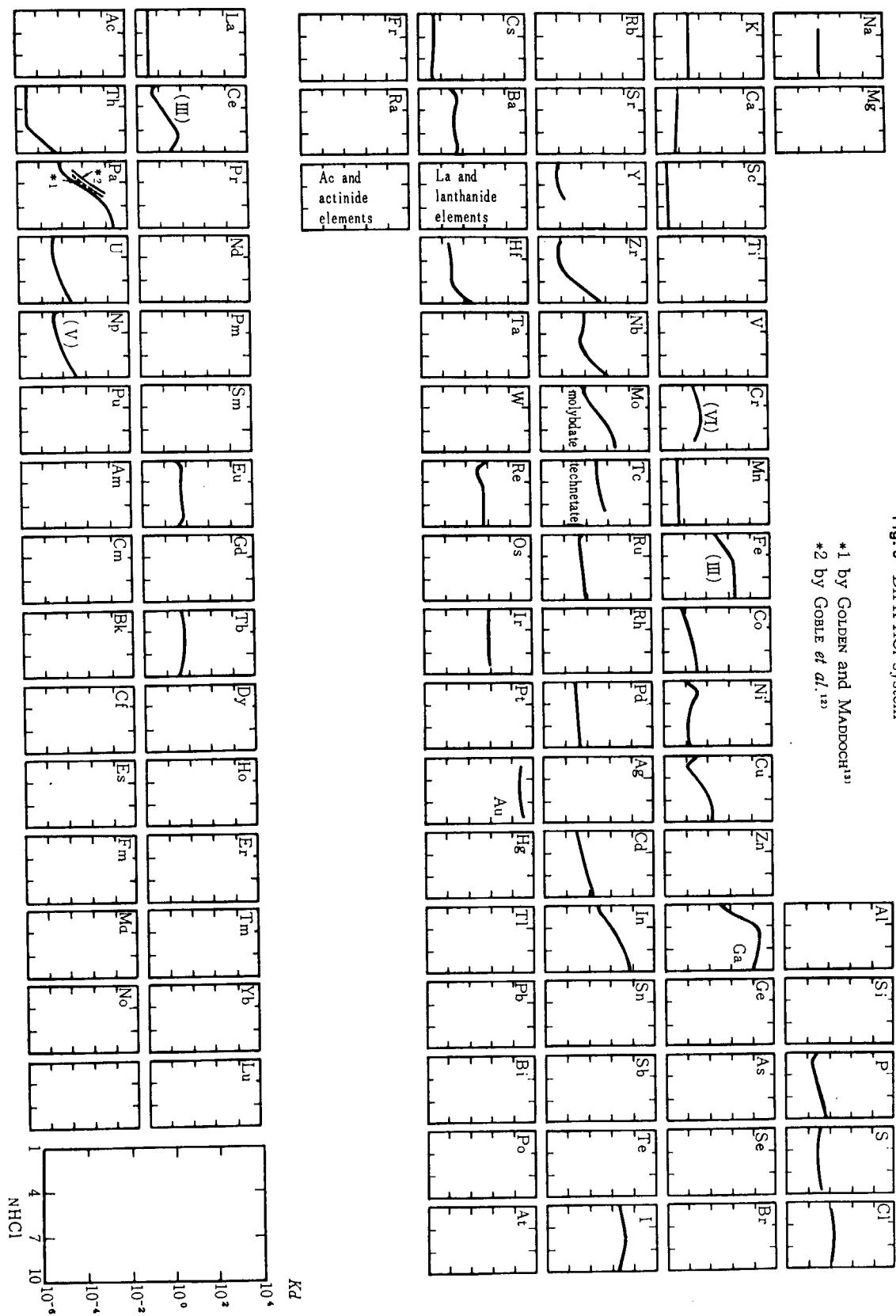
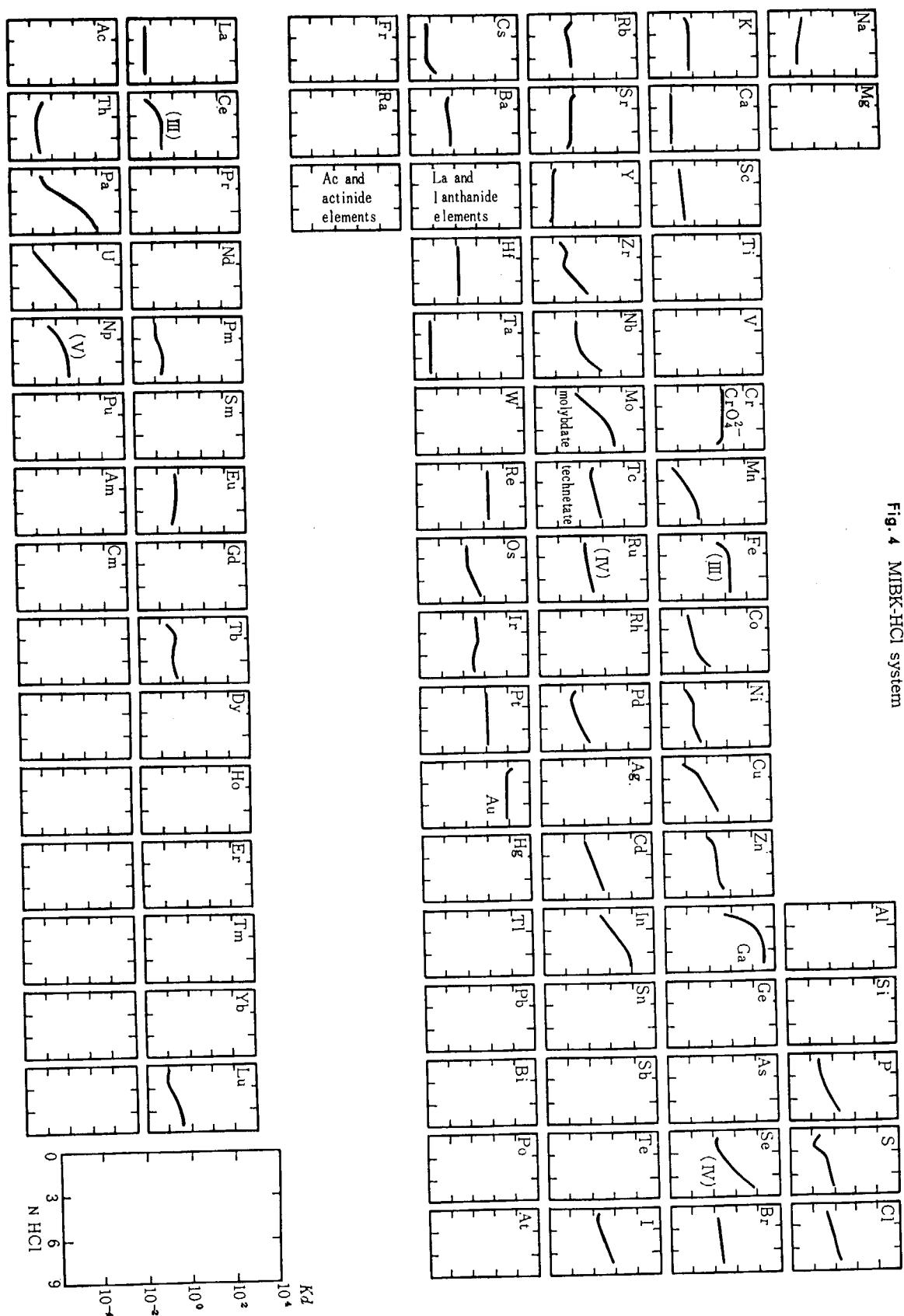


Fig. 2 Pentaether-NH₄NO₃ system





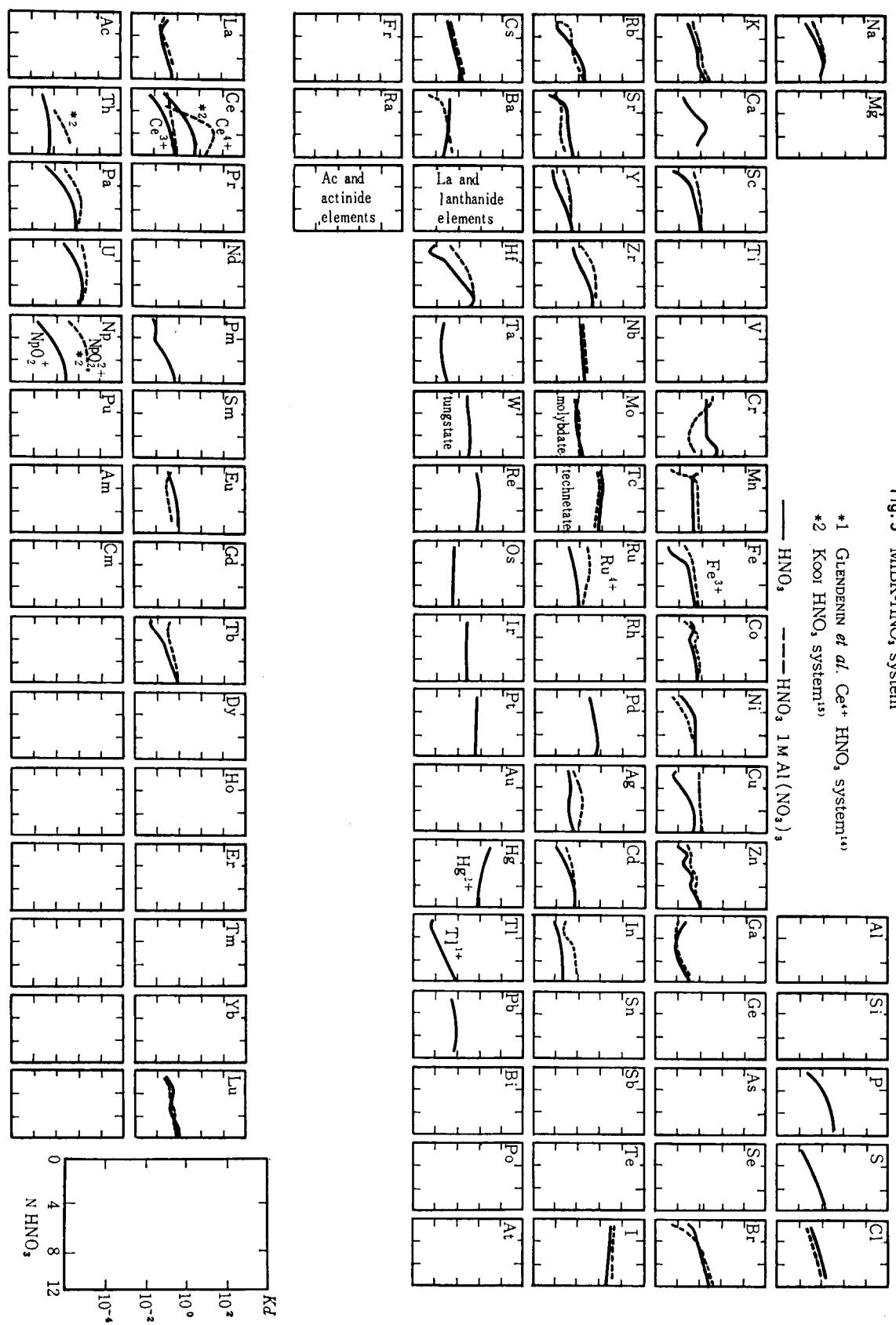
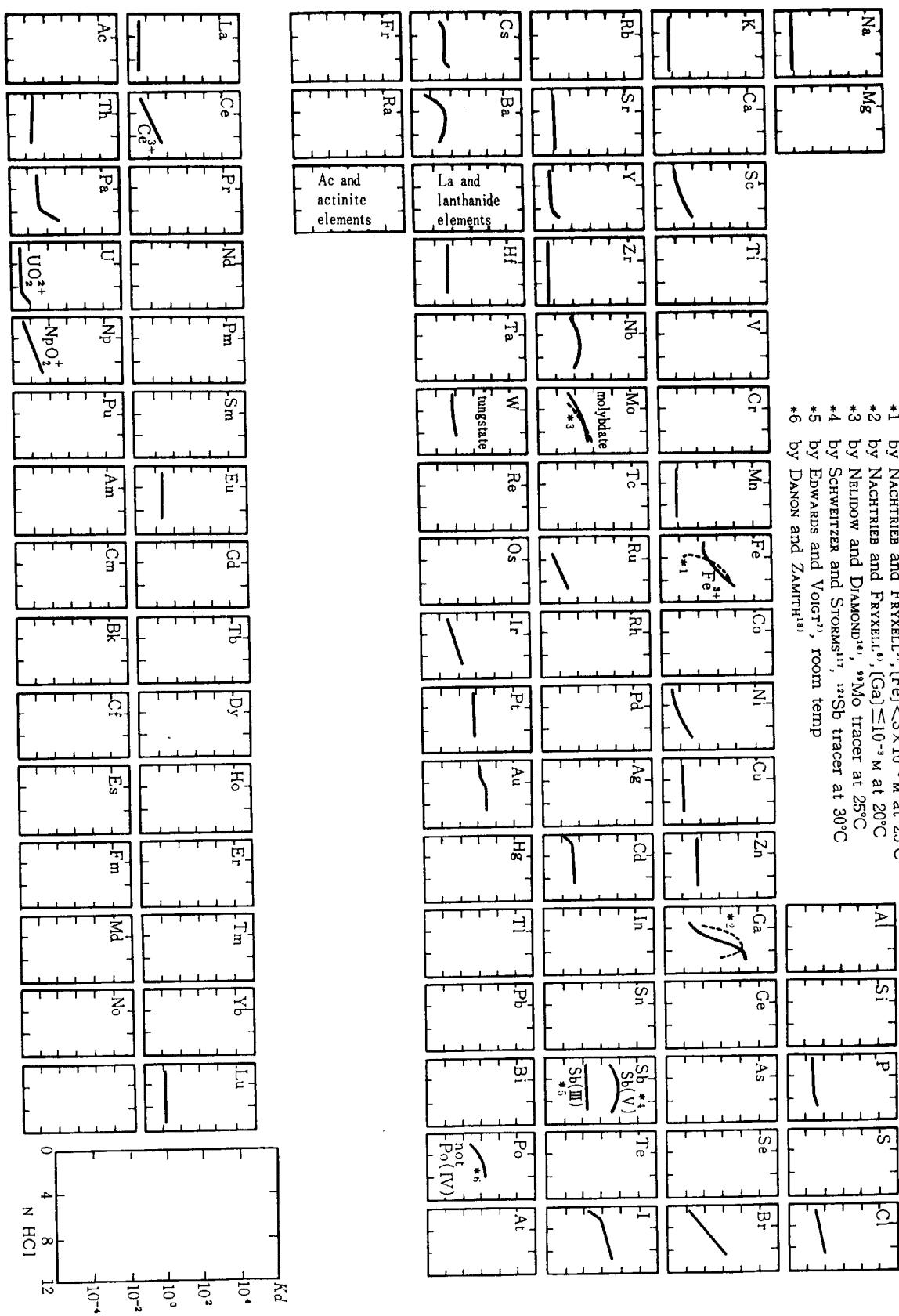
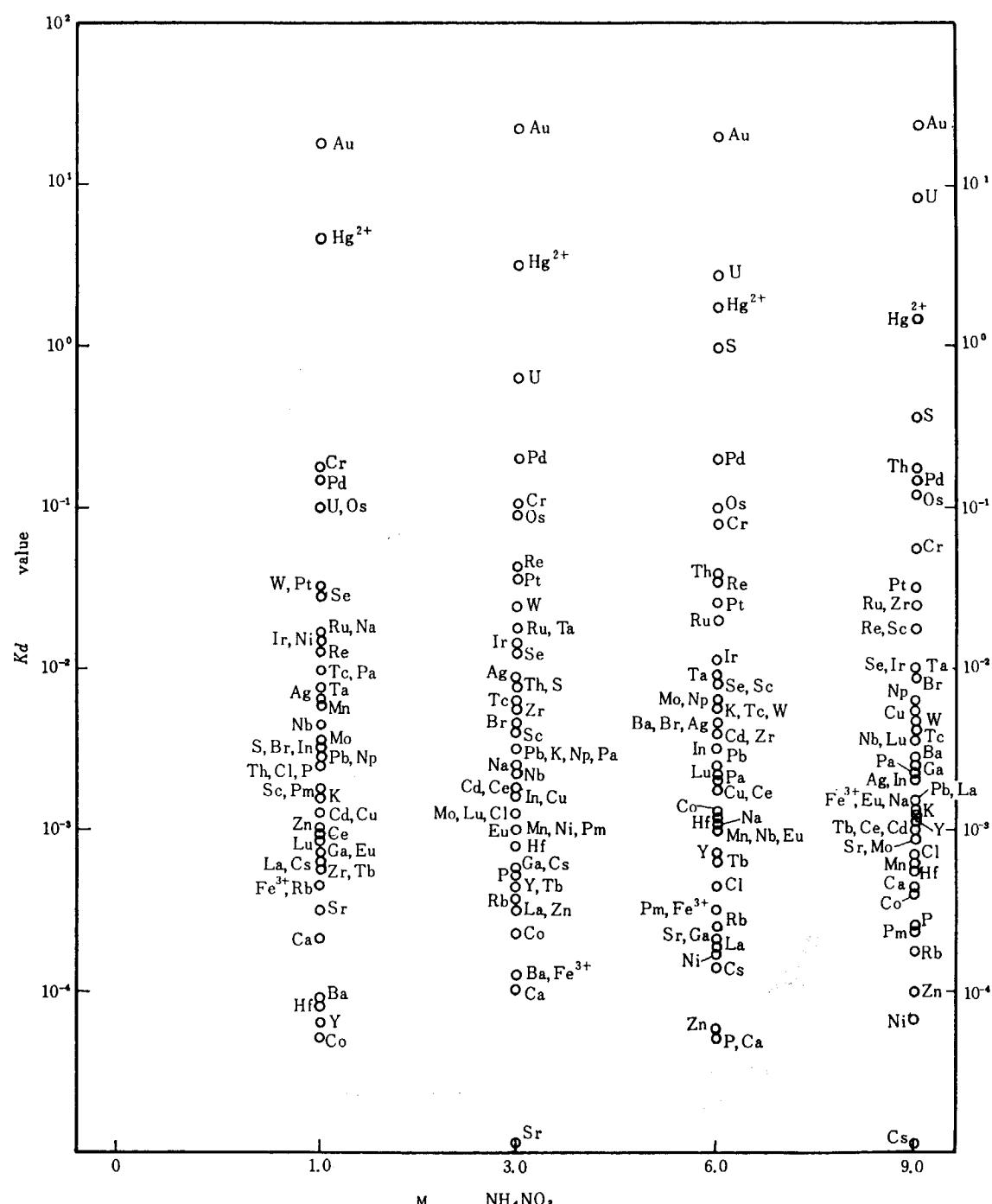


Fig. 6 Isopropyl ether-HCl system

*1 by NACHTRIEB and FRYXELL¹³, [Fe] < 3×10^{-3} M at 25°C
 *2 by NACHTRIEB and FRYXELL¹³, [Ga] $\leq 10^{-3}$ M at 20°C
 *3 by NEILDOW and DIAMOND¹⁴, 99m Mo tracer at 25°C
 *4 by SCHWEITZER and STORMS¹⁵, 113 Sb tracer at 30°C
 *5 by EDWARDS and VOIGT¹⁶, room temp
 *6 by DANON and ZAMIR¹⁸





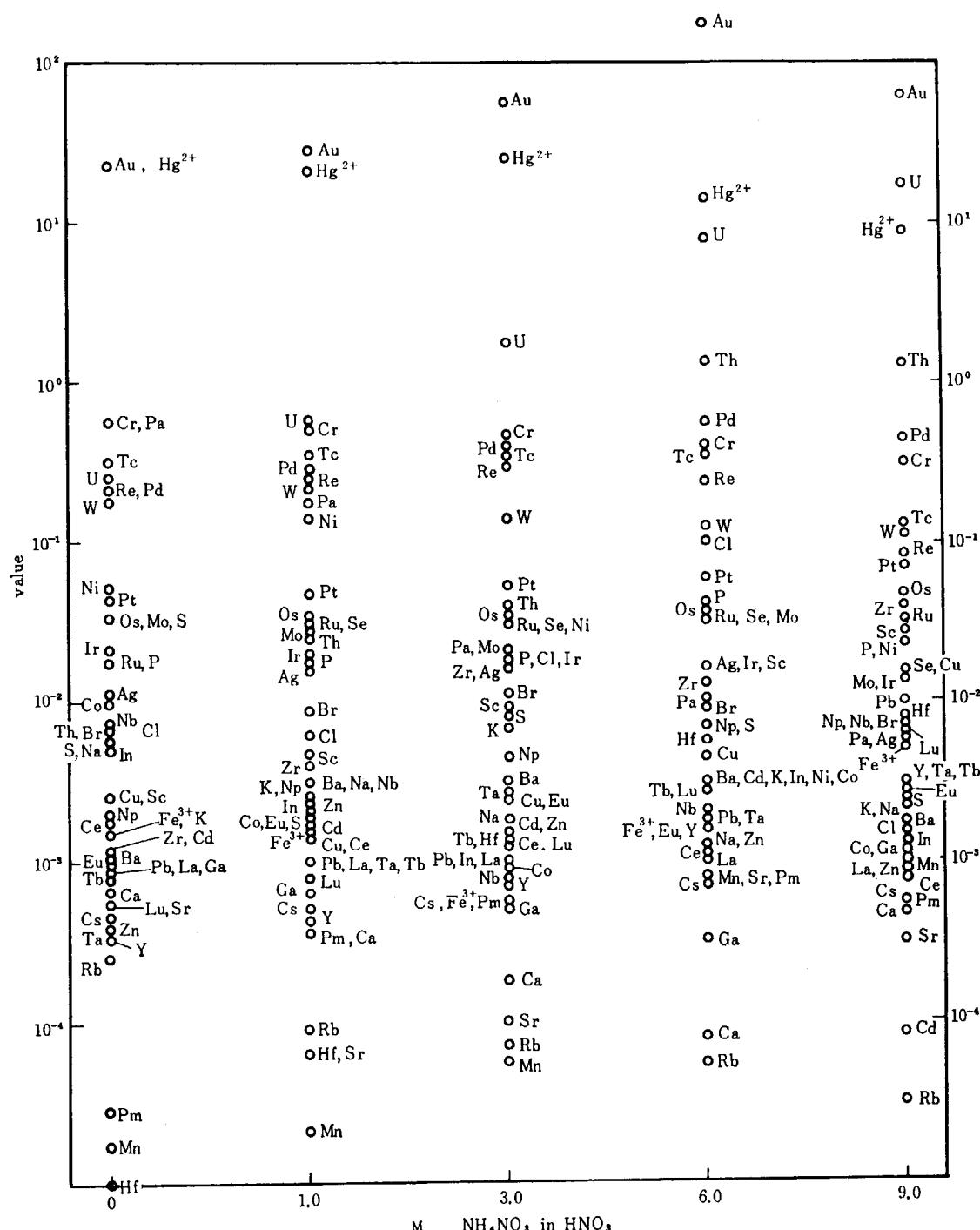
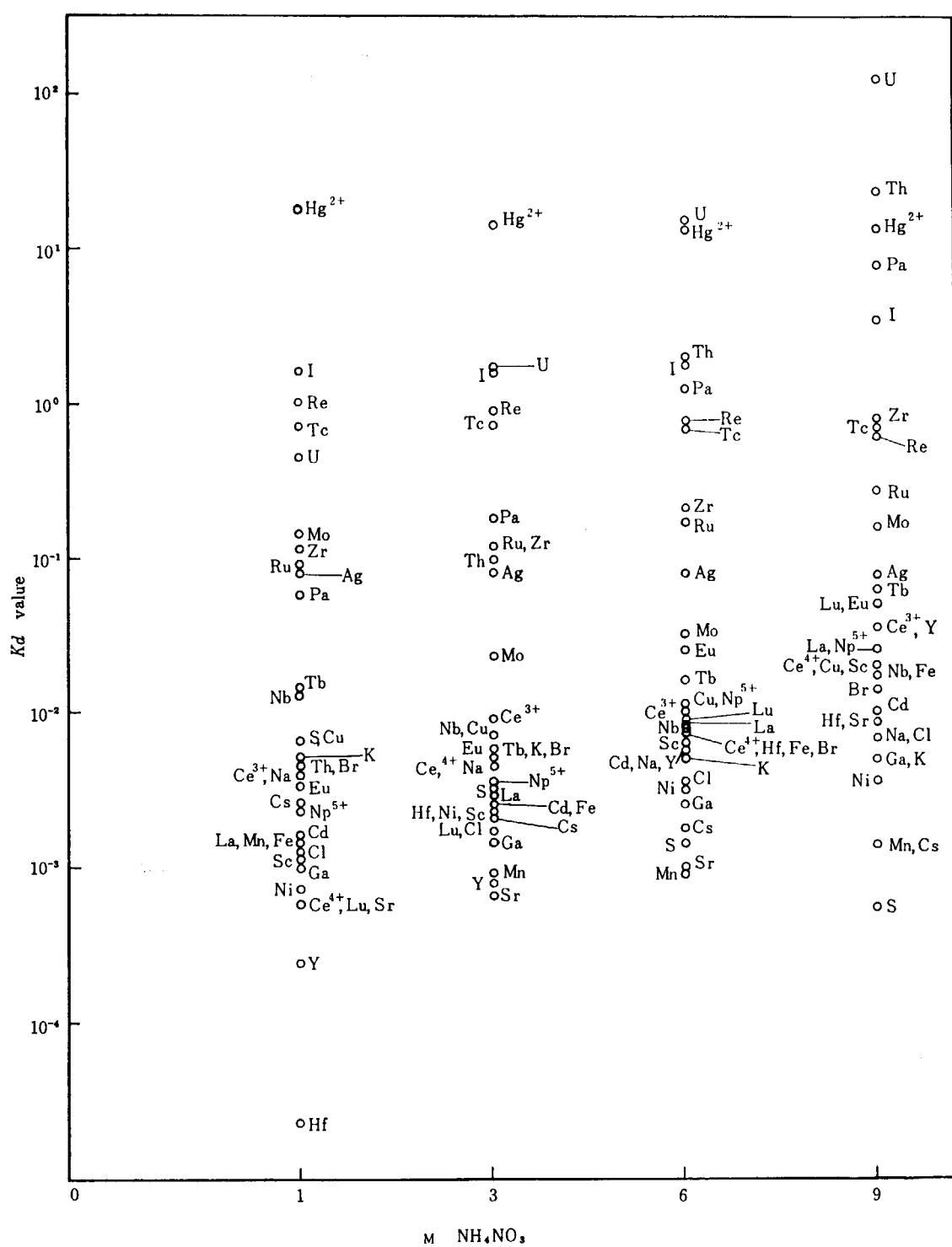
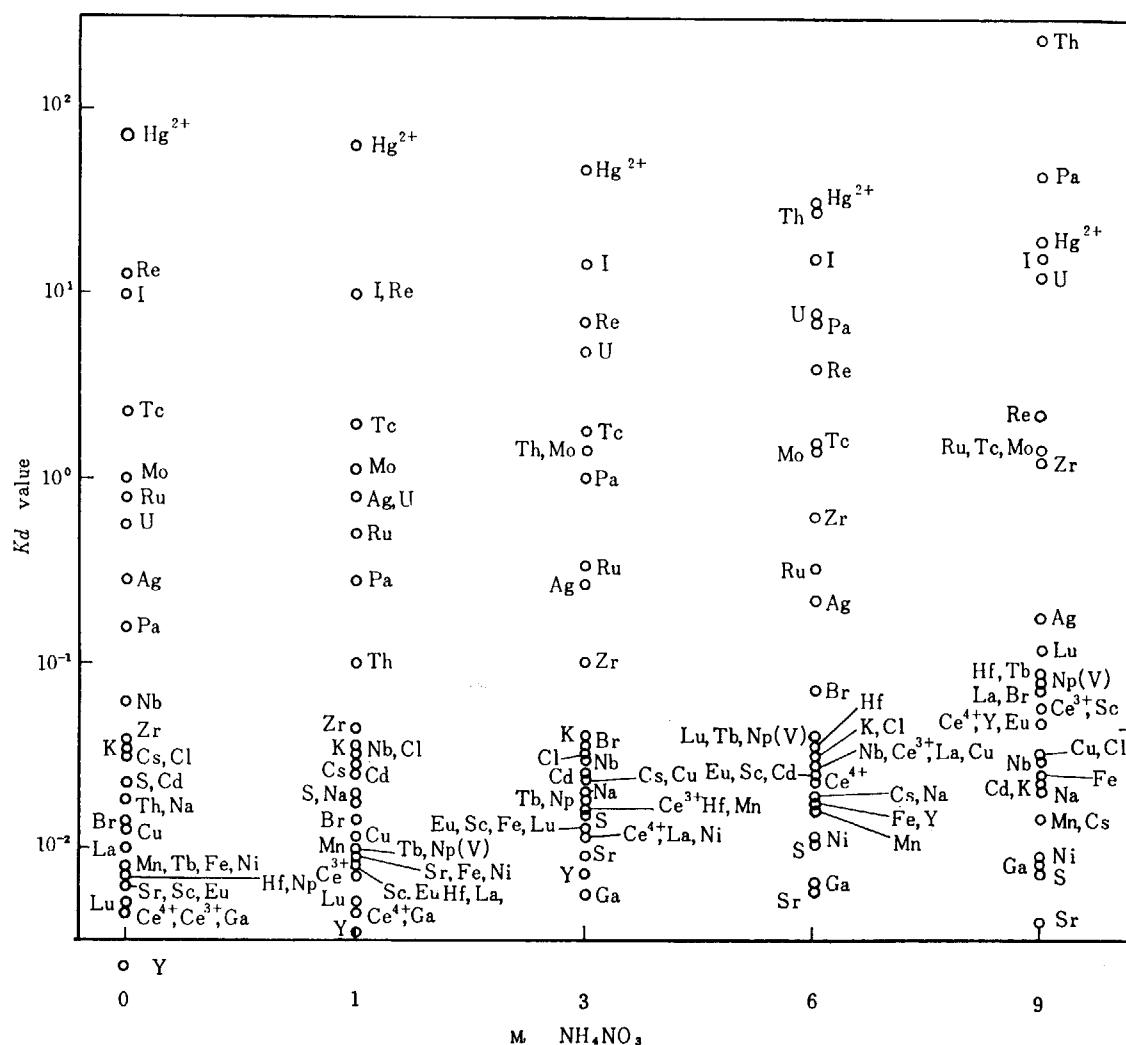


Fig. 8 K_d values in Diethyl Cellosolve- NH_4NO_3 -1N HNO_3 system

Fig. 9 K_d values in Pentaether- NH_4NO_3 system

Fig. 10 K_d values in Petaether- NH_4NO_3 -1N HNO_3 system

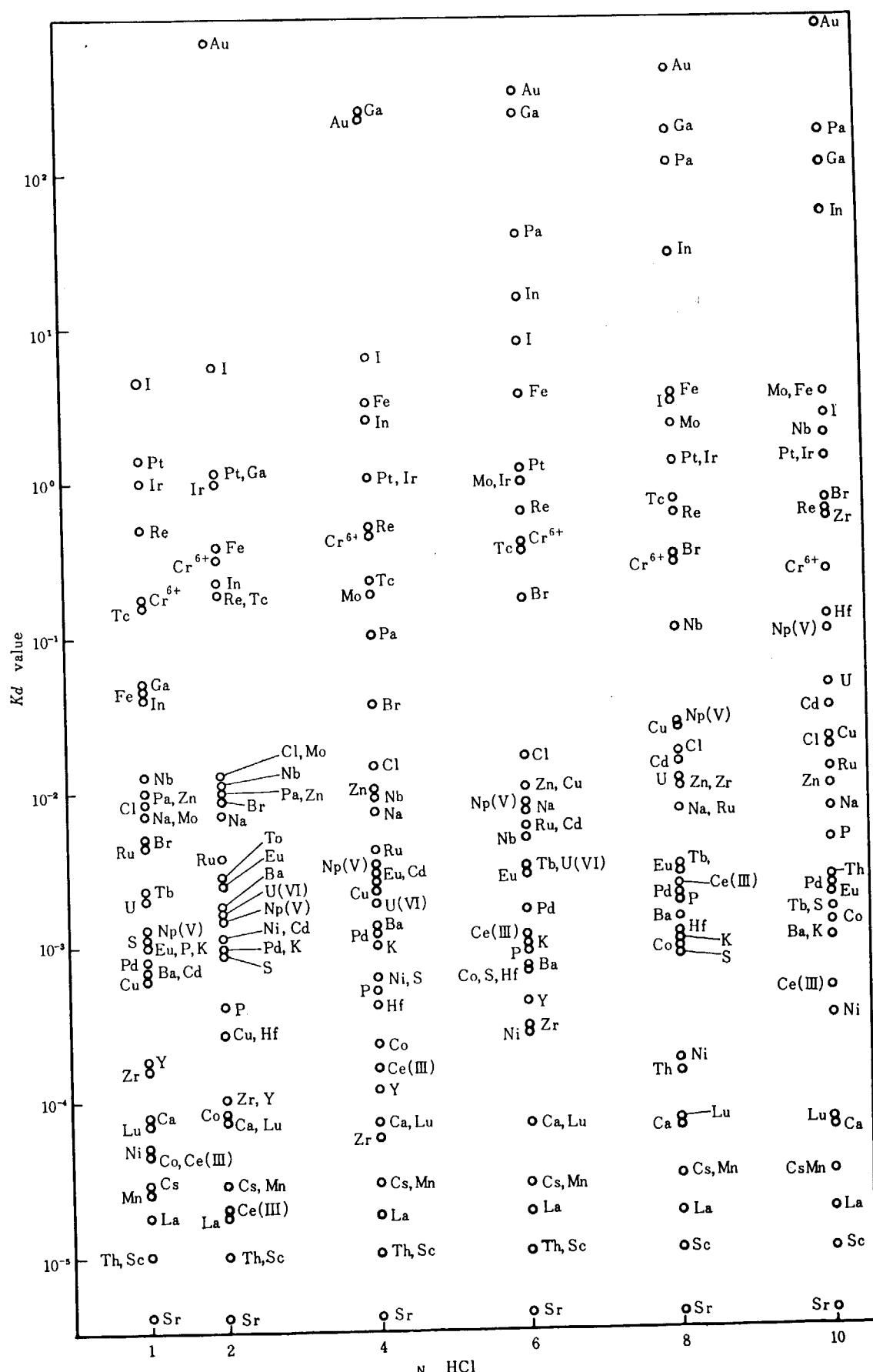
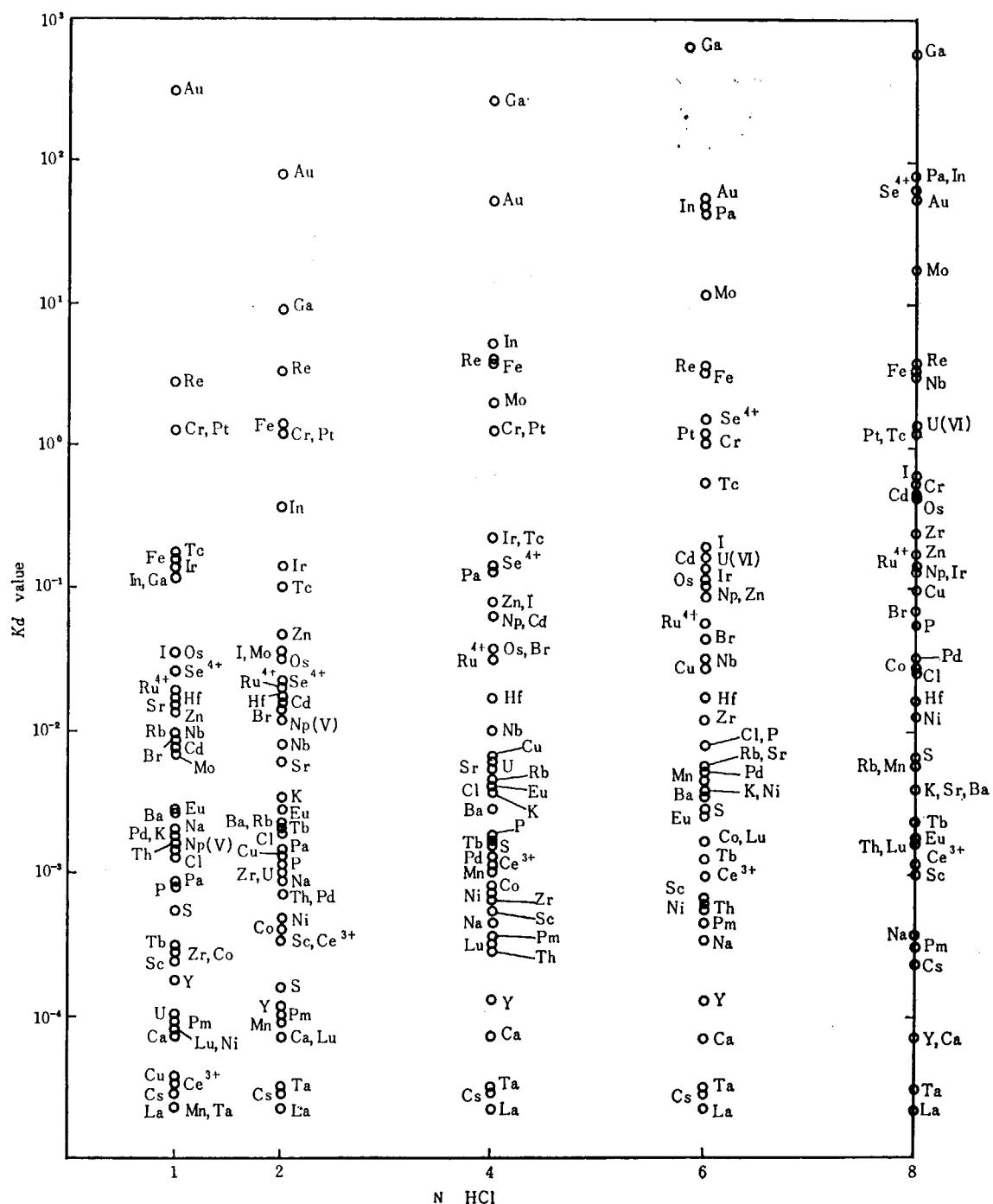
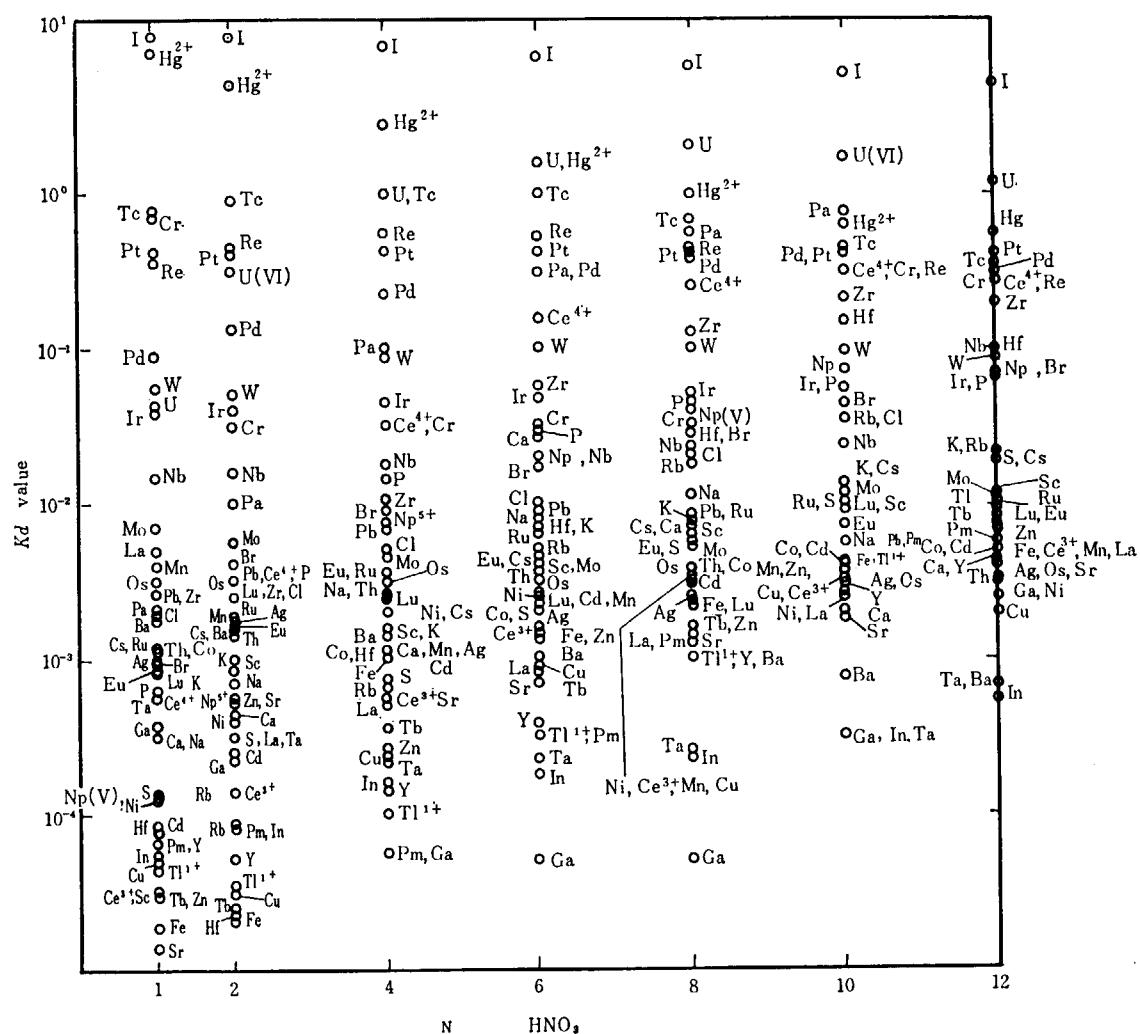


Fig. 11 K_d values in DIPK-HCl system

Fig. 12 K_d values in Hexone-HCl system

Fig. 13 Kd values in Hexone-HNO₃ system

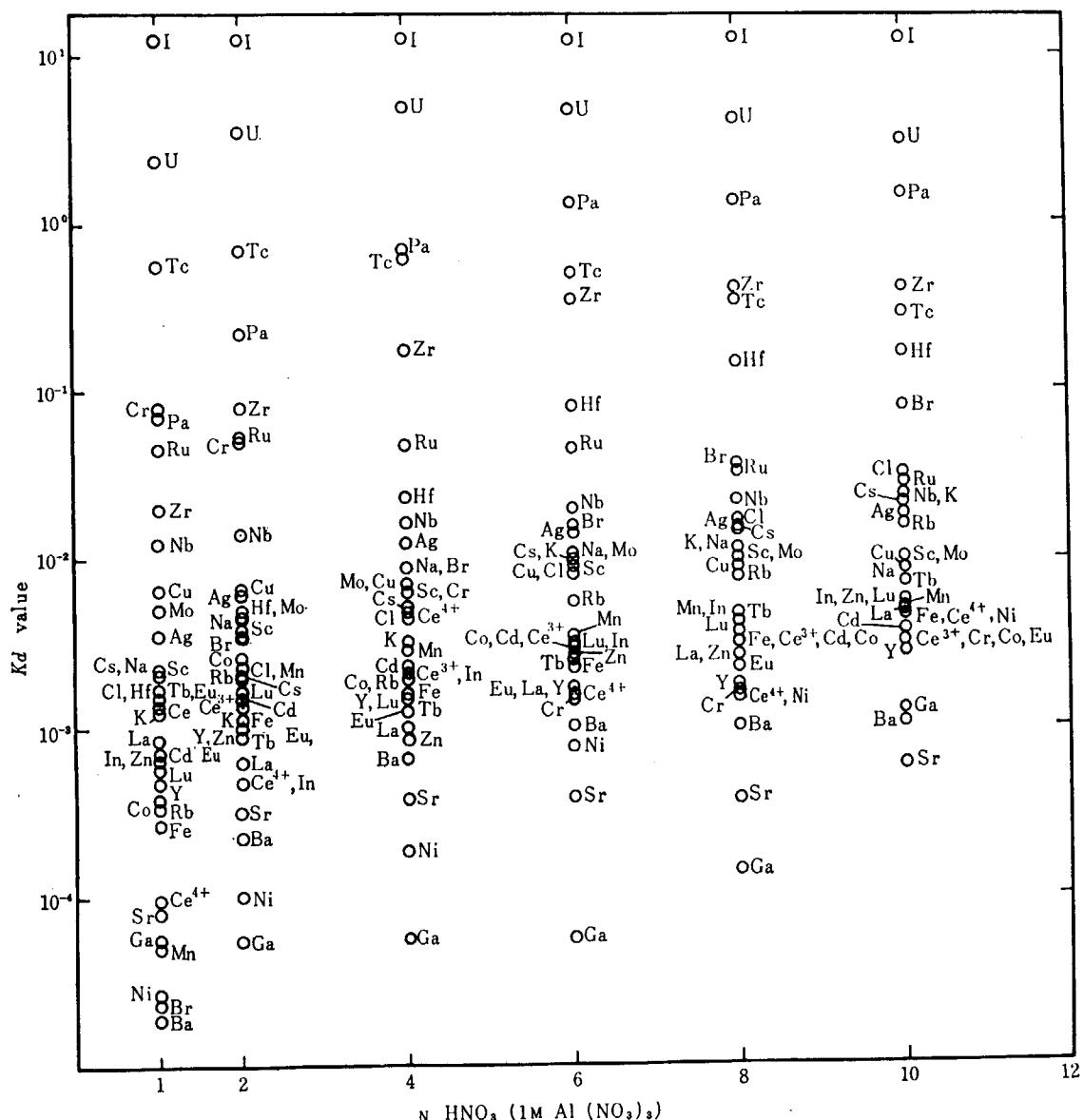
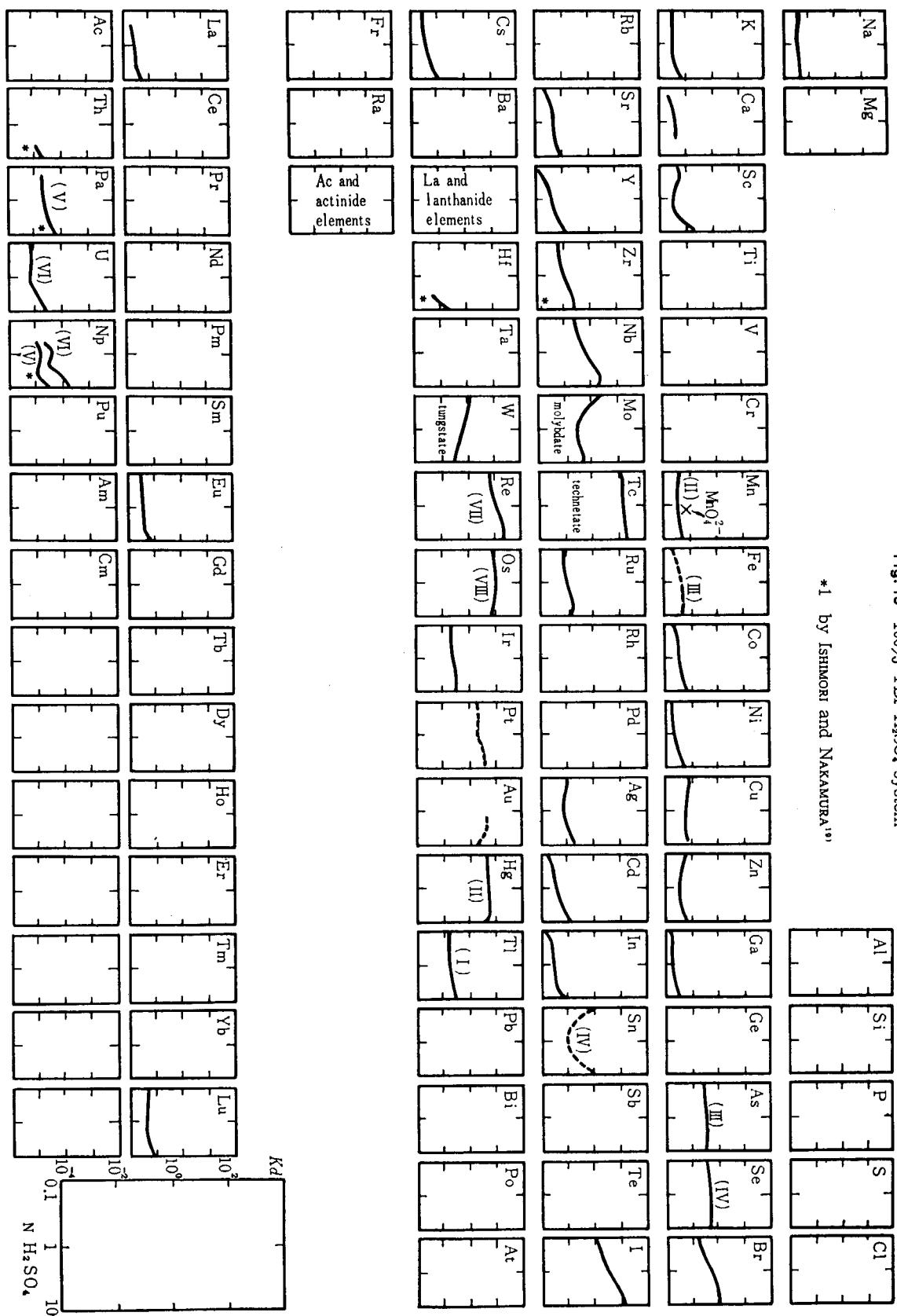
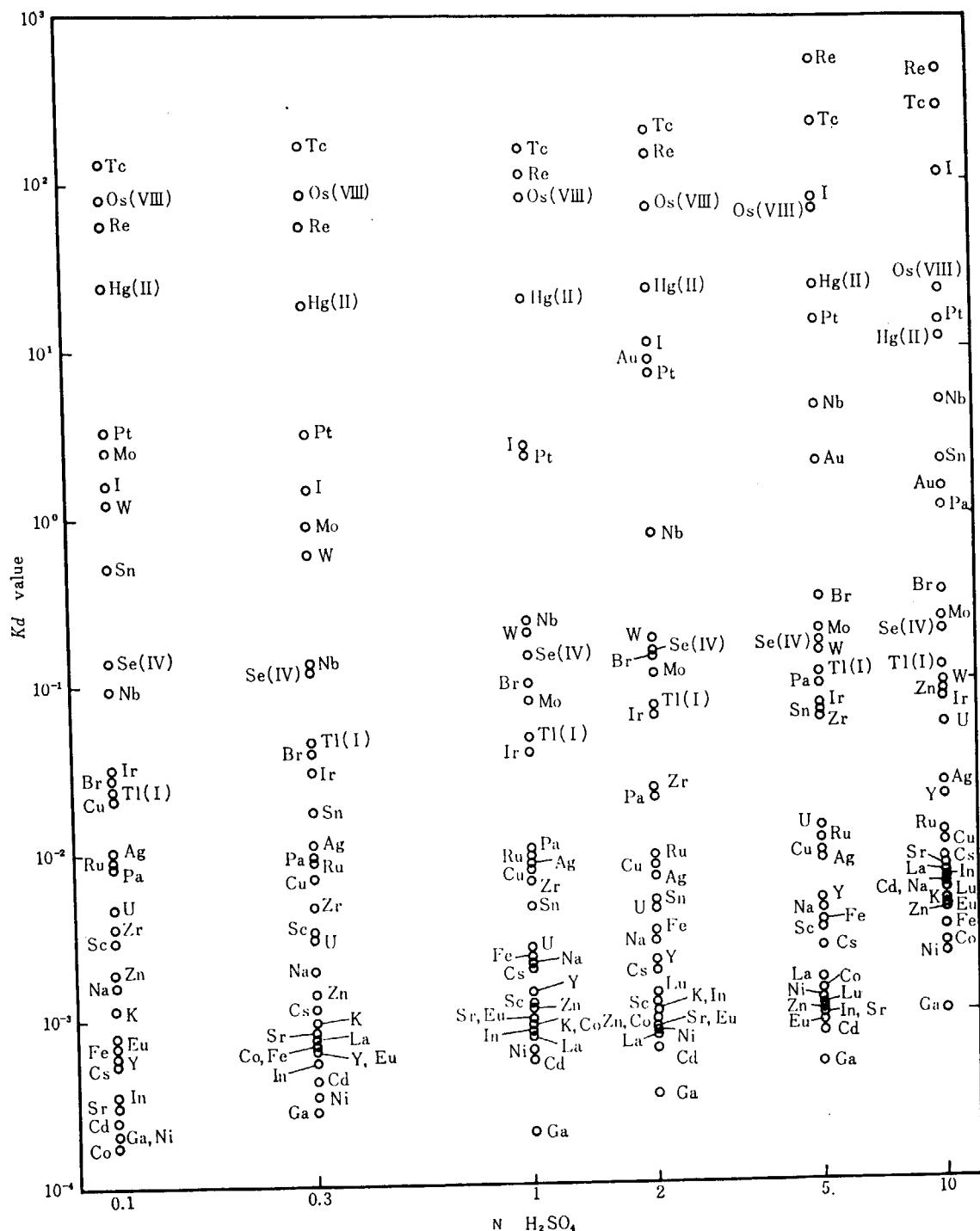
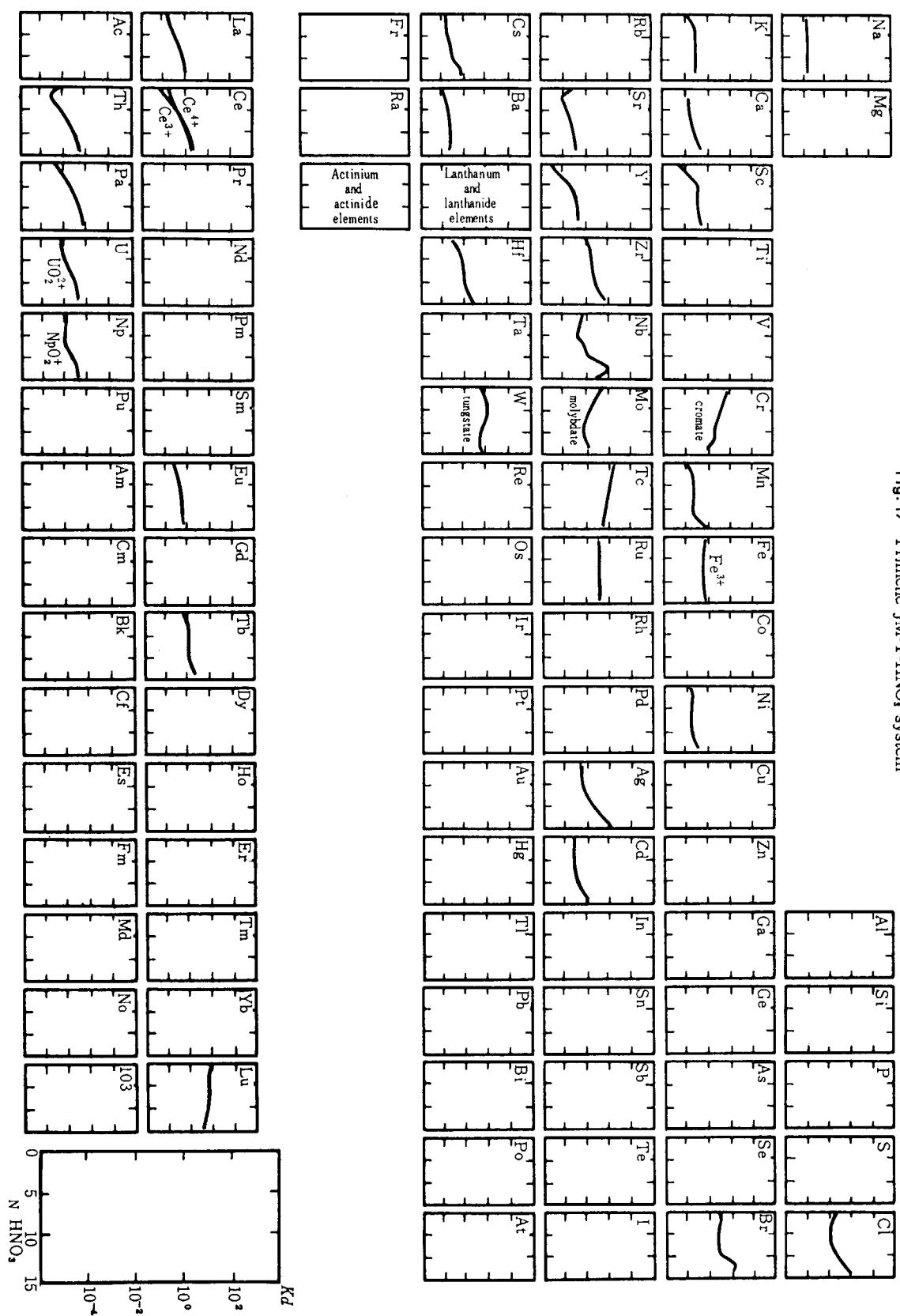


Fig. 14 K_d values in Hexone- HNO_3 -1 M $\text{Al}(\text{NO}_3)_3$ system



Fig. 16 K_d values in 100% TBP- H_2SO_4 system



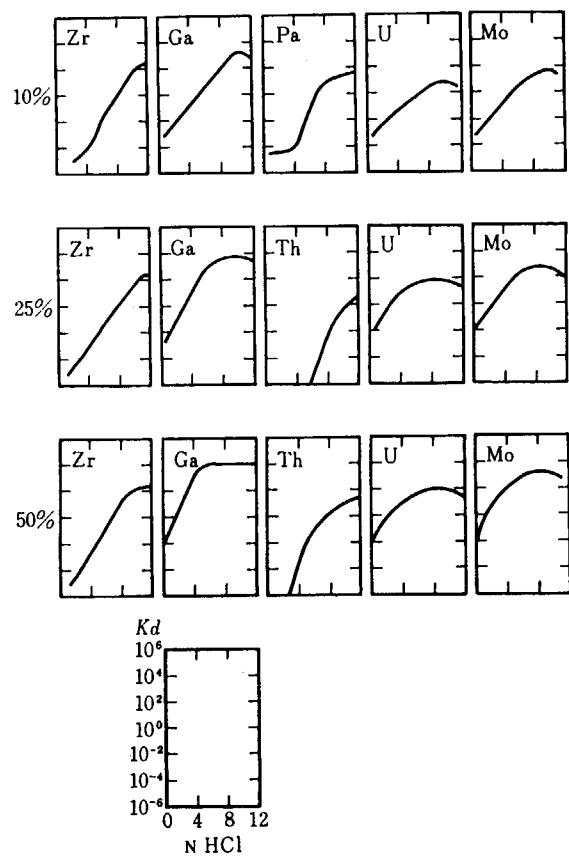
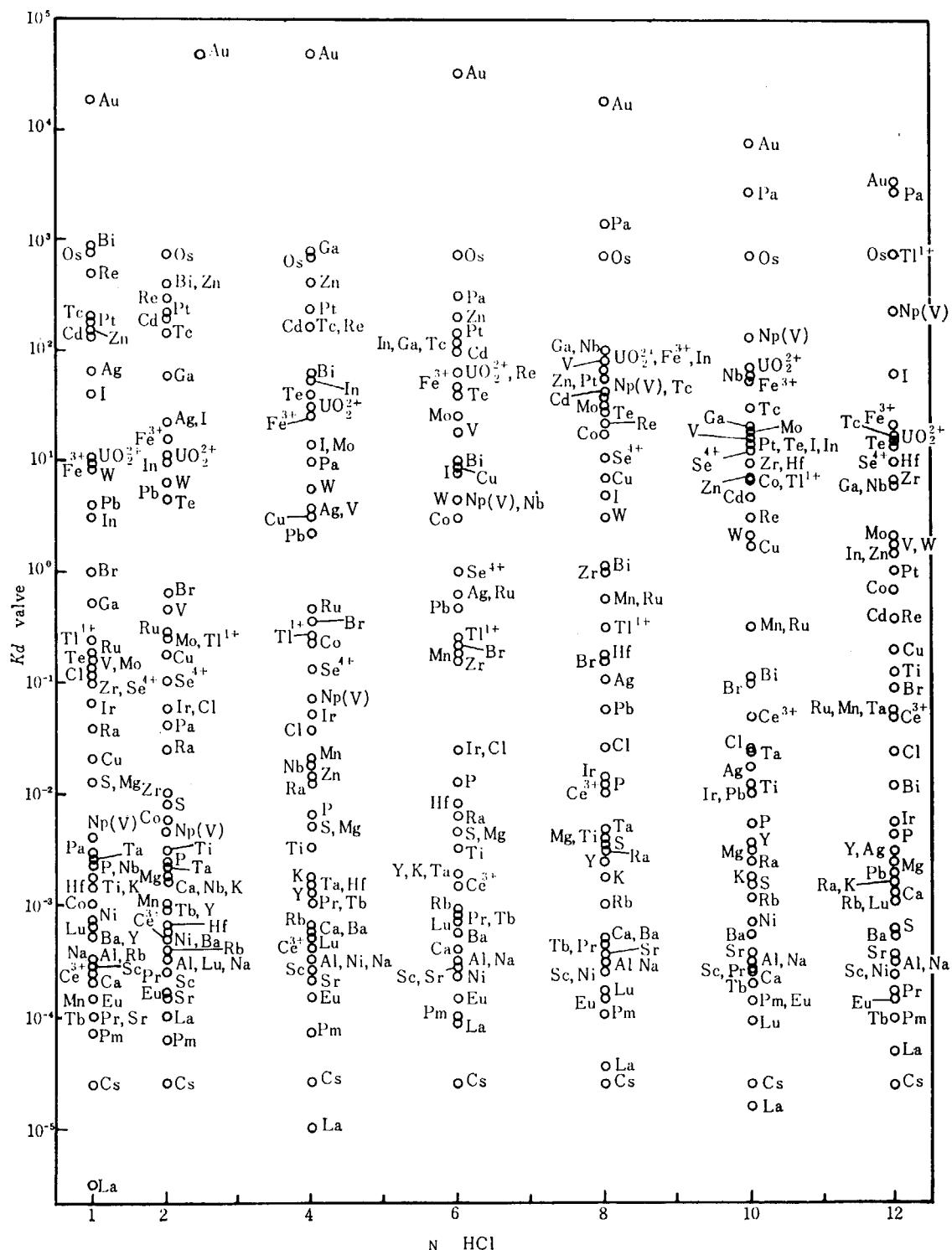


Fig. 18 Corrected data of TBP-HCl system

Fig. 19 K_d values in 5% TIOA-HCl system

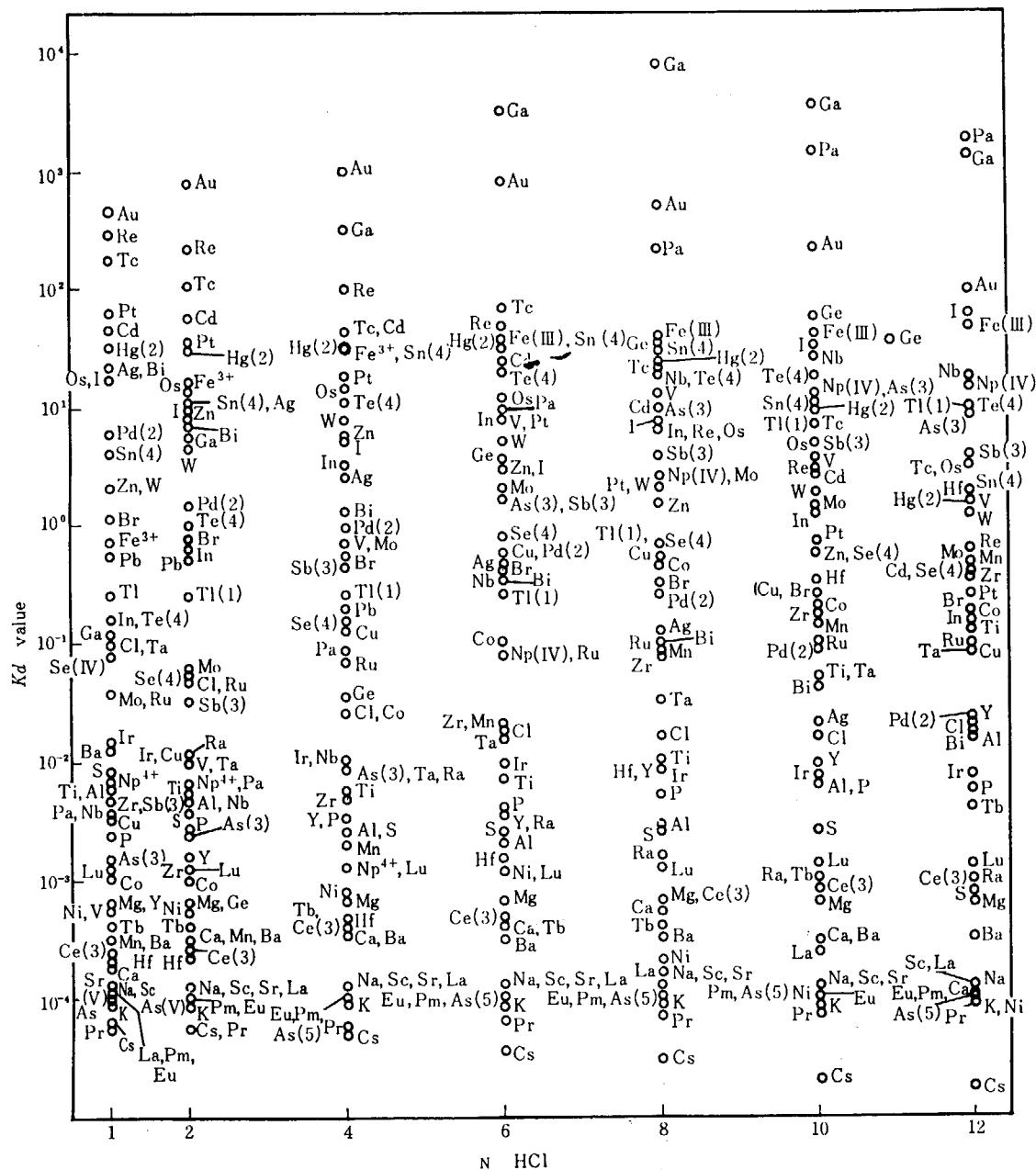
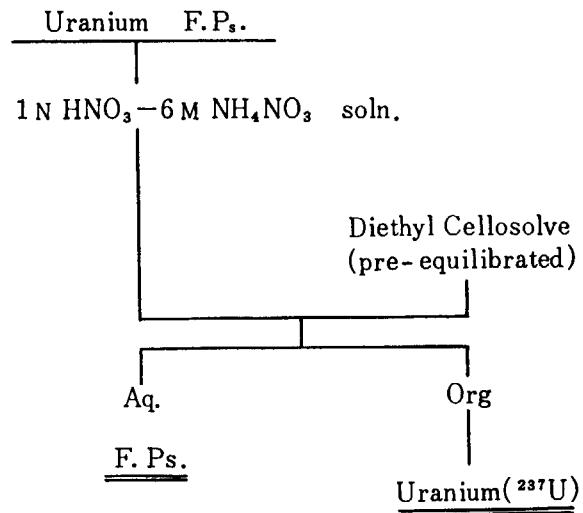
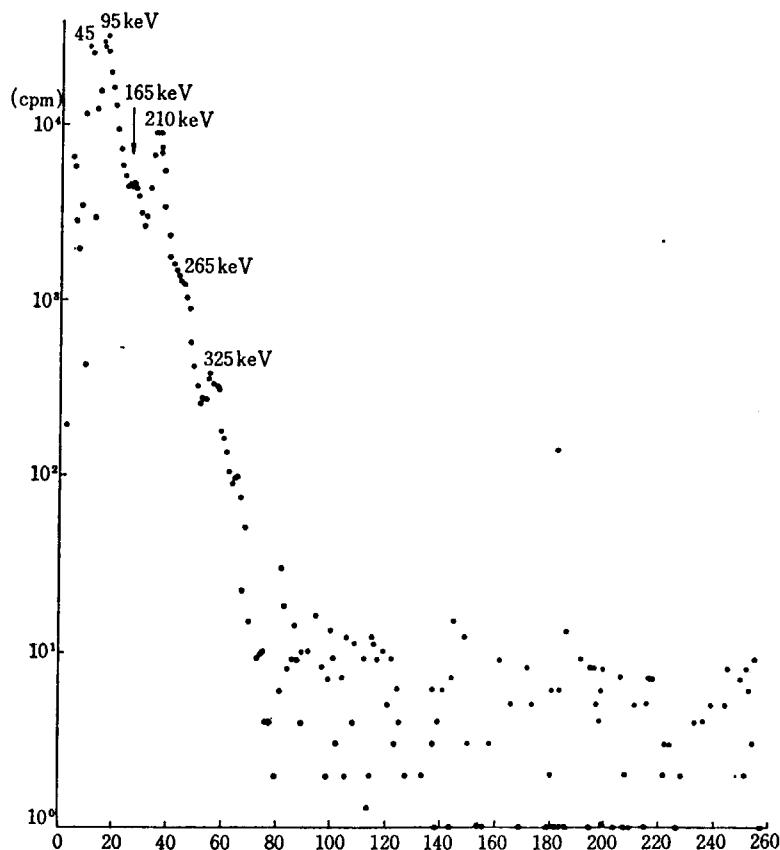
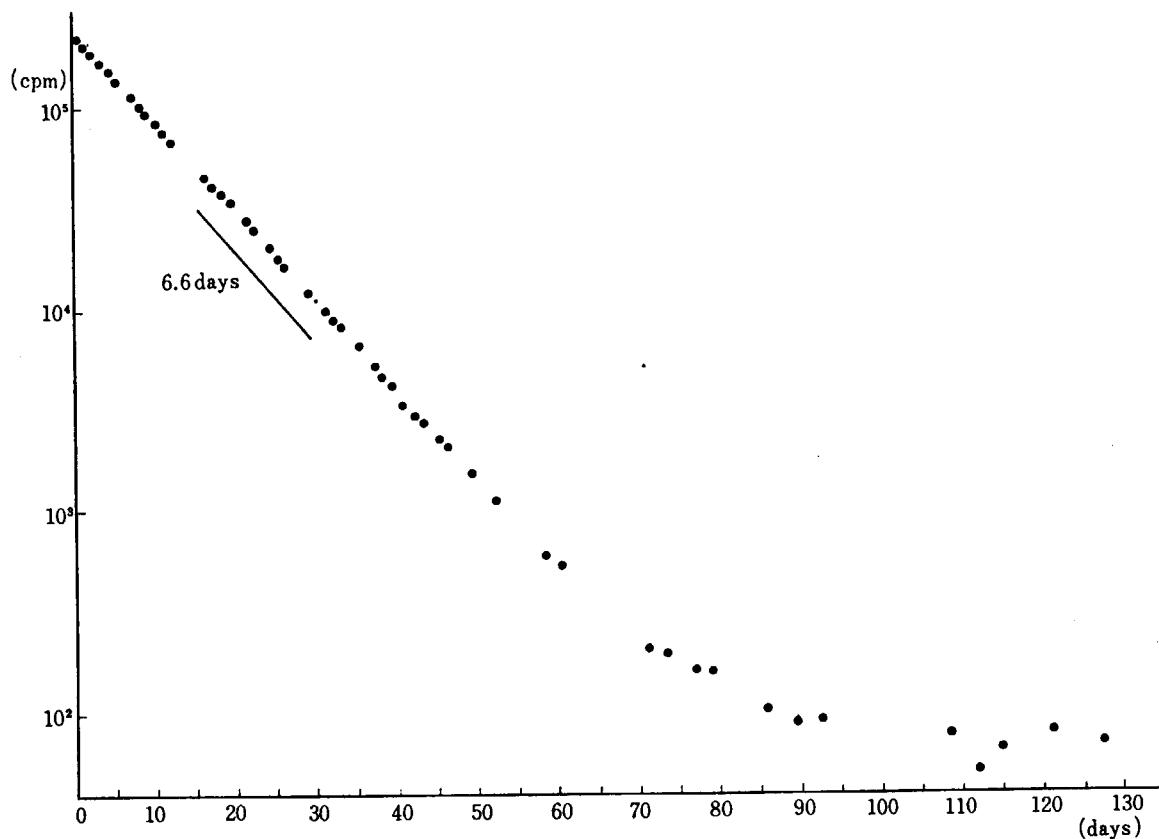
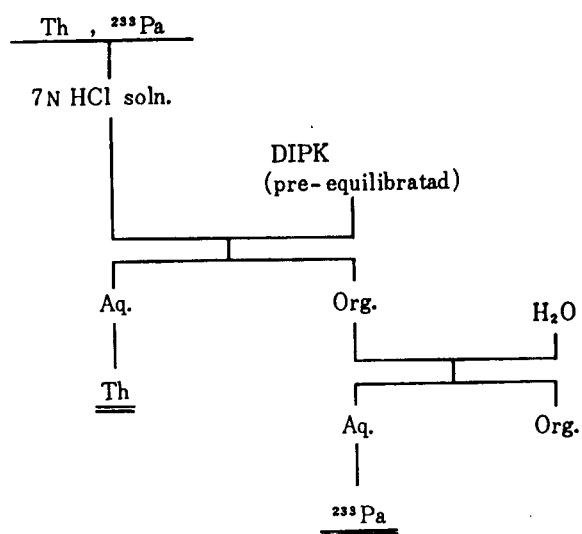


Fig. 20 K_d value in 10% Amberlite LA-1-HCl system

Fig. 21 The method of preparation of ^{237}U Fig. 22 Gamma ray spectrum of ^{237}U

Fig. 23 ^{233}U decay (Diethyl Cellosolve method)Fig. 24 The separation of ^{233}Pa from thorium

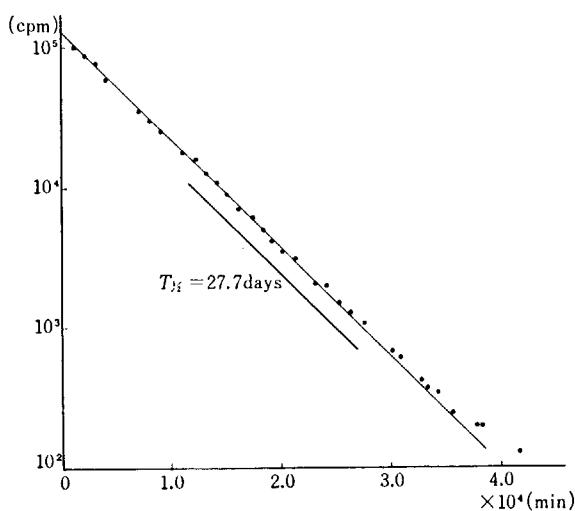
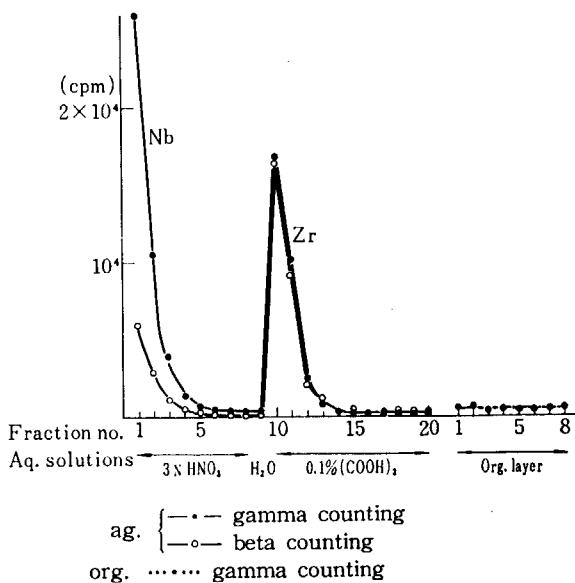
Fig. 25 The decay curve of ^{233}Pa prepared

Fig. 26 Results of Countercurrent Separation of Zr and Nb

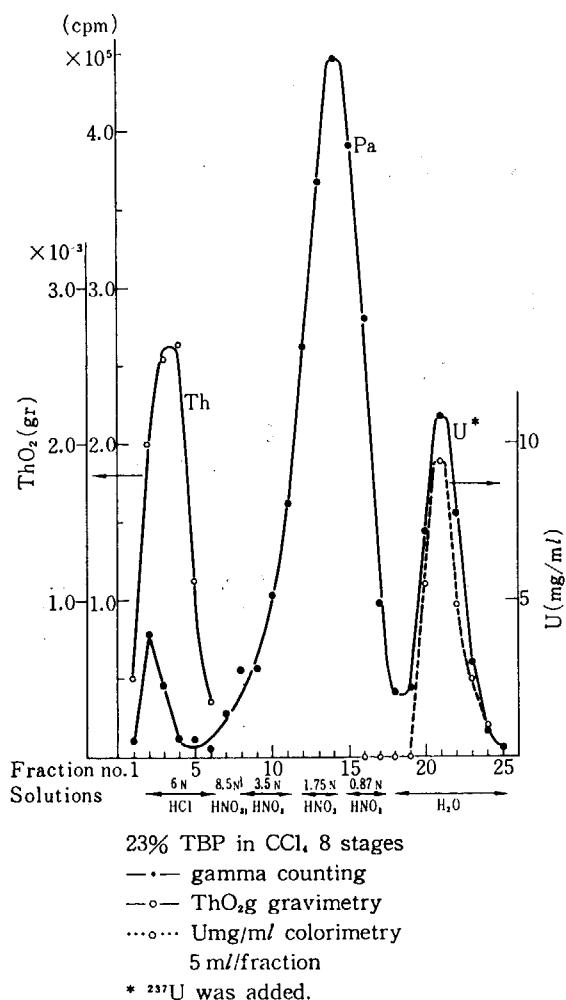


Fig. 27 Results of Countercurrent Separation of U, Pa and Th.

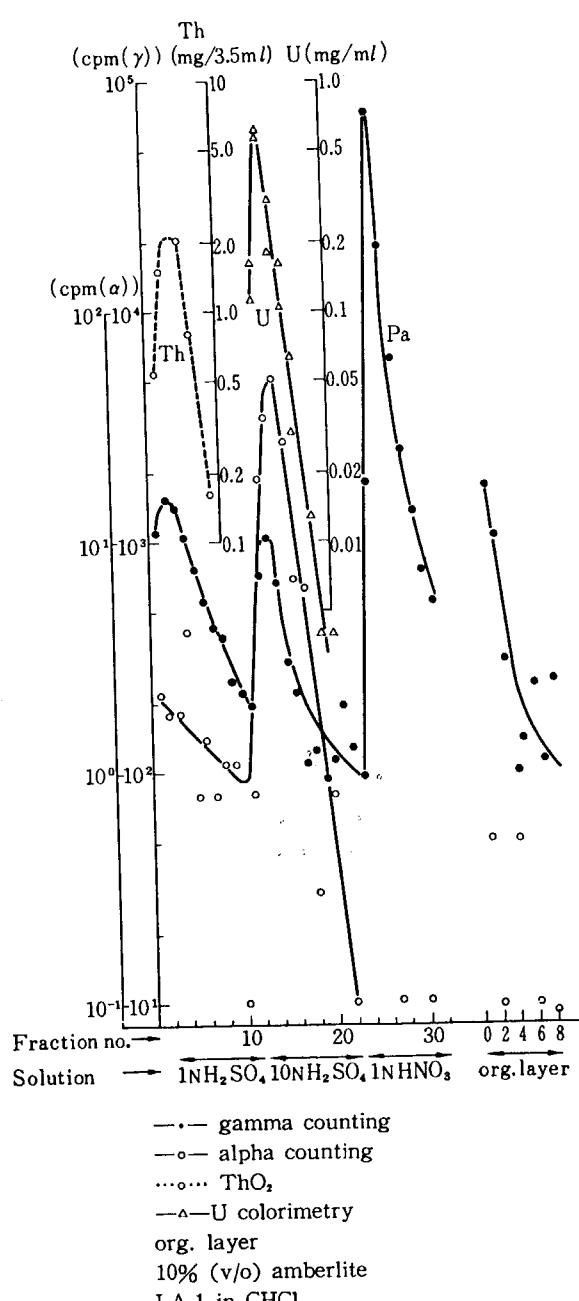


Fig. 28 Results of Countercurrent Separation of U, Pa and Th.

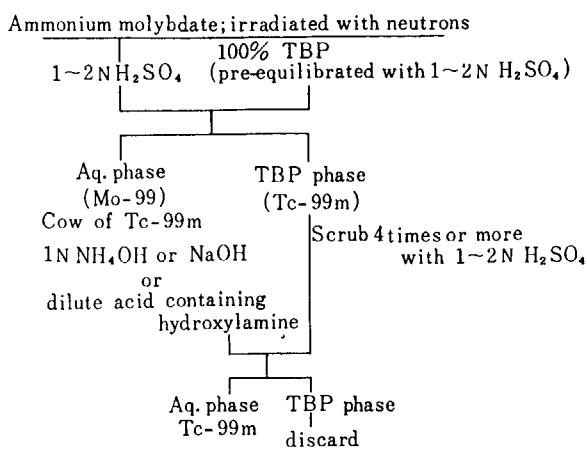


Fig. 29 The method of preparation of ^{99m}Tc

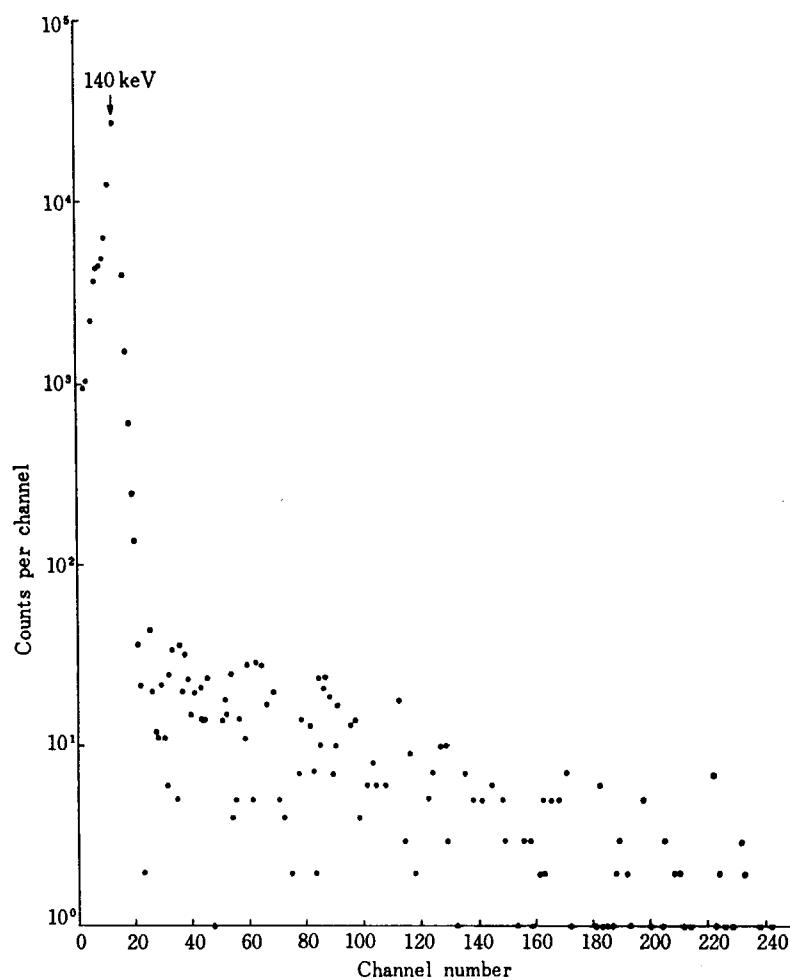
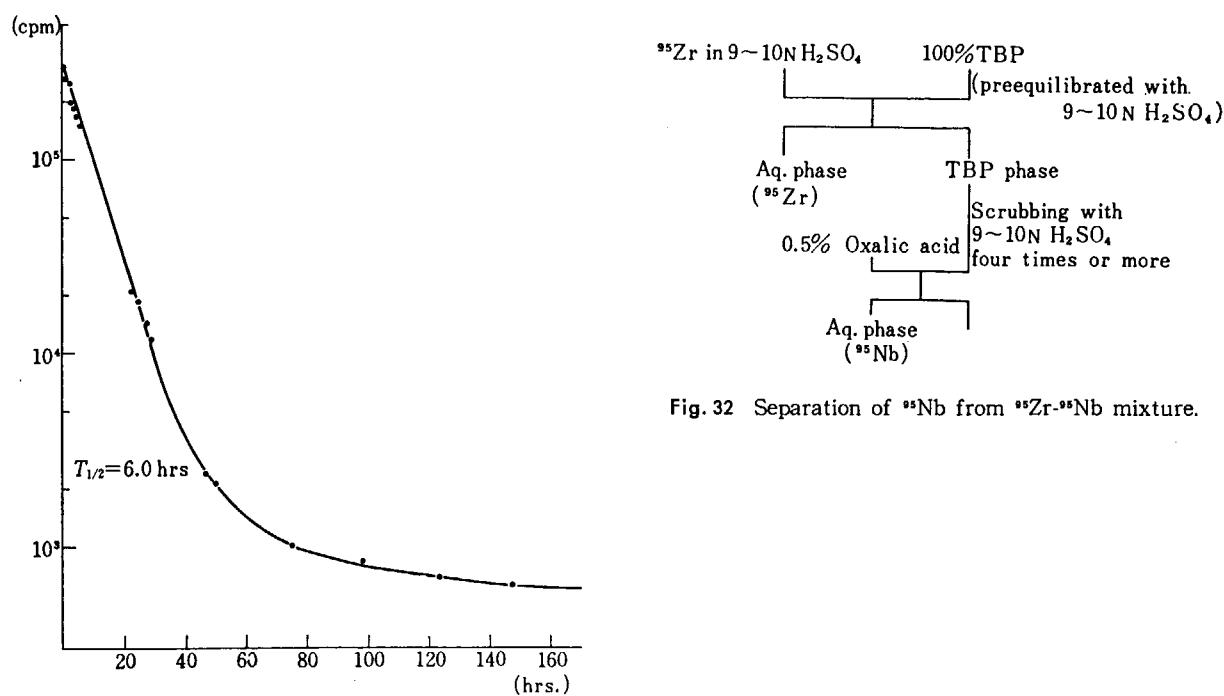
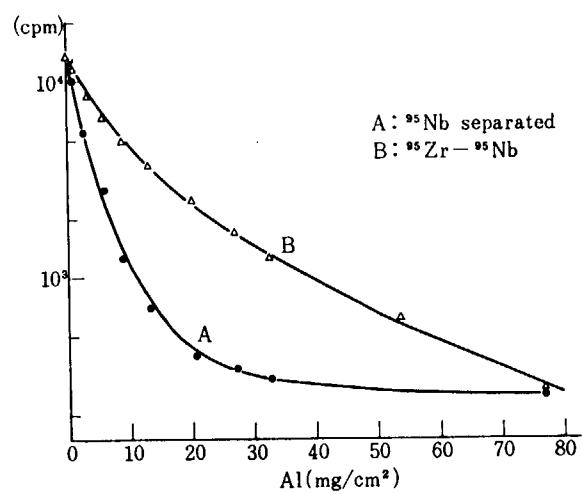
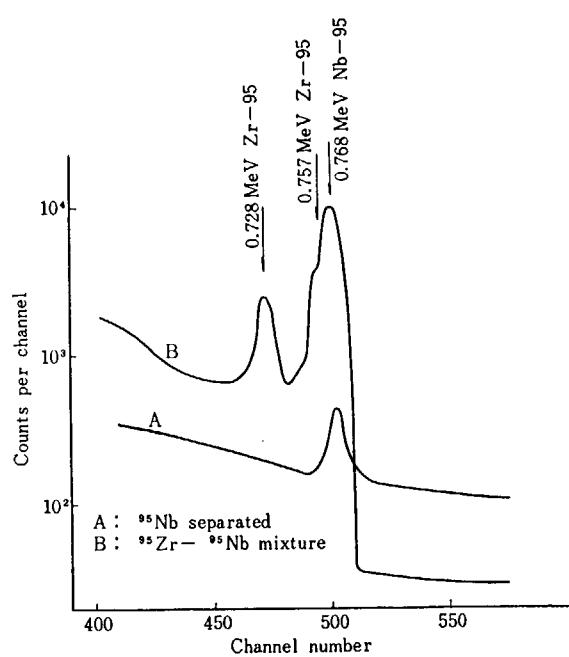
Fig. 30 Gamma ray spectrum of a ^{99m}Tc sample

Fig. 31 Decay curve of Tc-99m sample

Fig. 32 Separation of ^{95}Nb from $^{95}\text{Zr}-^{95}\text{Nb}$ mixture.

Fig. 33 β ray absorption curvesFig. 34 Gamma ray spectra of ^{95}Nb and $^{95}\text{Zr}-^{95}\text{Nb}$