

Studies on the Solvent Extraction of  
Actinide Elements  
by Organophosphorus Compounds

---

1967 年 3 月

---

日本原子力研究所

Japan Atomic Energy Research Institute

日本原子力研究所は、研究成果、調査結果の報告のため、つぎの3種の研究報告書を、それぞれの通しナンバーを付して、不定期に公刊しております。

- |         |                                  |                 |
|---------|----------------------------------|-----------------|
| 1. 研究報告 | まとまった研究の成果あるいはその一部における重要な結果の報告   | JAERI 1001-3999 |
| 2. 調査報告 | 総説、展望、紹介などを含め、研究の成果、調査の結果をまとめたもの | JAERI 4001-5999 |
| 3. 資料   | 研究成果の普及、開発状況の紹介<br>施設共同利用の手引など   | JAERI 6001-6999 |

このうち既刊分については「JAERI レポード一覧」にタイトル・要旨をまとめて掲載し、また新刊レポートは「原研びおりお」でその都度紹介しています。これらの研究報告書に関する頒布、版權、複写のお問合せは、日本原子力研究所技術情報部（茨城県那珂郡東海村）あてお申し越しください。

---

Japan Atomic Energy Research Institute publishes the nonperiodical reports with the following classification numbers:

1. **JAERI 1001-3999** Research reports,
2. **JAERI 4001-5999** Survey reports and reviews,
3. **JAERI 6001-6999** Information and Guiding Booklets.

Any inquiries concerning distribution copyright and reprint of the above reports should be directed to the Division of Technical Information, Japan Atomic Energy Research Institute, Tokai-mura, Naka-gun, Ibaraki-ken, Japan

Studies on the Solvent Extraction of Actinide Elements  
by Organophosphorus Compounds

Abstract

Radiochemical survey was performed on the extraction of actinide elements by TBP, TBPO and TOPO from hydrochloric and nitric acid solutions. In general, most of the elements studied were more extractable in the extraction systems of phosphine oxides than in those of phosphate. Influence of the variation of acid concentration on the distribution ratio of the elements was more remarkable in the former system than in the latter. The extraction of thorium and uranium chlorides by TBP or TOPO was studied. The composition of complexes extracted from the chloride solution of low acid concentration was established by partition study to be  $UO_2Cl_2(TOPO)_2$ ,  $UCl_4(TOPO)_2$ ,  $ThCl_4(TOPO)_2$  and  $UCl_4(TBP)_2$ . The composition of thorium complex in the TBP phase free from hydrochloric acid was revealed by infrared study to be  $ThCl_4(TBP)_4$ . Study on the extraction of curium from nitrate solution by TOPO suggested that the composition of complex extracted was  $Cm(NO_3)_3 \cdot (TOPO)_3$ .

The results obtained in the extraction of individual element were applied to the separation of the followings. (1) Small amounts of uranium-233 was separated from irradiated thorium by extraction with TBPO. Uranium and protactinium-233 were extracted by 1% TBPO from hydrochloric acid solution, leaving thorium in the aqueous phase. Protactinium was stripped from the organic phase by scrubbing with hydrochloric acid solution saturated with

ammonium fluoride. Then, uranium in the organic phase was back-extracted by contacting with acetic acid. Uranium-233 was purified by cation exchange method. (2) Uranium and plutonium were separated from each other by a continuous fractional extraction method using a couple of small pulse columns. The extraction of uranium was carried out with 20% TBP from 0.5N nitric acid solution of irradiated uranium. Under the condition, uranium could be extracted with the organic solution, whereas plutonium remained in the aqueous solution. After removing the main bulk of uranium, the acidity of the aqueous solution was raised up and then plutonium was extracted with 20 or 40% TBP from the resultant solution. The behavior of fission products possibly contaminating the uranium or plutonium fraction in these methods were also studied. (3) Reversed phase column chromatography was applied to the separation of americium from rare earths after coprecipitation. HDEHP and TOPO-xylene solutions held on kieselguhr were used as the stationary phase and the elutions were carried out with 0.1 to 1N nitric acid solutions. In the HDEHP system, americium was effectively separated from the rare earths except from praseodimium. Americium could also be separated from europium in the TOPO system.

Nov. 1966

Kenju Watanabe

Radiochemistry Laboratory, Tokai Research Establishment

Japan Atomic Energy Research Institute

## 有機リン化合物によるアクチニド元素の 溶媒抽出に関する研究

### 要 旨

有機リン化合物を用いた溶媒抽出法によるアクチニド元素の分離をしらべた。

- I) TBP, TBPO, TOPO-塩酸, 硝酸系におけるアクチニド元素の分配; 塩酸系では, 8, 4, 6 価のイオンを相互に分離できる。しかし, この系ではアクチニド以外の多くの元素が抽出されるから, アクチニドを他の元素から分離するに適さない。硝酸系では 8, 4, 6 価のイオンの相互分離に適さないが, アクチニド以外の元素が殆んど抽出されないので, 4, 6 価のアクチニドを他の元素から選択的に分離できる。
- II) 塩酸系における Th および U の行動; 少量の塩酸を含む NaCl または LiCl の水溶液から, TOPO および TBP による Th および U の抽出をしらべた。分配平衡の測定によれば, これらの系で Th および U は, それぞれ,  $\text{ThCl}_4 \cdot (\text{TOPO})_2$ ,  $\text{UCl}_4 \cdot (\text{TOPO})_2$ ,  $\text{UO}_2\text{Cl}_2 \cdot (\text{TOPO})_2$ ,  $\text{UCl}_4 \cdot (\text{TBP})_2$  として有機溶液中に抽出されると考えられる。また, 赤外線吸収スペクトル測定によれば, Th は塩酸を含まない TBP 中で  $\text{ThCl}_4 \cdot (\text{TBP})_4$  として存在すると考えられる。
- III) 硝酸系における Am および Cm の行動; 少量の硝酸を含む硝酸塩溶液と TOPO キシレン溶液との間の Am および Cm の分配を求めた。分配平衡測定により Cm は  $\text{Cm}(\text{NO}_3)_3 \cdot (\text{TOPO})_3$  として抽出されると考えられる。
- IV) 中性子照射した酸化トリウムより U-233 の単離; 4~6 N 塩酸溶液-1% TBPO 溶媒抽出系を用いることにより, 大量の Th を水層に残し, 微量の U-233 を抽出分離した。U-233 を逆抽出し, NaF を含む稀塩酸溶液にかえ, 陽イオン交換樹脂により精製した。
- V) TBP による Pu と U の分別溶媒抽出; 従来照射ウラン TBP 処理法では, 抽出の初段階で Pu を U とともに抽出する。ここに述べる方法では, 抽出の段階で Pu と U を分けて抽出する。照射ウランの約 0.5 N 硝酸溶液から 20% TBP で抽出を行なうと, 主に U が有機層に移り Pu の大部分は水層に残る。U を抽出したのち, 水層の酸濃度をあげて Pu を抽出する。核分裂生成物の大部分は水層に残り, U, Pu から分離される。
- VI) HDEHP を用いた逆相クロマトグラフィによる Am の分離; HDEHP をケイソウ土に保持させた逆相クロマトグラフィにより, Am と稀土類元素を分離するとともに, 各元素を単純な酸溶液として得た。溶媒抽出の分配比と逆相クロマトグラフィにおける溶出位置との間には比例関係があるので, 抽出データに基づいて金属イオンの相互分離の可否が判断できる。

1966年11月

日本原子力研究所 東海研究所  
研究部 放射化学研究室  
渡辺賢寿

The content of this thesis was published in the following journals.

- 1) T. Ishimori, K. Watanabe and E. Nakamura, Inorganic Extraction Studies on the System between Tri-n-butyl Phosphate and Hydrochloric Acid, Bull. Chem. Soc. Japan, 33 636-644 (1960)
- 2) T. Ishimori and K. Watanabe, Inorganic Extraction Studies on the System of Tri-n-butyl Phosphate-Nitric Acid, Bull. Chem. Soc. Japan, 33 1443-1448 (1960)
- 3) T. Ishimori, K. Watanabe and K. Kimura, Tracer-chemical Isolation of Uranium-233 from Irradiated Thorium by Solvent Extraction with Tributyl Phosphine Oxide, J. Atomic Energy Soc. Japan, 2 750-757 (1960)
- 4) T. Ishimori, K. Watanabe and T. Fujino, Inorganic Extraction Studies on the System between Tri-n-butyl Phosphine Oxide and Hydrochloric Acid., J. Atomic Energy Soc. Japan, 3 19-25 (1961)
- 5) T. Ishimori, K. Watanabe and T. Fujino, Fractional Extraction of Plutonium and Uranium with Tri-n-butyl Phosphate, J. Atomic Energy Soc. Japan, 3 507-512 (1961)
- 6) K. Watanabe and R. Ono, The Extraction of Curium and Americium by Tri-n-Octyl Phosphine Oxide, J. Nucl. Sci. Tech., 1 75-76 (1964)
- 7) K. Watanabe, Extraction of Thorium and Uranium from Chloride Solutions by Tri-n-Butyl Phosphate and Tri-n-Octyl Phosphine Oxide, J. Nucl. Sci. Tech., 1 155-162 (1964)
- 8) K. Watanabe, Separation of Americium and Some Rare Earths from Lanthanum by Reversed Phase Chromatography, J. Nucl. Sci. Tech., 2 45-50 (1965)

CONTENTS

I	Introduction	1
II	Distribution behavior in Various Extraction Systems	9
	i. Actinide Elements in Systems of Neutral Organophosphorus Compounds-Hydrochloric and Nitric Acids	9
	ii. Thorium and Uranium in System of Tri-n-octyl Phosphine Oxide-Chloride	20
	iii. Thorium, Uranium and Plutonium in System of Tri-n-butyl Phosphate-Chloride	26
	iv. Americium and Curium in System of Tri-n-octyl Phosphine Oxide-Chloride and Nitrate	33
III	Applications	35
	i. Separation of Uranium-233 from Irradiated Thorium by Tri-n-butyl Phosphine Oxide	35
	ii. Separation of Plutonium from Irradiated Uranium by Fractional Extraction using Tri-n-butyl phosphate	44
	iii. Separation of Americium from Rare Earths by Reversed Phase Chromatographies using Tri-n-octyl phosphine Oxide and Di-(2-ethylhexyl)phosphoric Acid	53

## 目 次

I	序 論 .....	1
II	種々の抽出系におけるアクチノイド元素の行動 .....	9
	I 中性有機リン化合物-塩酸・硝酸系における アクチノイド元素の分配 .....	9
	II TOPO-塩酸溶液系におけるトリウムおよび ウランの行動 .....	20
	III TBP-塩酸溶液系におけるトリウム, ウラン およびプルトニウムの行動 .....	26
IV	TOPO-塩酸および硝酸溶液系におけるアメ リシウムおよびキュリウムの行動 .....	33
III	応 用 例 .....	35
	I 照射トリウムからU-233のTBPOによる分離 .....	35
	II 照射ウランからプルトニウムのTBPによる分別 抽出分離 .....	44
	III HDEHPおよびTOPOを用いた逆相クロマトグラ フィによるアメリシウムと稀土類元素の分離 .....	53



## I. Introduction

Separation of actinide elements is one of the important subjects to be studied by chemists in atomic energy research. Nuclear fuel materials such as thorium, uranium and plutonium should be produced in high purity and by possibly inexpensive procedures. In the reprocessing of spent reactor fuel, particularly in separating the fuel elements from fission products, it is required to recover the materials with good yield and high purity. Effective separation methods for the actinide elements are also necessary in the chemical analyses of these elements.

Isolation and purification methods for the actinide elements have been widely investigated ever since they were discovered. At present the methods include such as precipitation, electrodeposition, solvent extraction, ion exchange, slagging, and volatilization of their halides and other compounds. To the production of thorium and uranium from ores, solvent extraction and ion exchange are applied. Both of wet and dry methods have been studied for the reprocessing of spent reactor fuel, but only solvent extraction is actually used in large scale. Ion exchange is mainly employed in the purification process of rough products. In laboratory scale, solvent extraction, ion exchange, and precipitation are frequently used for separating the actinide

elements. Particularly ion exchange is very useful to purify and identify the heavier actinide elements.

Solvent extraction method is finding more favor as separation technique for the actinide elements because of their speed, simplicity and efficiency. The method is very superior to precipitation method in the selectivity for separating metal ions.

Although the selectivity in the solvent extraction method is lower than in the ion exchange method, remote controlled techniques in the former are easier than in the latter.

A number of solvents have been used for separating actinide elements. For example, about three hundred tables and figures on extraction data for plutonium obtained by using various solvents and aqueous media are compiled by Smith<sup>(1-1)</sup> in the "Solvent Extraction Data for Plutonium". As is shown in this collection of data, the actinide elements may be extracted from either chelate- or ion association extraction systems, which are named by Morrison and Freiser<sup>(1-2)</sup>. Solvents for the chelating systems include TTA, cupferron, acetylacetone and others, while those for the ion association systems are TBP, hexone, diethylether and others. According to Morrison and Freiser, a metal ion may be extracted into organic phase through the following processes: The metal ion in aqueous phase is led to the formation of an extractable uncharged species by coordinating with an anion of a suitable chelating or coordinating agent, or by ion association with suitable ligand, cation and anion required to form the ion-pair.

The former is termed chelate extraction system and the latter ion association extraction system. The extractable species first distributes between the aqueous and the organic phases in accordance with the distribution law. Then, in the organic phase, reactions involving the extractable complex, e.g. polymerization or dissociation of the complex, interaction with other components, are caused. A difference, pointed out by Naito<sup>(1-3)</sup>, between the two extraction systems is that the organic phases used in the chelate extraction system are of inert substances in the Lewis's acid-base reaction theory, and the chelating agents to be added are soluble in aqueous phase, whereas those in the ion association extraction system are of active substances and are scarcely soluble in aqueous phase. Naito suggests that the extraction mechanism in the ion association extraction system, termed by Morrison and Freiser, is essentially similar to that in the chelate extraction system in meaning of the acid-base reaction in Lewis's theory, because in the former system the organic solvent itself acts as a base and in a manner of a chelating agent for inorganic ion to be extracted.

In most extraction systems, the multiplicity of oxidation states of actinide elements is effectively used for separating those from the other elements. For example, solvents, which form coordination complexes with metal nitrates, extract the actinide elements in the order of oxidation states (IV) > (VI) > (III) and (V). On the other hand, the order of extractability is

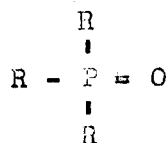
(VI) > (IV) > (III) and (V) for solvents which do not form coordination complexes with the nitrates. Accordingly, it is easy to separate tetra or hexa valent actinide elements from tri and penta valent metal elements by using these solvents.

Actually hexone, TTA and TBP are used for a large scale separation of plutonium from fission products and uranium. Hexa or tetra valent plutonium nitrate can be extracted by hexone or TTA and TBP, respectively, and then the plutonium is stripped from the organic phase to the aqueous phase after reducing the plutonium to trivalent state.

In these cases, extraction by hexone requires low concentration of nitric acid in aqueous phase because of the fairly high solubility of the nitric acid into hexone, and thus large amounts of salting out agent such as ammonium, magnesium, calcium or aluminum nitrate must be added into the aqueous phase in order to keep the concentration of nitrate high for extracting metal ions. In the TTA extraction method, plutonium is extracted into organic phase leaving uranium and essentially all fission products except zirconium, and no metal salting agent is employed. Thus, this method has merits of requiring only one cycle for the decontamination of plutonium and uranium, and of simplifying the waste disposal procedure. However, a disadvantage is that the rate of chelation is slow and a continuous operation takes much time. On the other hand, TBP shows high resistivity for oxidation by nitric acid and thus metal ions can be extracted from nitric acid solution

of relatively high concentration without an addition of a large amounts of other salting out agent. The TBP extraction method is up to date a most effective method for reprocessing spent reactor fuel.

Neutral organophosphorus compounds represented by TBP have the general formula



where R is an alkyl (or aryl) or an alkoxy group.

When all three substituents are alkyl groups, the compound is a phosphine oxide. The substitution of one, two and three alkoxy group for the alkyl groups gives phosphinates, phosphonates and phosphates, respectively. These neutral molecules are believed to coordinate to a metal through the oxygen atom. The substitution of hydroxy groups for R gives acidic organophosphorus compounds such as di-(2-ethylhexyl)phosphoric acid. The acidic organophosphorus compounds as well as the neutral one are frequently used for extracting metal ions.

Now, a systematic study on the solvent extraction of many elements relating to reactor fuel and material have been carried out in Radiochemistry Laboratory, Japan Atomic Energy Research Institute, since 1958. As a member of the group, the present author has mainly studied the extraction of actinide elements by organophosphorus compounds. The results obtained are given in the present paper.

An object of this work was to find effective methods for separating actinide elements mutually and from the other elements by solvent extraction using organophosphorus compounds. For the object, extraction behavior of individual elements in a particular system should be surveyed in the first step. Actually mutual separation of the elements is to be tried under a possibly suitable condition presumed on the basis of the results obtained in the distribution studies of the individual elements. In this work, Chapter II includes the distribution study on the actinide elements, and application of the results to the separation of those are described in Chapter III.

Extraction of the actinide elements from aqueous nitrate solutions by organophosphorus compounds, particularly TBP, has been studied in detail. In comparison with the extraction from nitrate media, only a few data for the elements have been given in the extraction by the organophosphorus compounds from aqueous chloride solutions. Thus, distribution of the elements between the organophosphorus compounds and the chloride solutions is mainly discussed in Chapter II. In this Chapter, data for phosphate and phosphine oxide are given. Generally, distribution ratio of metal ions increase in the order of phosphates, phosphonates, phosphinates and phosphine oxides<sup>(1-4)</sup>. Consequently, extraction behavior for phosphonates and phosphinates may roughly be estimated from the data for phosphates and phosphine oxides. Extraction of the elements by TBP, TBPO and TOPO from hydrochloric or nitric acid

is described in section 1. The distribution ratios of the elements obtained by the present author are compiled in a figure together with the results given in the published works by other investigators. General tendency of extraction behavior is roughly known from the results in these simple acid solution systems.

Studies on the extraction mechanism and on the effects of salting out agents on the extraction of metal ions are necessary to estimate the extraction capacities of solvents and to select the most suitable condition for the mutual separation of the metal ions. In section 2, 3 and 4, these studies on thorium, uranium, plutonium, americium and curium are given for systems of TBP and TOPO-chloride and nitrate solutions.

The subjects discussed in Chapter III are the following: In the extraction system of TBPO-chloride solutions, uranium can easily be extracted into the organic phase, while thorium can not. Protactinium is extracted from a hydrochloric acid solution of moderate concentration, but does not from a hydrochloric acid solution saturated with ammonium fluoride. On the basis of the facts, separation of uranium-233 from an irradiated thorium dioxide was carried out and the results obtained are described in section 1. In the extraction system of TBP-nitric acid, both of uranium and plutonium are easily extracted into TBP. However, when small amounts of plutonium is present in large amounts of uranium, the distribution ratio for plutonium are lower than those given in the extraction system in which plutonium alone

is present as metal ion. Accordingly, mutual separation of uranium and plutonium may be performed by fractional extraction using TBP and nitric acid under suitable conditions. This fractional extraction method was applied to the separation of plutonium from an irradiated uranium as is discussed in section 2. In this case, pulse columns were used for the fractional extraction. The fractional multiple extraction methods are frequently used for the mutual separation of the elements of which the values of distribution ratio are close each other. Reversed phase chromatography using extractant is, in a laboratory scale, one of the effective multiple extraction methods. In the reversed phase chromatography, the organic extractant is retained on a solid adsorbent and is used as a stationary phase. The separation of americium from rare earths by reversed phase chromatography using HDEHP and TOPO is discussed in section 3.



## II. Distribution behavior in Various Extraction Systems

### i. Actinide Elements in Systems of Neutral Organophosphorus Compounds-Hydrochloric and Nitric Acids

Distribution data for actinide elements in the systems of TBP and nitric acid solutions have been published by a number of investigators. Distribution of uranium(VI)<sup>(2-1)</sup> and thorium nitrates<sup>(2-2)</sup> between TBP and nitric acid solution has been studied at various concentrations of TBP, nitric acid and/or nitrate using aluminum, sodium or calcium nitrate as the salting out agent. Distribution data for protactinium<sup>(2-3)</sup>, neptunium<sup>(2-4)</sup> and plutonium<sup>(2-5)</sup> were also presented in the extraction with diluted TBP. According to Yakovlev and Kosyakov<sup>(2-6)</sup> extractabilities of americium and curium increase with increasing concentration of nitrate as salting out agent in the aqueous solution. Extraction of the elements by TOPO from nitric acid solution has been studied by White<sup>(2-7)</sup> and Ishimori<sup>(2-8)</sup>. TBPO was used for separating plutonium from nitric acid solution of irradiated uranium by Umezawa<sup>(2-9)</sup>. On the other hand, only a few distribution data are given for the elements in the system of the neutral organophosphorus compounds-hydrochloric acid.

In this section is presented the extraction of the elements by undiluted TBP, 1% TBPO and 1 or 5% TOPO from hydrochloric and nitric acid of various concentration.

### Experimental

Reagents --- TBP was purified in the usual way<sup>(2-2, 10, 11)</sup> and used without any dilution. TBPO received from Tama Chemicals Co. was diluted to 1 weight-volume % (w/v) with toluene and used without further purification. TOPO was obtained from Eastman Organic Chemicals and Dojindo & Co. Ltd. The TOPO was diluted to 1 or 5% (w/v) with xylene. Hydrochloric and nitric acid solutions were prepared by diluting commercial concentrated hydrochloric and nitric acid. The acidity was determined volumetrically whenever necessary. Other reagents were of A. R. grade.

Radioisotopes --- Radioisotopes used in this experiment are shown in Table 2-1. Protactinium-233, uranium-233, plutonium-239 and curium-242 were prepared by irradiating the respective targets. Uranium-237 was prepared by  $\gamma$  ray irradiation of natural uranium with a linear accelerator<sup>(2-12)</sup>. The imported plutonium was used after separating americium-241 by anion exchange method<sup>(2-13)</sup>.

Uranium and plutonium(IV) were prepared by reducing with zinc metal and by adding 0.2 M ammonium nitrite. Plutonium(III) was prepared by adding 0.2 M ferrous sulfamate or both of 0.1 M ammonium iodide and 0.1 M hydroquinone.

Determination of distribution ratio --- The distribution ratio,  $K_d$ , of a given nuclide (or nuclides), defined as the concentration of nuclide in the organic layer divided by that in the aqueous layer, was determined radiometrically. In the determination, a portion of an aqueous acid solution of a given concentration

containing the radioactive tracer was shaken with a portion of the solvent which had been previously equilibrated with the corresponding barren aqueous acid.

Details of the method of the determination were as follows. One to two millilitres of each of aqueous acid and pré-equilibrated TBP, TBPO or TOPO solution were placed in a 2 or 5 ml glass-stoppered measuring cylinder and shaken vigorously for 3 to 5 minutes. After the two layers were transferred together into a centrifuge tube, the mixture was centrifuged at about 3000 rpm for 1 minute. Nearly all of the aqueous layer was transferred with a transfer pipette to a new centrifuge tube. Both tubes were centrifuged for 1 minute again.

In several cases, a portion of the organic extract obtained was transferred to a new 2 or 5 ml cylinder, shaken with an equal volume of fresh aqueous acid, and treated again as beforementioned. Further scrubblings were made in a few cases. As a result of these scrubblings and the following redetermination of  $K_d$  values, difficulties caused by the formation of undesired metal hydrates or by the presence of other valent metal ions than the objective metal ion were obviated.

For the radio-assay of  $\alpha$  activity, aliquot portions from both layers were carefully dried up on a small platinum discs, with an induction furnace avoiding any loss of activity. In the case of  $\gamma$  ray emitters, aliquots of each layer were taken into two glass-stoppered tubes. The quantity of the aliquots were kept usually

1 ml. Alpha and  $\gamma$  ray activities were measured with a  $2\pi$  proportional and an well type  $\gamma$  ray scintillation counters, respectively.

### Results and Discussion

The results obtained are summarized in Fig. 2-1 as a series of graphs of  $\log K_d$  vs  $N$ , together with those cited in the works by other investigators. In this figure,  $K_d$  is the distribution ratio and  $N$  the acidity of hydrochloric and nitric acid solutions in normality. Data by other investigators are indicated with the initial letter of their names in boxes. Data for extraction of thorium and uranium(VI) from hydrochloric acid by undiluted TBP have also been published by Peppard<sup>(2-2)</sup> and Irving<sup>(2-17)</sup>, respectively. The results for these elements shown in the figure agree with their data. In the system of TOPO-HCl, data for thorium, uranium and plutonium are for extraction by 1% TOPO, and those for neptunium and americium are for extraction by 5% TOPO.

TBP-HCl System --- The  $K_d$  values for trivalent actinide elements, as pointed by Peppard et al<sup>(2-18)</sup>, increase with increasing atomic number and acidity of the ion as well as those for trivalent lanthanide elements. Although the  $K_d$  values for the individual element increase with increasing concentration of hydrochloric acid, those for all of the elements are generally low in all range of hydrochloric acid concentration and they are hardly extracted by undiluted TBP even from concentrated hydrochloric acid.

Thorium, uranium(IV), neptunium(IV) and plutonium(IV) are scarcely extracted from hydrochloric acid of low concentration, but they are easily extracted from the acid of high concentration. Shapes of their curves of  $K_d$  vs  $N$  resemble each other. The  $K_d$  values increase with increasing atomic number.

The  $K_d$  values for protactinium are higher than those for neptunium(V). Uranium(VI) and neptunium(VI) are practically completely extracted from hydrochloric acid above 4 N. The order of extractability of the hexavalent elements is neptunium(VI) > uranium(VI), and the order does not agree with that in the extraction system of TBI- $HNO_3$  and TBPO-HCl, in which is uranium(VI) > neptunium(VI) > plutonium(VI).

In the point of view of separation of actinide elements, the following are suggested by the results given in this extraction system. Tetravalent actinide elements except thorium may be separated from trivalent one by extraction with TBI from about 3 N hydrochloric acid. Mutual separation of trivalent actinide elements is difficult because of the similarity in the extraction behavior of the elements. In the tetravalent actinide elements, only thorium shows low  $K_d$  value in the extraction from hydrochloric acid of moderate concentration. Thus, thorium may be effectively separated from protactinium, uranium(VI), neptunium(VI) and plutonium(IV) by extraction from 5~6 N hydrochloric acid. Difference of  $K_d$  values between protactinium and neptunium(V) are large, and the mutual separation of these elements may be possible

in the extraction from about 5 N hydrochloric acid.

According to the other work<sup>(2-19)</sup> by the present author, tetra, penta, hexa and heptavalent elements except actinide elements show generally high Kd values as well as scandium, zinc, cadmium, mercury, gold, arsenic(III), antimony(III) and iron(III) in this extraction system. Therefore, it is not very effective to apply this extraction system for the separation of actinide elements from the other elements such as fission products.

TBP-HNO<sub>3</sub> system --- The behavior of americium in the extraction system of TBP-HNO<sub>3</sub> is similar to that of lanthanide elements<sup>(2-20,21)</sup>, and it is presumed that the other trivalent actinide elements also resemble to the lanthanide elements in the extraction behavior. As pointed out by other investigators<sup>(2-18)</sup>, the Kd values for the trivalent actinide elements increase with atomic number in this system. In general, the values in this system are larger than those in the TBP-HCl system. The values go up to a maximum and then fall, but increase again in the region of high nitric acid concentration. These facts are explained by the following reasons<sup>(2-22)</sup>; the decrease of Kd values for the elements is due to the competition between nitric acid and the metal ion for the active groups of the solvent. The formation of extractable anionic complexes of the metal with the acid causes final increase of the Kd values. In facts, the Kd values for americium and curium increase monotonously with nitrate concentration in the experiment by Yakovlev<sup>(2-6)</sup>, who measured the

values in various additional nitrate concentration under constant low nitric acid concentration. Accordingly, both of americium and curium can be extracted by TBP from  $>5$  M nitrate solutions at low acidity.

Tetravalent actinide elements are effectively extracted from nitric acid of moderate and high concentration. Although the order of extractability is not clear in this figure, it is thorium  $<$  neptunium(IV)  $<$  plutonium(IV), namely increasing with atomic number, according to the study by McKay on the system of 19% TBP and nitric acid<sup>(2-23)</sup>. The  $K_d$  values for protactinium are larger than those for neptunium(V) in this system as well as in the TBP-HCl system, whereas the order of extractability in hexavalent actinide elements is uranium(VI)  $>$  neptunium(VI)  $>$  plutonium(VI) in the TBP-HNO<sub>3</sub> system. All of these hexavalent elements are easily extracted by TBP in a wide range of nitric acid concentration.

In this extraction system, a mutual separation of tetra and hexavalent actinide elements except neptunium(IV) is difficult because all of the elements have high  $K_d$  values. In the TBP-HNO<sub>3</sub> extraction system, however, the  $K_d$  values for most of the other elements than actinide elements are low<sup>(2-24)</sup>, and thus tetra and hexavalent actinide elements can be selectively separated from the other elements by diluted TBP.

1% TBPO-HCl System --- Thorium is hardly extracted by 1% TBPO in all range of hydrochloric acid concentration. Neptunium(V) is

not extracted from hydrochloric acid of low concentration, while it is extracted in some degree from concentrated hydrochloric acid. Protactinium and uranium(VI), neptunium(IV) and (VI) are easily extracted. Accordingly, by extraction from about 6 N hydrochloric acid, thorium or neptunium(V) may be separated from protactinium and uranium(VI) or neptunium(IV) and (VI). In this extraction system, the  $K_d$  values for uranium(VI) are higher than those for neptunium(VI). This order of extractability is similar to that in the TBP- $\text{HNO}_3$  system. General tendency of extraction behavior of the other elements<sup>(2-25)</sup> resemble to that in the TBP-HCl system, and thus it is not expected to separate effectively the actinide elements from the other elements by using this extraction system.

1% TOPO - HCl System --- Concentration of 1% TOPO solution in molarity is 0.026, while that of undiluted TBP is 3.66. If we take into consideration the concentration of these extractants, the comparison of the results in TBP and TOPO extraction systems indicates that TOPO is a stronger extractant than TBP for metal ions. In the TOPO-HCl system, the  $K_d$  values for all of tetravalent actinide elements go through maxima at 7~8 N hydrochloric acid concentration and then fall. This is due to the competition between acid and metal ion as described in section 11. In the extraction from chloride solutions of low acidity, the  $K_d$  values for these elements increase monotonously with chloride concentration. Thorium can be easily extracted from chloride solution



at above 3 N containing small amounts of acid. Practically complete extraction of uranium(IV) and plutonium(IV) are possible from 7~8 N hydrochloric acid. Uranium (VI) can be extracted in the range of 2~10 N hydrochloric acid concentration. The element shows a maximum Kd at about 5 N hydrochloric acid concentration. However, in the extraction from chloride solutions of low acidity, it does not show a maximum value, but shows only increasing Kd values with increasing chloride concentration as is given in section ii. Chlorides of trivalent actinide elements are hardly extracted even by 5% TOPO.

In this TOPO-HCl system, trivalent actinide elements may be separated from the other valent one. However, the mutual separation of tetra, penta and hexavalent one is difficult because of high Kd values for all of these elements in the region of moderate and high acid concentration. Uranium(VI) may be separated from thorium and neptunium(V) by extracting from 1~2 N hydrochloric acid. The extraction behavior of the other elements<sup>(2-26)</sup> than actinide elements in this system resemble to that in TB-HCl and TBP-HCl systems, and thus the separation of actinide elements from the other elements by extraction in this system is not very selective.

5% TOPO-HNO<sub>3</sub> System --- The strong competition between nitric acid and metal ion for extractant is recognized in the 5% TOPO-HNO<sub>3</sub> system. Consequently, all of tri, tetra and hexavalent actinide elements show maximum Kd values at low concentration of nitric acid.

However, when acidity in aqueous phase is kept low, as described in section iv, the  $K_d$  values increase with nitrate concentration. Under this condition it is possible to extract trivalent elements into organic phase from nitrate solution above 2 M.

Americium and curium are separated from tetra and hexavalent actinide elements and protactinium in this extraction system. Mutual separation of protactinium and neptunium(V) may be performed by extraction from 1~4 N hydrochloric acid. The extraction behavior of the other elements<sup>(2-26)</sup> than actinide elements in this system is similar to that in the TBP-HNO<sub>3</sub> system. Therefore, a selective separation of tetra and hexavalent actinide elements from many other elements except a few elements such as zirconium and niobium is possible by extraction with TOPO from 1~5 N nitric acid solutions.

Based on the results mentioned above, trivalent ions are scarcely extracted in the extraction systems of hydrochloric acid, and remarkable increase of  $K_d$  values for these ions by adding salting out agents is not recognized. The  $K_d$  values for thorium are generally low. The element is hardly extracted by TBP and TBPO. Only TOPO extracts it from chloride solutions of high concentration. Protactinium, uranium(IV), neptunium(IV) and plutonium(IV) show low  $K_d$  values in low hydrochloric acid concentration, but show high values at moderate concentration. Uranium(VI) and neptunium(VI) are easily extracted from hydrochloric acid of moderate concentration. Accordingly, in these extraction systems,

trivalent actinide elements may be clearly separated from protactinium, uranium, neptunium and plutonium. Separation of uranium from thorium may be also easily carried out. However, a selective separation of actinide elements from the other elements are not expected in these systems.

On the other hand, in the extraction systems of nitric acid, both of tetra and hexavalent actinide elements show high  $K_d$  values, whereas most of the other elements than actinide elements show relatively low values. Consequently, tetra and hexavalent actinide elements can be selectively separated from the other elements, excepting a few elements. In these systems, trivalent actinide elements can be also extracted, when the acidity is kept low in the aqueous phase and suitable amounts of salting out agents are added.

A suitable combination of these systems will make a selective separation of a particular element possible. For example, thorium, uranium(VI) and plutonium(IV) are separated from many other elements by extraction with TBP or TOPO from nitric acid solution, and then thorium may be **selectively** recovered into aqueous phase by scrubbing with hydrochloric acid of a suitable concentration. Plutonium may be stripped from the organic phase by reducing to trivalent state, leaving uranium in the organic phase.

It is known in the extraction of metal ion by neutral organo-phosphorous compounds that tri or tetra and hexavalent metal ions are extracted into organic phase by the formation of **solvate**

complexes  $MX_3 \cdot 3S$  or  $MX_4 \cdot 2S$  and  $MO_2X_2 \cdot 2S$ , respectively, where M, X and S represent metal ion, anion such as  $Cl^-$  or  $NO_3^-$  and extractant. These solvation numbers fix the upper limit of a capacity of the extractant for metal ions. Solubility of TOPO in organic solvents is relatively low, for example, 0.92 M/l in cyclohexane at 25°C. This value corresponds to about only 1/4 of undiluted TBP concentration, 3.66 M/l. Capacity of TOPO solution for metal ions is fairly smaller than that of TBP. TBP is the more excellent extractant than TOPO for treatment of large amounts of metal ions. However, TOPO is the stronger extractant for most of metal ions than TBP, and the sufficiently high  $K_d$  values for extracting metal ions are occasionally obtained by using TOPO solution of very low concentration. Thus, TOPO is a suitable extractant for effective treatment of small amounts of metal ions.

#### ii. Thorium and Uranium in the System of Tri-n-octyl Phosphine Oxide-Chloride

The extraction behavior of thorium between TOPO and hydrochloric acid solutions was studied by Ross<sup>(2-7)</sup>, who determined the extracted species to be  $ThCl_4 \cdot HCl \cdot 3TOPO$ . He also studied the extraction of several metal ions including uranyl chloride by TOPO<sup>(2-27)</sup>. In most of the studies mentioned above, the metal ions were extracted from fairly concentrated acidic solutions,

where competitive extraction of the metal chloride and hydrochloric acid was observed.

The present section endeavors to elucidate the extraction mechanism by comparing the extraction of thorium and uranium chlorides by TOPO from chloride solutions with that from solutions containing only hydrochloric acid.

### Experimental

General techniques used were similar to those in the previous section. Measurements were made at a constant temperature of 25°C.

Reagents --- TOPO was obtained from Eastman Organic Chemicals and Cojindo Co., Ltd. The TOPO was purified to remove acidic impurities: A xylene solution of TOPO was successively scrubbed three times with 5% sodium bicarbonate solution, twice with water, twice with 1 N hydrochloric acid and three times with water. Other reagents were of A. R. grade.

Radioactive tracers --- The extraction of uranium and thorium was studied by the use of uranium-237 and thorium-231 prepared by  $\gamma$ -ray irradiation of natural uranium and thorium in a linear accelerator<sup>(2-12)</sup>. Thorium-234 milked from uranium-238<sup>(2-14)</sup> was also used as thorium tracer. Plutonium-239 was prepared by neutron irradiation of uranium in JRR-1<sup>(2-13,28)</sup>.

Uranium(IV) was prepared by reduction with zinc metal; and plutonium(IV) by the addition of 0.2 N ammonium nitrite.

### Results and Discussion

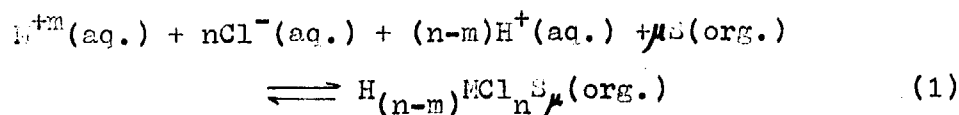
The measurements of the distribution ratio  $K_d$  for thorium, uranium(IV) and (VI) were made by the extraction from solutions of various concentrations of both hydrochloric acid and chloride. The chloride solutions was added with 0.1 M hydrochloric acid to prevent hydrolysis. In these cases, the concentration of metal ions in the aqueous phase was maintained at less than  $10^{-4}$  M. The results obtained are shown in Figs. 2-2, 3 and 4.

In Fig. 2-2, the dotted lines show the results obtained by the use of TOPO as received, while with TOPO scrubbed with sodium bicarbonate solution the results are as indicated by the solid lines. It is likely that the TOPO as received contains some impurities of acid form seeing that  $K_d$  values increase again with decreasing acidity in the region of hydrochloric acid concentration less than 1 M, while with TOPO scrubbed with alkali solution  $K_d$  continues to decrease down to lowest concentrations. Therefore, in this work, the purified TOPO was used to avoid the influence of acidic impurity.

As is shown in Figs. 2-2, 3 and 4 the  $K_d$  values for thorium, uranium(IV) and (VI) in the extraction from solutions of low hydrochloric acid concentration are approximately the same as those from the corresponding chloride solutions containing 0.1 M hydrochloric acid. In the region of more concentrated solution, however, the  $K_d$  values in the hydrochloric acid system show a maximum, whereas those in the chloride solution system do not and

continue to increase evenly with the chloride concentration. The decrease of Kd values in the region of high acid concentration may be explained as competitive extraction of the metal ions and hydrochloric acid, as pointed out by some investigators<sup>(2-20,22,29,30)</sup>. According to Naito<sup>(2-29)</sup>, Kd values for metal ions of same valency extracted in the same extraction system should have a maximum at nearly the same acid concentration. In fact, in the extraction by TOPO of thorium and uranium chlorides, both tetravalent, the Kd values for these metal ions assume maximum values at about the same hydrochloric acid concentration of 7.5~8 M (Figs. 2-2 and 3).

Mechanism of extraction --- In the present systems, the extraction mechanism of metal chloride may be expressed by the equation



where  $M^{+m}$  indicates a metal ion and S an extracting reagent, while n and m are integers. When the solute concentration in the organic phase is low and it is assumed that the all metal ions in the organic phase contribute to the formation of the complex, the following equation for the distribution ratio, Kd(M), can be derived:

$$Kd(M) = \text{const.} \cdot \left[ (f_{H^{+}})^{n-m} \cdot (f_{M^{+m}}) \cdot (f_{Cl^{-}})^n \cdot \frac{(f_S^0)^{\mu}}{(f_{\text{complex}})} \right] \times \left[ (C_{H^{+}})^{n-m} \cdot (C_{Cl^{-}})^n \cdot (C_S^0)^{\mu} \right] \quad (2)$$

where f and C respectively are the activity coefficient and

equilibrium concentration of the corresponding term indicated by the suffix, and  $C_S^0$  is the initial concentration of the solvent in the organic phase. The extraction mechanism can be determined by finding the values of  $n$ ,  $(n-m)$  and  $\mu$ . Since the presence of hydrochloric acid causes competitive extraction of metal ion and acid which complicates the analysis of extraction mechanism, the concentration of acid must be kept as low as possible to simplify the analysis. On the other hand, it is known that hydrolysis of Th begins from about pH 2<sup>(2-31)~(2-33)</sup>. Bearing these facts in mind, an acidity of 0.1 M was chosen as experimental condition for the chloride solution system. The amount of hydrochloric acid extracted into TOPO phase is very small under this condition<sup>(2-26)</sup>.

Acid dependence --- If the  $K_d$  is measured at constant concentrations of the TOPO and chloride, Eq. (2) becomes

$$K_d(M) = \text{const.} \cdot (f_{H^+})^{n-m} \cdot (C_{H^+})^{n-m} \quad (3)$$

where it is assumed that  $(f_{\text{complex}})$  is constant because the complex concentration in the organic phase is low. If the measurement is made in the region where little variation of  $(f_{H^+})$  is expected, one can determine approximately the value of  $(n-m)$  from the slope of the curve relating  $\log K_d(M)$  to  $\log C_{H^+}$ . Such curves are reproduced in Fig. 2-5 for the case where sodium chloride was added to maintain the constant chloride concentration. From this figure, it is concluded that the values of  $(n-m)$  are zero for thorium, uranium(IV) and (VI), thus establishing that the complexes of TOPO and these metal ions do not contain hydrogen ion.



Solvent dependence --- When the  $K_d(M)$  is measured while keeping the concentration of chloride and hydrochloric acid constant, Eq. (2) becomes

$$K_d(M) = \text{const.} \cdot (f_s^0)^{\mu} \cdot (C_s^0)^{\mu} \quad (4)$$

If the measurement is made at low solvent concentration, the value of  $\mu$  is obtained by plotting  $\log K_d(M)$  vs.  $\log C_s^0$  since the variation of  $f_s^0$  is small under this condition. The solvent dependence curves for thorium, uranium(IV) and (VI) are shown in Fig. 2-6. From the slopes of these lines the value of  $\mu$  is determined to be 2 for all these metal chlorides,

Chloride dependence --- In a similar way, one can determine the chloride dependence  $n$  by measuring  $K_d(M)$  under constant concentration of solvent and hydrochloric acid, and varying the concentration of chloride. In this case, Eq. (2) becomes

$$K_d(M) = \text{const.} \cdot (f_{Cl^-})^n \cdot (C_{Cl^-})^n \quad (5)$$

It is seen from Fig. 2-4 that in the region of chloride concentration less than 1 M,  $K_d$  values for uranium(VI) vary at a rate of about the second power of chloride concentration. This suggests that the value of  $n$  is 2 for uranyl chloride. Precise  $K_d$  values for thorium and uranium(IV) were unfortunately not obtained in the region of chloride concentration less than 1 M, where the variation of  $(f_{Cl^-})$  is expected to be small, because  $K_d$  was very low in this region and the values for tetravalent metal ions were seriously influenced even by very small amounts of acidic impurity. Thus the chloride dependence for the extraction

of thorium and uranium(IV) were not determined directly by the method. However, since it was already known that  $(n-m)$  was equal to zero, the value of  $n$  could be assumed to be 4 for tetravalent metal ion in so far as Eq. (1) represented the extraction mechanisms of thorium and uranium(IV) in TOPO-chloride system.

Composition of complexes --- It is established by these analyses that the composition of the complexes formed in the extraction of thorium, uranium(IV) and (VI) by TOPO are  $\text{ThCl}_4(\text{TOPO})_2$ ,  $\text{UCl}_4(\text{TOPO})_2$  and  $\text{UO}_2\text{Cl}_2(\text{TOPO})_2$ . These are for the species extracted in the region of low acid concentration. While Ross<sup>(2-7)</sup> reported that the composition of the species of  $\text{ThCl}_4$  extracted by TOPO was  $\text{ThCl}_4 \cdot \text{HCl} \cdot (\text{TOPO})_3$ , it is recalled that this was done in fairly high acid solution such as 7 N.

### iii. Thorium, Uranium and Plutonium in the System of Tri-n-butyl Phosphate-Chloride

The distribution of uranyl chloride between TBP and hydrochloric acid was reported by Reilly<sup>(2-34)</sup>, Irving<sup>(2-17)</sup>, and Larsen<sup>(2-35)</sup>. Naito proposed the composition of the extracted complex to be  $\text{UO}_2\text{Cl}_2(\text{TBP})_2$ <sup>(2-29)</sup>. According to Iwase<sup>(2-36)</sup>, in the extraction of uranium tetrachloride from hydrochloric acid solution by TBP, the composition of the species extracted is  $\text{UCl}_4 \cdot 3\text{TBP}$ . The extraction behavior of thorium chloride between

the aqueous and TBP phases was investigated by Leppard<sup>(2-2)</sup>, but the extraction mechanism still remains uncertain.

In these studies on the TBP system as well as those on the TOD system, excepting the one by Naito, the metal ions were also extracted from fairly concentrated acidic solutions.

In the present section, extraction of thorium and uranium by TBP from chloride solutions of low acid concentration are mainly discussed. The extraction of plutonium chloride by TBP is also described.

#### Experimental

TBP was purified by the usual method<sup>(2-2, 10, 11)</sup>. Other reagents, radioactive tracers and general techniques were the same as those described in the previous section.

Infrared measurement --- A Koken DS Type 301 spectrometer equipped with a rock salt prism was used in the infrared measurements. The techniques were essentially the same as described in the reports<sup>(2-29, 37)</sup> by Naito, et al.

Determination of thorium in TBP phase --- In the infrared study, the concentration of thorium in TBP phase was determined as follows: Thorium in TBP solution of a known volume was stripped into aqueous solution and precipitated with oxalic acid. Then the thorium oxalate was ignited to oxide, and weighed.

#### Results and Discussion

The distribution ratios for thorium, uranium(IV) and plutonium(IV) in the extraction from hydrochloric acid solutions by TBP are shown in Fig. 2-7. These metal ions resemble each other in the shape of the curve of  $\log K_d(M)$  vs.  $\log C_{HCl}$ , except that the  $K_d$  value for thorium does not have a maximum. The  $K_d$  values of these metals increase with atomic number. The values for uranium(IV) and plutonium(IV) have maxima at about 9~10 M hydrochloric acid concentration. The values for thorium on the other hand have no maximum value in the region studied, and those in the system of 20% TBP and hydrochloric acid solutions scarcely differ from those in the system of undiluted TBP and lithium chloride solutions containing 0.1 M hydrochloric acid. The dissimilar behavior of thorium to that of tetravalent uranium and plutonium suggests that the extraction mechanism of thorium be different from that of tetravalent uranium or plutonium. In fact, the composition of the complex of thorium extracted into TBP from concentrated chloride solution containing hydrochloric acid differs from that of uranium(IV) as described below.

Mechanism of extraction --- In a way similar to the case of TOPO extraction,  $n-m$  and  $\mu$  were determined from the slopes of the acid dependence and solvent dependence curves.

Acid dependence --- Acid dependence curves of thorium and uranium(IV) are shown in Fig. 2-8 together with those for the extraction by TOPO from 10 M chloride solutions. Since the  $K_d$  values for uranium(IV) in the extraction from 5 M chloride solutions are

nearly constant, it is concluded that  $(n-m)=0$  for uranium(IV). On the other hand, the value of  $\log K_d$  for thorium in the extraction from 10 or 5 M chloride solutions is in proportion to the value of  $\log C_{H^+}$ . The solid lines show the results obtained by the use of thorium-234 tracer, while the broken line shows those with  $1.5 \times 10^{-3}$  M thorium tetrachloride solution containing thorium-234 tracer. Macro amounts of thorium were added to avoid the formation of radiocolloidal thorium in the aqueous phase. The behavior of thorium in the system of TBP and chloride solution apparently differs from that of uranium(IV) in the same extraction system, as well as from those of thorium and uranium(IV) in the system of TOPO and chloride solution. In the latter three cases, the  $K_d$  values in the extraction from 10 M chloride solutions decrease gradually with the increase in hydrochloric acid concentration. An acid dependence curve obtained for thorium in 5 M aqueous chloride concentration is less accurate because the values are too low. Thus, it remains uncertain whether the formation of thorium chloride-TBP complex is acid dependent in moderate chloride concentrations.

Solvent dependence --- The effect of TBP concentration on the  $K_d$  values of thorium, uranium(IV) and plutonium(IV) chlorides at constant acid concentration in the aqueous phase are shown in Fig. 2-9. The  $K_d$  values for uranium(IV) and plutonium(IV) vary approximately with the second power of TBP concentration, whereas those of thorium vary with the third power in the region of low

concentration of TBP, and the slope of this solvent dependence curve decreases with TBP concentration in the more concentrated region. In Fig. 2-10 are shown solvent dependence curves of thorium and uranium(IV) in the system of TBP and chloride solution. The value of  $\mu$  for uranium(IV) is established to be 2. On the other hand, in the case of thorium, the values of the slope of the solvent dependence curves vary between 3 and 4 according to the variation of acid concentration of the aqueous phase. The broken line in this figure represents the results obtained by the use of carbon tetrachloride as diluent. Carbon tetrachloride is a more reliable diluent for determining the value of the slope of solvent dependence curve than other diluents in the region of TBP concentration above 10~20%<sup>(2-29)</sup>. As is shown in Figs. 2-9 and 10, the value of the slope of the solvent dependence curves for thorium increases with decreasing acid concentration in the aqueous phase and approaches 4 in the case of aqueous solution containing 0.1 M hydrochloric acid.

To determine the value of  $\mu$  directly, infrared examination of this system was also tried. In general, the absorption band due to the  $\nu = 0$  group at  $1,230 \text{ cm}^{-1}$  is shifted to the longer wavelength by the formation of a complex with inorganic salt. The intensity of the band due to free TBP decreases with increase in the thorium concentration in the TBP phase. Since the decrease of the concentration of free TBP is related to the composition of the complex formed, the composition of the complex can be determined

by plotting the decrease of the concentration of free TBP against the increase of the concentration of thorium in the TBP phase<sup>(2-29)</sup>.

The infrared spectra obtained for the  $\text{ThCl}_4$ -TBP system are shown in Fig. 2-11. The samples were prepared by dissolving thorium tetrachloride crystals in the TBP phase to concentrations of 0.074, 0.111, 0.147, 0.221, 0.295 and 0.442 M. The spectra were obtained by capillary samples and their thickness was adjusted so as to give a constant intensity in the absorption band due to  $\text{CH}_3$  and  $\text{CH}_2$  deformation vibration at  $1,470 \text{ cm}^{-1}$ . The decrease in the concentration of free TBP with the increase in concentration of thorium chloride in the organic phase is shown in Fig. 2-12. The initial slope is 4.0, so the solvation number  $\mu$  can be determined in this case to be  $\mu = 4$ . Figure 2-13 represents the change of the intensity of absorption due to the formation of the complex at  $1,205 \text{ cm}^{-1}$ . It is observed that intensity of this absorption band increases in proportion to the concentration of thorium in the organic phase, except the value for 0.442 M. The results obtained by this infrared study indicate that the composition of the complex of thorium chloride dissolved in TBP phase is  $\text{ThCl}_4(\text{TBP})_4$ . However, it should be noted that, in this system, no hydrochloric acid or any chloride other than thorium chloride is present.

The value of  $\mu$  for the complex of thorium extracted into TBP phase from a chloride solution containing a small amount of hydrochloric acid is determined to be 4 by considering the

solvation number in the infrared study and from the fact that the slope of the solvent dependence curves of thorium approaches 4 with the decrease of acid concentration.

Chloride dependence and the composition of complexes --- The

value of  $n$ , i.e. chloride dependence, was not directly determined for the same reasons as in the case of TOPO extraction. However, the value of  $n$  may be determined indirectly from the values of  $m$  and  $(n-m)$  in so far as Eq. (1) can be applied to this system.

Accordingly, as it was earlier established that  $n-m = 0$  and  $m = 4$ ,  $n$  is 4 for uranium(IV), and the composition of the complex formed in the extraction by TBP from chloride solution is determined to be  $UCl_4(TBP)_2$ . This does not agree with the results obtained by Iwase (2-36), who reported the composition of the complex to be  $UCl_4 \cdot (TBP)_3$ . The results by Iwase were obtained from the solubility of  $UCl_4$  into TBP phase from 6 M hydrochloric acid solution. In the case of the extraction of thorium by TBP, it was observed from partition study (Fig. 2-3) that the  $K_d$  values vary with the first power of the acid concentration in the aqueous phase.

Accordingly, it is likely that the composition of the Th complex extracted by TBP from the concentrated chloride solution is  $ThCl_5(TBP)_4$ . Although details of the extraction mechanism of thorium in concentrated chloride solution was not clarified by the present work, it is likely that, in the extraction by TBP from concentrated chloride solution, the hydrogen ion contributes to the formation of thorium complex, and that the extraction mechanism of thorium is more complicated than that of uranium.



iv. Americium and Curium in the Systems of Tri-n-octyl phosphine Oxide-Chloride and Nitrate

The extraction of americium by TOPO from nitric acid solutions has been investigated by Martin<sup>(2-38)</sup> and Ishimori<sup>(2-39)</sup>. The present section deals with the extraction behavior of curium in the system of TOPO and nitric acid solutions, together with the extraction of americium and europium from ammonium nitrate solutions. The distribution of americium between TOPO and hydrochloric acid was also studied.

#### Experimental

TOPO was dissolved in xylene and used as 1~5% (weight by volume) solutions. The distribution ratio  $K_d$  was determined radiochemically by the usual method<sup>(2-39)</sup>, using radioactive tracers of curium-242, americium-241 and europium-152, 159. The curium tracer was separated from irradiated americium-241 by the cation exchange method<sup>(2-16)</sup>. The experiments were carried out at room temperature, about 20°C.

#### Results and Discussion

Figure 2-14 shows the extraction of curium by 5% TOPO from solutions in various concentrations of nitric acid. The  $K_d$  values for curium decrease with increase in acid concentration after passing through a maximum value at low acidity. This extraction

behavior is very similar to that of americium and trivalent lanthanide elements (2-8, 39).

Figure 2-15 shows the variation of  $K_d$  values for curium with concentration of TOPO in the organic phase, keeping the concentration of both acid and nitrate in the aqueous phase constant. The  $K_d$  values for curium vary at a rate of about the third power of TOPO concentration. This suggests that an extracted species has a value of 3 : 1 for the mole ratio of TOPO to curium.

The effects of salting agent on the extraction of curium, americium and europium are shown in Fig. 2-16. Measurements of the  $K_d$  values were made for the extraction from solutions in various concentrations of both nitric acid and ammonium nitrate. When the concentration of nitrate ion in the aqueous phase is kept constant, the  $K_d$  values for these elements increase with decreasing acid concentration under the conditions prevailing in the present work. The  $K_d$  values for curium and americium are slightly lower than that of europium. As shown in this figure, these elements are easily extracted by 5% TOPO from ammonium nitrate solutions in concentrations above 2M containing nitric acid of less than 0.1 M.

Figure 2-17 shows the distribution of americium between 5% TOPO and hydrochloric acid solutions.

The  $K_d$  values for americium, as in the case of trivalent lanthanide elements (2-8), are very low in the extraction from hydrochloric acid solutions.

### III. Applications

#### 1. Separation of Uranium-233 from Irradiated Thorium by Tri-n-butyl phosphine Oxide

As uranium-233 is supposed to be an important source material of the nuclear energy, the chemical separation and purification of uranium-233 from irradiated thorium have been extensively studied. Earlier significant works on uranium-233 were compiled by Katzin<sup>(3-1)</sup>.

Irradiation of thorium-232 with slow neutrons brings about the formation of uranium-233 through two intermediate nuclides, thorium-233 and protactinium-233. Although 23.5 min thorium-233 decay completely in a few hours, some of 27.4 day protactinium-233 still remain after cooling for several months. Accordingly, the separation of uranium-233 from both a large amount of thorium and a tracer amount of protactinium-233 becomes a main problem in the chemical processing of irradiated thorium target cooled for several months.

Although several processes, including precipitation<sup>(3-2, 3)</sup>, solvent extraction<sup>(3-4)~(3-10)</sup>, and ion exchange techniques<sup>(3-11)~(3-14)</sup> have been developed for the recovery of uranium-233, a solvent extraction has been beneficially used for the preliminary separation of uranium-233 from the highly radioactive protactinium-233 and a large amount of thorium. For example, in the case of Thorex process<sup>(3-15)</sup>, uranium-233 and thorium are separated from

protactinium-233 and fission products by the tributyl phosphate extraction, and the thorium is removed from uranium-233 by the scrubbing with diluted nitric acid.

It is well known that the phosphine oxides are the strongest extractants for uranium among many organophosphorous compounds (3-16)~(3-18). As is shown in the previous chapter, uranium is easily extracted with 1% TBPO-toluene solution, while thorium is hardly extracted with TBPO solution from hydrochloric acid media. These facts indicate that TBPO is available for the separation of uranium-233 and the recovery of thorium from the irradiated thorium.

In the present work is described the separation process for a small amount of uranium-233 by the solvent extraction with 1% TBPO in toluene from hydrochloric acid solution of thorium oxide irradiated in JRR-1. Final purification of uranium-233 was carried out by a cation exchange method.

#### Experimental

Materials --- Thorium dioxide was received from Mitsui Kinzoku Kogyo Co. Ltd. Tributyl phosphine oxide was obtained from Tama Kagaku Co. Ltd. One percent TBPO solution was prepared by dissolving 1g TBPO in 100 ml of toluene. Hydrochloric acid solutions were prepared by diluting concentrated hydrochloric acid. Acetic acid solution was prepared by diluting glacial acetic acid.

Thorium-234 was prepared by the Isotope Production Group, JAERI, and protactinium-233 was prepared from irradiated thorium nitrate.

Determination of distribution ratio --- The distribution ratio,  $K_d$ , was determined usually by the ordinary radiometric method (3-19)~(3-21). Some of the distribution data for uranium were obtained by activation analysis: Aliquots of organic or aqueous phases and a standard solution of uranium were irradiated at the same time for 30 min in JRR-1. After cooling for 1 day, the activity at photoelectron peak of neptunium-239 was measured with a  $\gamma$ -ray pulse height analyser.

Irradiation of thorium dioxide --- Five grams of thorium dioxide enclosed in a glass tube was packed in an aluminium can. Nine cans containing 45 g of thorium dioxide were irradiated in JRR-1 for 173 hr at the neutron flux of  $10^{11}$  n/cm<sup>2</sup>.sec.

Procedure --- After cooling for 5 months, the irradiated samples were treated for the separation of uranium-233 according to the process shown in Fig. 3-1. The details for this process are described in the following.

### Results and Discussion

Distribution data ---  $K_d$  values for thorium, protactinium and uranium in the system of 1% TBPO-hydrochloric acid are shown in Fig. 3-2. The data for protactinium is cited from the work of Fujino (3-22). Broken lines in Fig. 3-2 indicate  $K_d$  values for uranium or protactinium in the system of 1% TBPO vs. hydrochloric acid solution saturated with sodium fluoride.

As shown in Fig. 3-2 thorium is hardly extracted with 1% TBPO

from any concentration of hydrochloric acid, while uranium is extracted quantitatively from 2~7 N hydrochloric acid solution. Accordingly, a separation of uranium from thorium may be easily achieved by the solvent extraction of 1% TBPO-hydrochloric acid system. However, protactinium is taken into 1% TBPO phase together with uranium.

In the extraction from hydrochloric acid solution saturated with sodium fluoride, Kd values for protactinium become considerably low whereas uranium keeps still high Kd values under the same condition. Protactinium extracted into the organic phase together with uranium can be easily washed out with 4~6 N hydrochloric acid solution saturated with sodium fluoride, while uranium is left in the organic phase.

According to the above results, the isolation of uranium-233 from protactinium-233 and thorium was carried out by the solvent extraction with 1% TBPO.

Dissolution of thorium dioxide --- The dissolution of thorium dioxide in hydrochloric acid is the first step in the TBPO processing for the isolation of uranium-233. As is well known<sup>(3-23)</sup>, it is not easy to dissolve thorium dioxide in mineral acids. Thorium dioxide used in the present study also could not be dissolved in concentrated hydrochloric acid by boiling for 5 hr. However, the addition of fluoride ion makes the dissolution possible, and the preliminary experiment showed the fluoride concentration range of 0.01~0.001 M was most suitable for the rapid dissolution.

The dissolver consisted of a 100 ml glass flask with a reflux condenser. After 5 g of the irradiated thorium dioxide and 50 ml of concentrated hydrochloric acid were charged in the flask, an optimum amount of potassium fluoride solution was added, and the mixture was heated on a hot plate. It took 1.5~3 hr for the complete dissolution. In order to expel the excess hydrogen chloride and fluoride, the solution was heated for about 2 hr without reflux condenser.

Extraction of protactinium-233 and uranium-233 --- The solution of irradiated thorium in about 6 N hydrochloric acid was shaken three to five times with 5 ml of 1% TBEO. Both uranium-233 and protactinium-233 were extracted into the organic phase. For example,  $3.6 \times 10^8$  cpm of protactinium-233 was found in 20 ml of the organic phase after four successive extractions, while  $4.9 \times 10^5$  cpm was left in 45 ml of the aqueous phase. Although uranium-233 remained in the aqueous phase could not be determined by the interference of a large amount of thorium, it was supposed that uranium-233 was completely extracted into the organic phase according to the higher Kd value than that of protactinium at the 6 N hydrochloric acid.

Scrubbing of the organic phase --- The organic phase containing both uranium-233 and protactinium-233 was washed twice with a few milliliters of 4~6 N hydrochloric acid in order to remove the contaminant of thorium. Then, the organic phase was scrubbed two to four times with 5 ml of 4~6 N hydrochloric acid solution.

saturated with sodium fluoride. Most part of the protactinium-233 was washed out from the organic phase. Table 3-1 gives some results of the scrubbing with 4~6 N hydrochloric acid solution saturated with sodium fluoride. Table 3-1 shows that 90 to 99 % of protactinium-233 is removed from organic phase.

Although it is difficult to remove a small contaminant of protactinium-233 completely from the organic phase, this scrubbing method is convenient for the preliminary separation of uranium-233 from most part of protactinium-233.

Back extraction of uranium-233 --- The uranium-233 was easily stripped with 4 N acetic acid solution from the organic phase. An example of back extraction of uranium-233 is shown in Table 3-2. The organic phase (5.8 ml) was contacted three times with about 2 ml of 4 N acetic acid solution. Most part of uranium-233 was stripped in the first contact. As is shown in Table 3-2 the stripping of uranium-233 was practically completed by three contacts. A carbonate solution was also used for the stripping of uranium-233, but large amounts of chloride salt was yielded after acidifying the carbonate solution with hydrochloric acid. It was troublesome to remove the salt produced by converting the solution of uranium-233 into an acidic solution to be used for the recycle of solvent extraction or the final purification by ion exchange. On the other hand the acetic acid solution was evaporated by heating and converted easily into the hydrochloric acid solution by dissolving the uranium-233 remained. Consequently,



the acetic acid was chosen as the stripping solution for uranium-233.

Ion exchange --- Uranium-233 obtained by the 1% TBPO extraction method still contained an activity of protactinium-233 which corresponded to about 1/50~1/100 of that initially present.

A final purification of uranium-233 was achieved by the cation exchange technique of Chesne, et al<sup>(3-13)</sup>. The solution of uranium-233 was brought to the condition of 0.1 N hydrochloric acid and 0.02 M sodium fluoride. The resultant solution was passed through a column of Dowex-50 in the RH form. The elution for the removal of protactinium-233 was carried out with additional 50 ml of 0.1 N hydrochloric acid solution containing 0.02 M sodium fluoride. The elution curve obtained is shown in Fig. 3-3.

Uranium-233 was eluted with 20 ml of 2 N hydrochloric acid. A first 2 ml eluent was discarded, because this fraction contained a tolerable amount of protactinium-233 and a small amount of uranium-233 as shown in Fig. 3-3. The following 18 ml of 2 N hydrochloric acid was collected as the uranium-233 fraction.

Recycle of solvent extraction --- Although the decontamination factor of solvent extraction is smaller than that of ion exchange, the repeated solvent extraction is another method for the purification of uranium-233. Uranium-233 is extracted from a 4~6 N hydrochloric acid saturated with sodium fluoride again. Table 3-3 shows an example for the extraction of uranium-233 with three portions of 2 ml, 1% TBPO from 8 ml, 6 N hydrochloric acid solution saturated with sodium fluoride containing uranium-233 and

protactinium-233. In the first extraction, 88% of uranium-233 was extracted into the organic phase, while 17% of protactinium-233 was extracted.

The results obtained by scrubbing are given in Table 3-4. The comparison between Tables 3-1 and 3-4 shows that the decontamination factor for protactinium-233 decreases with decreasing activity of protactinium-233.

decontamination of protactinium-233 from Uranium-233 --- Any particular procedure for separation of fission products from uranium-233 was not tried in the present work, because the fission products were not found in the  $\gamma$ -ray spectrum of the irradiated thorium oxide (Fig. 3-4). Therefore, the decontamination of protactinium-233 from uranium-233 becomes a main subject in the work. Protactinium-233 was removed from uranium-233 through two steps described above: The scrubbing of the organic phase containing these nuclides with hydrochloric acid saturated with sodium fluoride and then the cation exchange using a dilute hydrochloric acid containing fluoride. The decontamination factor for protactinium-233 from Uranium-233 in the scrubbing was usually 50 to 450 as shown in Table 3-1. That in the ion exchange was about 200 to 500 as shown in Table 3-5.

Table 3-6 shows the  $\alpha$  and  $\beta$  activities of the final products. The decontamination factor for protactinium-233 all through the procedure was about  $10^4$  to  $10^5$ .

If the irradiated sample is allowed to cool for a longer

period, the contamination of uranium-233 with protactinium-233 will be reduced more than that given in the present work because the activity of protactinium-233 will decay considerably during the longer cooling period while that of uranium-233 will remain practically constant.

Identification of the final product --- The radiochemical purity of the final product was checked by the measurement of  $\alpha$  ray energy and by the 1% TBPO extraction from hydrochloric acid.

Alpha-ray energy spectra measured by Sakai and Doke are shown in Figs. 3-5 and 3-6. In these Figs, the spectra for polonium-210 and plutonium-239 are added in order to compare with the  $\alpha$ -energy of final product. Patterns in Figs. 3-5 and 3-6 show that the  $\alpha$  ray energy of the final product is  $4.8 \pm 0.05$  MeV, which corresponds to that of uranium-233, 4.316 and 4.779 MeV.

The solvent extraction behavior of the final product in the system of 1% TBPO-hydrochloric acid was checked. The results are shown in Fig. 3-2. The distribution data for the final product agree with those for uranyl chloride obtained by the activation analysis.

According to the results of the  $\alpha$ -ray spectra and the solvent extraction behavior, it is shown that the  $\alpha$ -emitter of the final product is uranium-233 and the chemical form of that is uranyl chloride.

ii. Separation of Plutonium from Irradiated Uranium by Fractional Extraction using Tri-n-butyl Phosphate

Liquid-liquid extraction for separation of plutonium from irradiated uranium has been extensively studied. Especially, TBP extraction has been widely employed for the reprocessing of spent reactor fuel. In the usual TBP extraction, as represented by thePUREX process<sup>(3-24, 25)</sup>, nitric acid solution of irradiated uranium is primarily contacted with the solvent which extracts both uranium and plutonium, leaving the bulk of fission products in aqueous solution. The uranium and plutonium extracted together are then separated in the stripping stage, where plutonium is transferred into aqueous phase by being reduced to trivalent state while uranium remains in organic phase.

The present author suggested previously in his work<sup>(3-26)</sup>, that a fractional extraction would be available to separate plutonium from the bulk of uranium at the first extraction stage of irradiated uranium processing. From 2 N nitric acid solution, uranium-plutonium extraction was continuously performed with 20% TBP in kerosene using a couple of small continuous pulse columns. The results shown in Fig. 3-7 were obtained. Uranium was found in the first 100 ml portion of organic solution whereas plutonium was concentrated in the region of solvent between 100 to 200 ml. Thus it may be concluded that the most part of uranium and plutonium could be separated from each other. Under such conditions,

the plutonium contamination in the uranium fraction came up to about 14% of the total plutonium extracted, and that of uranium in the plutonium fraction amounted to about 5% of total uranium. Accordingly, something is still left to be examined for the mutual separation of uranium and plutonium by extraction from 2 N nitric acid solution.

In the present work, more convenient conditions for the sharp mutual separation of uranium and plutonium by the fractional extraction from more dilute nitric acid solutions are described.

#### Experimental

Materials --- Commercial TBP and kerosene were used as received. Plutonium-239 tracer was prepared by irradiation of uranium in JRR-1 (3-26). In fractional extraction experiments were used depleted uranium oxide targets (3-26) irradiated in JRR-1 for a period of 75 to 194 hr.

Determination of extraction data --- Extraction of plutonium in the presence of uranium was studied using both plutonium-239 tracer and natural uranium. General techniques used were similar to those described in the previous chapter. Values for a percent extraction of plutonium in the presence of uranium were calculated from the data obtained by analysis of plutonium (3-27) in aqueous and organic phases.

Apparatus --- The small pulse extraction apparatus used is shown in Plate 3-1. It consists mainly of two glass columns of about

50 ml capacity connected to an air pulse generator.

Experimental procedure for fractional extraction --- Experiments on fractional extractions of uranium and plutonium were performed on approximately 0.5 N nitric acid solutions of irradiated uranium; the initial uranium concentration being about 0.21 to 1.26 M. 25~35 ml of the 0.5 N nitric acid solution was charged in the first column of the extraction apparatus, while the second column was filled with about 30 ml of 0.5 N nitric acid for scrubbing. Twenty percent solution of TBP in kerosene after pre-equilibration with 0.5 N nitric acid was then dropped into the first column as the pulse generator was operated. The flow rate of the extractant was controlled to be about 2 ml/min. At this stage, only uranium was extracted into the organic phase leaving plutonium in the aqueous solution. Extraction with the 20% TBP solution was continued until practically all uranium has been extracted and the aqueous phase became colorless. Usually, about 400 ml of 20% TBP was needed for extraction of most of the uranium.

After uranium had been extracted, two methods were chosen for extraction of plutonium from the aqueous solution: (I) The acidity of the aqueous phase was left as it was, and the concentration of organic solution to be supplied was increased to 40% in TBP-kerosene and was pre-equilibrated with 3 N nitric acid; (II) The acidities of the aqueous phases in both columns were raised up to about 4 N by the addition of concentrated nitric

acid; 20% TBP in kerosene pre-equilibrated with 4 M nitric acid being used as an extracting agent. In both methods, plutonium was completely transferred into the organic phase by continuous extraction with about 400 ml.

The amount of uranium or plutonium extracted in the organic solutions was determined by the colorimetric<sup>(3-28)</sup> or radiometric<sup>(3-27)</sup> method, respectively. Fission products extracted together with uranium or plutonium were studied by  $\gamma$  ray spectrometry. In some stages of the process the acidity of the aqueous solutions were determined volumetrically after precipitating uranium peroxide by the addition of hydrogen peroxide<sup>(3-29)</sup>.

The bulk of uranium, which was separated from plutonium in the extraction stage, was recovered into an aqueous phase by contacting with an ammonium carbonate solution. Further purifications of plutonium were performed by the usual method<sup>(3-26)</sup>. However, stripping of plutonium from the organic phase was tried without a particular consideration for separating uranium because most part of uranium was already removed from plutonium fraction in the extraction stage.

### Results and Discussion

Extraction for uranium and plutonium were examined for the purpose of finding better conditions for mutual separation of these two elements by a fractional extraction method. Some extraction data for uranyl and plutonium(IV) nitrates in

TBP-extraction are compiled in Fig. 3-8. Values for uranium(VI) and plutonium(IV), which are rewritten on the basis of the works of Naito<sup>(3-30)</sup>, McKay, et al<sup>(3-31, 32)</sup> and Goldschmidt, et al.<sup>(3-33)</sup> are also shown in this figure. The present data for plutonium in the presence of uranium were obtained in the extraction from nitric acid solutions containing macro amounts of uranium and tracer amounts of plutonium. No procedure was taken to keep plutonium in a definite oxidation state in order to compare the results with those of fractional extractions obtained for irradiated uranium dissolved into nitric acid without any further treatment.

It has been known that the extractability of plutonium into TBP phase in the presence of uranium decreases with increasing uranium concentration in nitric<sup>(3-33)~(3-35)</sup> or hydrochloric<sup>(3-36)</sup> acid media. When extraction is tried from nitric acid solution containing plutonium alone, plutonium can be easily extracted into TBP. In the presence of more than 0.1 M uranium, however, only a little amount of plutonium is extracted into 20% TBP from dilute nitric acid solutions (Fig. 3-8). In other words, when continuous extraction is tried from dilute nitric acid solution containing both macro quantities of uranium and trace quantity of plutonium, uranium is mainly extracted at first and as the uranium concentration in the aqueous phase is decreased, extraction of plutonium is gradually increased.



Furthermore the extractability of plutonium is affected by acidity and nitrate ion concentration in the aqueous solution as well as by uranium concentration. In the usual TBP-extraction of irradiated uranium, as for example in the Purex process, the conditions under which both plutonium and uranium are extracted have been selected. Under such conditions, it is not possible to separate plutonium from uranium in the extraction stage. On the other hand, the fractional extraction of plutonium from irradiated uranium requires a suitable acidity under which uranium is easily extracted into organic phase whereas the whole bulk of plutonium remains in aqueous phase until uranium concentration becomes very low. As Fig. 3-8 shows, plutonium gives higher extractability as uranium concentration goes down at above 1 N acidity. However, at 0.5 N acid, the extractability of plutonium is not practically affected by the concentration of uranium present. Thus it is suitable to choose the acidity region of 0.5 N nitric acid for performing the fractional extraction. Figs. 3-9 and 10 show typical variation of uranium and plutonium concentrations and of  $\gamma$ -activity extracted in the organic solutions. In Fig. 3-9 the results of the fractional extraction from about 0.5 N nitric acid solution of irradiated uranium (0.21 M uranium) are given. Extraction of uranium was carried out with 20% TBP in kerosene pre-equilibrated with 0.5 N nitric acid. The bulk of uranium was extracted with about 400 ml of 20% TBP. During this process, plutonium extracted

with 20% TBP increased slightly with decreasing uranium concentration, whereas most of plutonium remained in the aqueous phase. The result shown in Fig. 3-9 was obtained by Method (I), in which plutonium was extracted using 40% TBP in kerosene pre-equilibrated with 3 N nitric acid. The acidity of aqueous phase in the extraction apparatus was gradually raised up with nitric acid added through pre-equilibrated TBP. The extractability of plutonium was enhanced by increasing acidity in the aqueous phase, also by increasing the TBP concentration from 20 to 40% in the organic phase. Fig. 3-9 shows a gradual increase of the plutonium extracted with increasing volume of extractant (40% TBP) and that the bulk of plutonium is collected in the fractions between 100 to 400 ml. When plutonium extraction was finished, the final acidities of aqueous phases amounted to 5.6 and 2.6 N in the sample and scrubbing solutions, respectively.

The results given in Fig. 3-10 represent the extraction from a solution having an initial acidity of 0.5 N and the concentration of irradiated uranium of 0.82 M. These results were obtained by Method(II). Uranium was extracted in the same way as in Method (I) using 20% TBP and 0.5 N nitric acid solution. Therefore, uranium extraction curve in Fig. 3-10 is similar to that of Fig. 3-9. On the other hand, plutonium was extracted from the sample and scrubbing solution, after adding concentrated nitric acid to raise the acidities to 4 N. Twenty percent TBP in kerosene pre-equilibrated with 4 N nitric acid

was used for the extraction of plutonium. According to the high  $K_D$  value at 4 M nitric acid, plutonium was extracted into the first 200 ml of organic solution.

Extraction of uranium from 0.5 M nitric acid solution was generally achieved by using about 300 to 400 ml of 20% TBP. However, larger volumes of about 600 ml were required for solutions of 1.26 M initial uranium concentration. Uranium contaminations in the plutonium fractions came to about 0.6 and 1.5 % of total uranium when extraction was carried out from solutions of initial uranium concentrations of 0.21~0.32 and 0.32~1.26 M, respectively. On the other hand, the amount of plutonium extracted into uranium fractions were less than 1% of total plutonium from higher uranium concentrations and came to about 1 to 2% for lower concentrations.

A remarkable difference between the results obtained by Method (I) and (II) is that the main bulk of plutonium can be extracted in a smaller volume of TBP in Method (II). However, most of uranium contamination in the plutonium fraction is extracted in the earlier portion. Fig. 3-9 shows that the amount of uranium in the first 100 ml of plutonium fraction comes to about 80% of that in the total plutonium fraction having 400 ml volume. Hence, better results are obtained by Method (I) rather than by Method (II) as regards separation of the main fraction of plutonium from uranium contamination.

Gamma-activities extracted in the uranium fraction showed

maximum intensity in the first 100 ml. In the plutonium fractions, two patterns for the variation of  $\gamma$ -activity were shown according to the method applied. In method (I), the  $\gamma$ -activity increased gradually with increasing acidity of the aqueous phase. Method (II) gave decreasing activity as the extraction proceeded. Fig. 3-11 shows  $\gamma$ -ray spectra for uranium and plutonium fractions as compared with that for the original solution. Zirconium-95, niobium-95, ruthenium-103 and cerium-144 were the major nuclides found in **these** spectra because of 3 to 6 months cooling. Ruthenium-103 was extracted in the uranium fraction from 0.5 N nitric acid solution, while zirconium-niobium-95 were mainly extracted together with plutonium from about 4 N nitric acid solution. In the plutonium fraction in Method (I), the mixture of ruthenium-103 and zirconium-niobium-95 was extracted at an earlier stage and then the latter became more predominant with increase of acidity of the aqueous phase.

Some examples of  $\gamma$ -contamination in uranium or plutonium fraction are given in Table 3-7. About 2 and 5% of the  $\gamma$ -activity in the original solutions were found in the uranium and plutonium fractions, respectively. The uranium fraction could be further purified from fission products by scrubbing with moderate nitric acid solutions, removing ruthenium from the organic phase.

The results obtained in this work show that plutonium can be separated from uranium in TBP extraction stage of irradiated uranium processing at least on a laboratory scale, by the

fractional extraction method from 0.5 M nitric acid solution.

iii. Separation of Americium from Rare Earths by Reversed Phase Chromatographies using Tri-n-octyl Phosphine Oxide and Di-(2-ethylhexyl) phosphoric Acid

During the purification of americium, it is occasionally required to separate americium from macroamounts of lanthanum after coprecipitating americium with the lanthanum carrier. It is well known that americium can be recovered with good yield and high purity by ion exchange and solvent extraction from solutions containing large amounts of lanthanum and other elements. Now, in most cases of these procedures, aqueous solutions of high concentration of salts such as 10 M lithium chloride<sup>(3-37)</sup> and 5 M ammonium thiocyanate<sup>(3-38)</sup> are used, and this necessitates further separation of americium and lanthanum from the salts. On the other hand, in recent years, reversed phase chromatography has received attention for the separation of rare earths, for its good efficiency in the mutual separation of these elements, and it does not involve the use of acid solutions containing complexing reagents. Siekierski<sup>(3-39)(3-40)</sup> has successfully separated rare earths from each other using a column of TBE held on kieselguhr and eluting with nitric acid solutions. Di(2-ethylhexyl)orthophosphoric acid (HDEHP) on

alumina<sup>(3-41)(3-42)</sup>, on kieselguhr<sup>(3-43)</sup>, on Kel-F<sup>(3-44)</sup> and on Corvic<sup>(3-45)~(3-48)</sup> has also been used by some investigators for the mutual separation of rare earths with hydrochloric<sup>(3-41)~(3-44)</sup> or perchloric<sup>(3-45)~(3-48)</sup> acid solutions. In these works only microamounts of rare earths have been used for the mutual separation owing to the low capacities of the columns for metal ions.

In the present work, the separation of americium from promethium, samarium, europium and lanthanum by means of reversed phase chromatography was studied, using columns of HDEHP and TOPO held on kieselguhr treated with dimethyl-dichlorosilane and eluting with nitric acid solutions of low concentrations.

#### Experimental

Reagents --- HDEHP received from Virginia Chemicals, Co. was purified according to the method described by Peppard<sup>(3-49)</sup>. TOPO supplied from Dojindo Co. Ltd. was used without further purification. Other reagents used were of A. R. Grade. The kieselguhr "Shimalite" obtained from Shimadzu Seisakusho Co. was ground and sieved to 100~150, 150~230 and 200~400 mesh. Americium-241, lanthanum-140, praseodimium-142, promethium-147, -149, samarium-153 and europium-152, -154 were used as radioactive tracers.

Column preparation --- The kieselguhr was dried at 110°C and then placed for a day in a desiccator containing an open bottle

of dimethyldichlorosilane in order to make the surface hydrophobic. The treated kieselguhr was heated to remove hydrogen chloride. To the product, an acetone solution of HDEHP or TOPO-xylene was added to a ratio of about 0.5 ml of undiluted HDEHP or 0.8 ml TOPO-xylene solution to 1g of kieselguhr. The resultant mixture was well stirred and left until the acetone was gone. A dilute nitric acid solution was added to the ostensibly dry product and heated on a water bath until all particles settled out. The final product was stocked in water. The column beds were packed by settling the slurry of this product and slightly pressing the beds with a glass rod after addition of small portions of this kieselguhr. The column beds were of 3 to 6 mm in diameter and 7 to 14 cm in length. Some of the columns were prepared by introducing 50% HDEHP toluene solutions into the kieselguhr beds without treating with acetone and dilute nitric acid solutions. These columns were washed with water under slight pressure to remove air.

Procedure --- 0.1~4.3 ml of the sample solutions were introduced from the top of the columns, which had been previously washed with nitric acid solutions of suitable concentrations, and then eluted with nitric acid solution of concentrations required to separate the metal ions. In the case of elution using columns of 3 mm diameter packed with 200~400 mesh kieselguhr, some pressure amounting to a fraction of atmospheric was required. One drop in 0.25 to 10 ml of eluate was sampled and evaporated

on a platinum or stainless steel plate by means of induction heating, and its activity was measured.  $\alpha$  activity was counted with a proportional counter, and  $\beta$  activity with an end window G. M. counter.

The free column volumes were determined by using lanthanum-140 of 1 N nitric acid solution, under such condition that the lanthanum would not be adsorbed on the column bed.

The experiments were carried out at room temperature, about 20°C.

#### Results and Discussion

Characteristics of columns --- It is necessary in chromatographic separation for the column to be reproducible in form and that the same element always be eluted with the same eluate volume under similar conditions. For reference in checking the reliability of the method used in this work, elution data obtained for americium with an HDEHP-kieselguhr column under the same conditions during two months have been collected in table 3-8. Those for promethium and europium with a TOPO-kieselguhr column during a week are also given in this table. The values of peak eluate volume in the elution of promethium or europium agree with each other with a variation of less than 5%. This variation may be considered within the limits of experimental error. For americium it is less than  $\pm 10\%$  from the mean value. The discrepancy is permissible for the mutual separation of rare



earths by reversed phase chromatography using HDEHP, because the separation factors are close to 2.5 for adjacent elements (3-43)~(3-44).

Distribution of metal ion between HDEHP and aqueous solution depends solely on the acidity in the aqueous solution. Consequently, in reversed phase chromatography using HDEHP, elution of metal ion should similarly be influenced only by eluant acidity and not by the species and concentration of the anion. In fact, elution curves for promethium and europium with 0.3 N nitric, sulphuric and hydrochloric acid solutions resemble each other very closely in Fig. 3-12.

Figures 3-13 and 3-14 show the relationships between the peak eluate volumes in HDEHP- and TOPO-reversed phase chromatographies and the distribution ratio  $K_d$  in the corresponding solvent extraction systems. Hydrochloric acid solutions were used as eluants from the HDEHP-kieselguhr columns for comparison with the  $K_d$  values cited from the work by Kimura (3-50), who obtained the data with a system of 50% HDEHP and hydrochloric acid. But for the reason mentioned earlier, the relationships thus obtained in the HDEHP-hydrochloric acid system must be converted for application to either HDEHP-nitric or -sulphuric acid system. In these figures, the peak eluate volumes are proportional to the values of  $K_d$ , and the values obtained lie along straight lines with only small deviation. This fact speaks for the good reliability of the HDEHP and TOPO reversed phase chromatographies. In other words, when the relationship between

$K_d$  value in solvent extraction and peak eluate volume from a column are known for a metal ion, peak eluate volumes from the column for other metal ions of which the  $K_d$  values are known for the same extraction system can be easily estimated from the same relationship. Accordingly, whether a metal ion is separated or not from other ions through reversed phase chromatography using a given solvent system can be estimated from the extraction data obtained on that system.

In order to measure the loading capacity of a HDEHP-kieselguhr column for metal ion, a series of columns with different HDEHP loadings **was** prepared by directly introducing HDEHP toluene solutions into the column beds. The capacities were measured by saturating lanthanum nitrate in a 0.05 N nitric acid solution. The results are shown in Table 3-9, together with the calculated values from the amount of HDEHP, assuming the HDEHP to be dimeric in toluene. It is seen that in all cases the values found are somewhat higher than calculated. The reason for this has not been investigated in this work, but similar results using HDEHP-Corvic mixtures have been reported also by Pierce<sup>(3-47)</sup>, who obtained values 1.3~1.6 as ratio between observed and calculated loading capacities.

In generally, reversed phase chromatography has the defect of small loading capacity for metal ion, and thus it has so far been used only for the separation of microamounts of rare earths. In the present work, an experiment was designed to examine the

effect on the elution of americium produced by the presence of mg amounts of rare earth. On the basis of the extraction data for americium and rare earths reported by Peppard<sup>(3-49)</sup>, it may be deduced that HDEHP reversed phase chromatography can easily separate americium from rare earths of atomic number larger than 61. Separation with HDEHP-kieselguhr column was tried on a sample containing microamounts of americium, promethium and europium and 1 mg of irradiated samarium corresponding to about 10% of the loading capacity of the 3 mm $\phi$  x 7 cm column. The results are shown in Fig. 3-15. Americium is satisfactorily separated from the rare earths. Separation factors for the adjacent rare earths are 2.0 under the conditions of the experiment, and are smaller than the value of 2.5 reported in previous studies<sup>(3-43,44,48)</sup> with microamounts of the elements. Thus, while the increase of sample size to mg amount affects the elution of metal ions in some degree, it still would not be an obstruction to the mutual separation of the elements.

Separation of americium and some rare earths from lanthanum

carrier in HDEHP system --- In the HDEHP system, it is possible to separate amounts below mg order of americium and certain rare earths from lanthanum carrier after coprecipitation, if conditions are chosen such that the former are absorbed on the HDEHP-column bed and the latter passes through. The conditions should be determined on the basis of both extraction data<sup>(3-49,50)</sup> (Fig. 3-16) and the characteristics of the column. Typical examples are shown

in Figs. 3-17 and 3-18.

Figure 3-17 shows the separation of americium, praseodimium and promethium from lanthanum. Tracer amounts of americium and promethium and 1 mg of irradiated praseodimium were coprecipitated as hydroxide with 5 mg of lanthanum. The precipitate was centrifuged and then dissolved in a fraction of ml of nitric acid. After repeated coprecipitation, the precipitate was dissolved with a few drops of 1 N nitric acid and then diluted to 0.6 ml with 0.1 N nitric acid solution. The resultant solution was about 0.15 N in acidity. The solution was introduced into a 3 mm  $\phi$  x 7 cm, HDEHP-kieselguhr column with 200~400 mesh, and the column bed was washed successively with 3.6 ml of 0.3 N and 2.5 ml of 0.5 N nitric acid.

Although the peak eluate volume of americium in this figure is less than in Fig. 3-15, americium is still effectively separated from the lanthanum carrier. The elution curve for americium overlaps with that for praseodimium. The shoulders appearing on the elution curves for americium in Figs. 3-15 and 3-17 are due to the presence of curium-242. Mutual separation of americium from curium by this method is more difficult than for the rare earths. It is likely that the separation factor between curium and americium is about 1.5 under the conditions of the present experiments, and is smaller than in other mutual separation methods such as cation exchange with  $\alpha$ -hydroxy isobutylate.

Next, a tracer amount of promethium and 0.3 mg of europium

were coprecipitated as hydroxide with 110 mg of lanthanum carrier. The precipitate was treated in the same way as above. A 4.3 ml sample was finally prepared as 0.25 N nitric acid solution. The solution was passed through a 6 mm $\phi$  x 14 cm HDEHP-kieselguhr column, 100~150 mesh, and then eluted successively with 16 ml of 0.3 N, 30 ml of 0.4 N and 15 ml of 1 N nitric acid solutions. The results are shown in Fig. 3-18. Promethium and europium are clearly separated from the lanthanum carrier, but these elution curves are broad in comparison with those shown in Figs. 3-15 and 3-17. The column used in this experiment had a free column volume of about 30% of the geometrical volume, while the corresponding values were 50~70% in the other experiments. It would thus appear that the free column volume, in other words the space available for the contact of organic solvent with aqueous solution, should occupy about 50~70% of the geometrical volume in order to obtain a sharp elution curve for metal ion. During the present work, increasing the loading capacity, namely the solvent volume adsorbed on kieselguhr, frequently brought about a decrease in the free column volume and lowered on the sharpness of the elution curve. The tendency was particularly marked in the region where the ratios of solvent volumes to kieselguhr weight were above 1/2(ml/g).

Separation of Am from some rare earths in TOPO system ---

According to extraction data on the TOPO system<sup>(3-51,52)</sup>, the ratio of K<sub>d</sub> value between europium and americium is about 2 at

3 N aqueous nitrate concentration, while at 0.25 N nitric acid concentration the  $K_d$  value for americium is close to that for europium, and the  $\text{Eu/La}$   $K_d$  ratio is about 10. Thus it can be deduced that the TOPO reversed phase chromatography could effectively be applied to the separation of americium from lanthanum with 0.25 N nitric acid solution, and from europium with 3 N nitrate solution.

Figure 3-19 (a) shows the separation of americium from lanthanum. A tracer amount of americium was coprecipitated with 5 mg of lanthanum carrier and treated similarly to the previous cases. The sample and eluant were 0.25 N nitric acid solutions. As seen from this figure, americium has been successfully separated from 5 mg of lanthanum. A sharper elution curve for americium was obtained by using a longer column and fine supporting material below 150 mesh. When lanthanum was present to an amount of 25 mg, americium could not be separated with a 3 mm  $\phi$  x 7 cm column, but a column of larger loading capacity might prove successful, as in the case of the HDEHP method (Fig. 3-18).

The separation of americium from europium is shown in Fig. 3-19 (b). A separation factor of 2 can be obtained by eluting with 3 N nitrate solution containing 0.25 N nitric acid. In this case the elution curve for promethium overlaps those for americium and europium.

It is proved from the foregoing that americium can be effectively separated from lanthanum carrier by means of reversed phase chromatography with TOPO as well as with HDEHP, using diluted nitric acid solutions as eluants. For the separation of americium from promethium and europium, however, the HDEHP system is better than the TOPO system because of the higher separation factors between these metal ions and for the possibility of using an eluant of simple acid solution.

## References

- 1-1) L.L. Smith, Solvent Extraction Data for Plutonium, DP-700 (1962).
- 1-2) G.H. Morrison and H. Freiser, Solvent Extraction in Analytical Chemistry, Wiley, New York, (1957).
- 1-3) K. Naito, Studies on Chemical Separation of Actinide Elements, the thesis for degree, (1960).
- 1-4) K. Oshima, J. Atomic Energy Soc. Japan, 4, 166 (1962).
- 2-1) for example, K. Naito, Bull. Chem. Soc. Japan, 33, 363 (1960).
- 2-2) for example, D.F. Peppard, C.W. Mason and J.L. Maier, J. Inorg. Nucl. Chem., 3, 215 (1956).
- 2-3) for example, C.J. Hardy, D. Scargill and J.M. Fletcher, *ibid.*, 7, 257 (1958).
- 2-4) for example, T. Ishimori and E. Nakamura, Bull. Chem. Soc. Japan, 32, 713 (1959).
- 2-5) for example, G.F. Best, H.A.C. McKay and P.R. Woodgate, J. Inorg. Nucl. Chem., 4, 315 (1957).
- 2-6) G.N. Yakovlev and V.N. Kosyakov, Proceedings of the Second International Conference on Peaceful Uses of Atomic Energy, Vol. XXVIII P/2127, United Nations Publication, New York, (1959).
- 2-7) W.J. Ross and J.C. White, ORNL-2627 (1958).
- 2-8) T. Ishimori, K. Kimura, T. Fujino and H. Murakami, J. Atomic Energy Soc. Japan, 4, 117 (1962).
- 2-9) H. Umezawa, *ibid.*, 2, 478 (1960).



- 2-10) K. Alcock, S.S. Grimley, T.V. Healy, J. Kennedy and H.A.C. McKay, Trans. Faraday Soc., 52, 39 (1956).
- 2-11) D.F. Leppard, W.J. Driscoll, R.J. Sironen and S. McCarty, *ibid.*, 4, 326 (1957).
- 2-12) S. Nakamura, Radiochimica Acta, 2, 66 (1963).
- 2-13) K. Watanabe, J. Atomic Energy Soc. Japan, 3, 497 (1961).
- 2-14) D. Dyrssen, Svensk. Kem. Tid., 62, 153 (1950).
- 2-15) T. Ishimori, K. Watanabe and K. Kimura, J. Atomic Energy Soc. Japan, 2, 750 (1960).
- 2-16) T. Fujino, *ibid.*, 5, 640 (1963).
- 2-17) H. Irving and D.W. Edgington, J. Inorg. Nucl. Chem., 10, 306 (1959).
- 2-18) D.F. Leppard, F.R. Gray and W.M. Markus, J. Am. Chem. Soc., 75, 6063 (1953).
- 2-19) T. Ishimori, K. Watanabe and S. Nakamura, Bull. Chem. Soc. Japan, 33, 636 (1960).
- 2-20) D. Scargill, K. Alcock, J.M. Fletcher, E. Hesford and H.A.C. McKay, J. Inorg. Nucl. Chem., 4, 304 (1957).
- 2-21) E. Hesford, E.E. Jackson and H.A.C. McKay, *ibid.*, 2, 279 (1959).
- 2-22) E. Glueckauf, Bel. Chem. Ind., 23, 1215 (1958).
- 2-23) K. Alcock, G.F. Best, E. Hesford and H.A.C. McKay, J. Inorg. Nucl. Chem., 6, 328 (1958).
- 2-24) T. Ishimori and K. Watanabe, Bull. Chem. Soc. Japan, 33, 1443 (1960).

- 2-25) T. Ishimori, K. Watanabe and T. Fujino, J. Atomic Energ. Soc. Japan, 3, 19 (1961).
- 2-26) T. Ishimori, K. Kimura, T. Fujino and H. Murakami, *ibid.*, 4, 117 (1962).
- 2-27) W.J. Ross and J.C. White, ORNL-CF-56-9-18 (1956).
- 2-28) K. Kimura, T. Ishimori, K. Naito, H. Umezawa and K. Watanabe, J. Atomic Energy Soc. Japan, 2, 328 (1960).
- 2-29) K. Naito and T. Suzuki, J. Phys. Chem., 66, 989 (1962).
- 2-30) L. Kaplan, R.A. Hildebrand and M. Ader, ANL-4521 (1950).
- 2-31) S. Hietanam, Acta Chem. Scand., 8, 1626 (1954).
- 2-32) K.A. Kraus, A/Conf. P/731, 7, 245 (1955).
- 2-33) K.A. Kraus and R.W. Holmberg. J. Phys. Chem., 58, 325 (1954).
- 2-34) E. Reilly, ANL-5254 (1954).
- 2-35) R.P. Larsen and C.A. Seils, Anal. Chem., 32, 1863 (1960).
- 2-36) E. Iwase and T. Isono, Sci, Pap. I.P.C.R., 53, 13 (1959).
- 2-37) K. Nukada, K. Naito and U. Maeda, Bull. Chem. Soc. Japan, 33, 894 (1960).
- 2-38) B. Martin, D.W. Ockenden and J.K. Foreman, J. Inorg. Nucl. Chem., 21, 96 (1961).
- 2-39) T. Ishimori, C.T. Rhee and T. Fujino, J. Atomic Energy Soc. Japan, 4, 837 (1962).
- 3-1) L.I. Katzin, TID-5223 (1952).
- 3-2) G.T. Seaborg. J.W. Gofman and R.W. Stoughton, U.S. Patent 2,861,866 (1958).

- 3-3) G.T. Seaborg, J.W. Gofman and R.W. Stoughton, U.S. Patent 2,900,228 (1959).
- 3-4) D.F. Peppard, G.W. Mason and M.V. Gergel, J. Inorg. Nucl. Chem., 3, 370 (1957).
- 3-5) W.H. Hardwick and M. Moreton-Smith, Analyst, 83, 9 (1958).
- 3-6) R.F. Clayton, W.H. Hardwick, M. Moreton Smith and R. Todd, *ibid.*, 83, 13 (1958).
- 3-7) A. Van Winkle, U.S. Patent 2,895, 791 (1959).
- 3-8) O.K. Neville, U.S. Patent, 2,902,503 (1959).
- 3-9) Brit. Patent 800, 791, Nucl. Eng., 4, 188 (1959).
- 3-10) Brit. Patent 809,282 (1959).
- 3-11) I.L. Jenkins and R.J. Richardson, AERE-C/R-1217, (1953).
- 3-12) K.A. Kraus, G.E. Moore and F. Nelson, J. Am. Chem. Soc., 78, 2692 (1956).
- 3-13) A. Chesne and P. Regnant, A/Conf., 8P/350 (1955).
- 3-14) R.W. Bane, U.S. Patent 2,902,338 (1959).
- 3-15) A.T. Gresky, CF-56-2-157 (1956).
- 3-16) C.D. Susano, H.S. House and M.A. Marler, TID-7555, (1958).
- 3-17) L.L. Burger, J. Phys. Chem., 62, 590 (1958).
- 3-18) S. Nomura and R. Hara, (Unpublished).
- 3-19) D.F. Peppard, G.W. Mason and J.L. Maier, J. Inorg. Nucl. chem., 3, 215 (1956).
- 3-20) D.F. Peppard, W.J. Driscoll, R.J. Sironen and S. McCarty, *ibid.*, 4, 326 (1957).
- 3-21) T. Ishimori and E. Nakamura, Bull. Chem. Soc. Japan, 32, 713 (1959).

- 3-22) T. Ishimori, K. Watanabe and T. Fujino, J. Atomic Energ. Soc. Japan, 3, 19 (1961).
- 3-23) Gmelins Handbuch der anorganischen Chemie, 44, Thorium und Isotope, 225 (1955), Verlag Chemie, GMBH, Weinheim.
- 3-24) F.L. Culler, A/Conf., 9, P/822, 465 (1956), United Nations, New York.
- 3-25) E.R. Irish, HW-60116, (1959).
- 3-26) K. Kimura, T. Ishimori, K. Naito, H. Umezawa and K. Watanabe, J. Atomic Energy Soc. Japan, 2, 328 (1960).
- 3-27) K. Watanabe, *ibid.*, 3, 497 (1961).
- 3-28) E.B. Sandell, "Colorimetric Determination of Traces of Metals", 915 (1959), Interscience Publishers, Inc., New York.
- 3-29) R.E. Connic, MDDC-1245 (1945).
- 3-30) K. Naito, unpublished.
- 3-31) G.F. Best, H.A.C. McKay and P.R. Woodgate, J. Inorg. Nucl. Chem., 4, 315 (1957).
- 3-32) K. Alcock, G.F. Best, E. Hesfor and H.A.C. McKay, *ibid.*, 6, 328 (1958).
- 3-33) B. Goldschmidt, P. Regnaut and I. Prevot, A/Conf., 9, P/349, 492 (1956), United Nations, New York.
- 3-34) J.T. Wood and J.A. Williams, J. Brit. Nucl. Energy Conf., 3, 315 (1958).
- 3-35) J.R. Flanary, A/Conf., 9, P/539, 528 (1956), United Nations, New York.
- 3-36) M. Beederman and C. Kesser, ANL-5254 10-17 (1954).

- 3-37) for example, M.H. Loyd and R.E. Leuze, CF-60-3-23 (1960).
- 3-38) for example, V.A. Ryan and J.W. Pringle, RFP-130 (1960).
- 3-39) S. Siekierski and I. Fidelis, J. Chromatog., 4, 60 (1960).
- 3-40) idem., NP-9643 (1960).
- 3-41) J.W. Winchester, CF-58-12-43 (1958).
- 3-42) idem., CF-60-3-158 (1960).
- 3-43) idem., J. Chromatog., 10, 502 (1963).
- 3-44) E. Cerrai and C. Testa, J. Inorg. Nucl. Chem., 25, 1045 (1963).
- 3-45) T.B. Pierce and P.F. Peck, Nature 194, Apr. 84 (1962).
- 3-46) T.B. Pierce and P.F. Peck, *ibid.*, 194, Aug. 597 (1962).
- 3-47) T.B. Pierce and R.S. Hobbs, J. Chromatog., 12, 74 (1963).
- 3-48) T.B. Pierce, R.F. Peck and R.S. Hobbs, *ibid.*, 12, 81 (1963).
- 3-49) D.F. Peppard, G.W. Mason, J. L. Maier and W.J. Driscoll, J. Inorg. Nucl. Chem., 4, 334 (1957).
- 3-50) K. Kimura, Bull. Chem. Soc. Japan, 33, 1038 (1960).
- 3-51) K. Watanabe and R. Ono, J. Nucl. Sci. Tech., 1, 75 (1963).
- 3-52) T. Ishimori and C.T. Rhee, unpublished.

Table 2-1. Sources of Radioactive Tracers used

Element	Tracer	Target	Method for checking Radiochemical Purity	Remarks
Th	$^{234}\text{Th}$		$\gamma$ spectrum and decay curve	milked from $^{238}\text{U}$ by extraction (2-14)
Pa	$^{233}\text{Pa}$	$\text{ThO}_2$	$\gamma$ spectrum	processed by solvent extraction (2-15)
U	$^{233}\text{U}$	$\text{ThO}_2$	$\alpha$ spectrum	processed by solvent extraction (2-15)
	$^{237}\text{U}$	natural U	$\gamma$ spectrum and decay curve	prepared by E. Nakamura
Pu	$^{239}\text{Pu}$	deplete U	$\alpha$ spectrum	Processed by ion exchange (2-13, 28)
	mixture of Pu isotopes		$\alpha$ spectrum	imported
Am	$^{241}\text{Am}$		$\alpha$ and $\gamma$ spectra	imported
Cm	$^{242}\text{Cm}$	$^{241}\text{Am}$	$\alpha$ spectrum	processed by cation exchange (2-16)

Table 3 - 1 Scrubbing of  $^{233}\text{Pa}$  from 1 %TBPO with HCl saturated with NaF

Vol. of org. phase (ml)	Total vol. of aq. phase (ml)	Acidity of aq. phase (N)	Number of scrubbing	Activity (cpm)			
				$^{233}\text{Pa}(\beta)$		$^{233}\text{U}(\alpha)$ in org. phase	
				In org. phase	In aq. phase	Before scrubbing	After scrubbing
20	20	6	4	$8 \times 10^5$	$3.6 \times 10^5$	$4.6 \times 10^4$	$3.8 \times 10^4$
24	12	6	2	$7.7 \times 10^6$	$4 \times 10^5$	$5.9 \times 10^4$	$5.4 \times 10^4$
25	20	6	4	$2.4 \times 10^6$	$4 \times 10^5$		-
24	20	6	4	$8 \times 10^6$	$7 \times 10^5$	$1.6 \times 10^4$	$1.3 \times 10^4$

Table 3 - 2 Stripping of  $^{233}\text{U}$  from 1 %TBPO with 4 N acetic acid

	Vol. of org. phase (ml)	Vol. of aq. phase (ml)	Activity (cpm)			
			$^{233}\text{Pa}(\beta)$		$^{233}\text{U}(\alpha)$	
			In aq. phase	In org. phase	In aq. phase	In org. phase
1	5.8	1.8	$2.2 \times 10^5$	-	$4.2 \times 10^4$	-
2	-	2.0	$2.0 \times 10^4$	-	$5 \times 10^3$	-
3	-	1.8	$3.2 \times 10^3$	$2.9 \times 10^3$	$1.3 \times 10^3$	$1.1 \times 10^3$

Table 3 — 3 Extractions of  $^{234}\text{Pa}$  and  $^{238}\text{U}$  with 1% TBPO from 6 N HCl saturated with NaF

	Vol. of aq. phase (ml)	Vol. of org. phase (ml)	Activity (cpm)			
			$^{234}\text{Pa}$ ( $\gamma$ )		$^{238}\text{U}$ ( $\alpha$ )	
			In org. phase	In aq. phase	In org. phase	In aq. phase
1	8	2	$1 \times 10^6$	$5.0 \times 10^6$	$5 \times 10^4$	-
2		2	$1.4 \times 10^6$	$3.6 \times 10^6$	$6 \times 10^4$	-
3		2	$1.4 \times 10^6$	$2.2 \times 10^6$	$6 \times 10^2$	$3 \times 10^2$

Table 3 — 4 Scrubbing of  $^{234}\text{Pa}$  with HCl saturated with NaF in second cycle

	Vol. of org. phase (ml)	Total vol. of aq. phase (ml)	Acidity of aq. phase (N)	Number of scrubbing	Activity (cpm)			
					$^{234}\text{Pa}$ ( $\beta$ )		$^{238}\text{U}$ ( $\alpha$ )	
					In org. phase	In aq. phase	Before scrubbing	After scrubbing
1	2.4	5.5	6	3	$1.2 \times 10^4$	$1.3 \times 10^5$	$1.0 \times 10^4$	$1.0 \times 10^4$
2	6	6	6	3	$2.0 \times 10^5$	$1.1 \times 10^7$	-	-
3	4.5	4.5	4	3	$3.4 \times 10^4$	$5.5 \times 10^5$	$1.23 \times 10^4$	$1.19 \times 10^4$



Table 3-5 Decontamination of  $^{233}\text{Pa}$  from  $^{233}\text{U}$  by cation exchange

	Initial activity (cpm)		$^{233}\text{Pa}$ eluted in 0.1 N HCl, 0.02 M $\text{NaF}$ fraction	Final product (2 N HCl fraction)	
	$^{233}\text{Pa}$ ( $\beta$ )	$^{233}\text{U}$ ( $\alpha$ )		$\beta$	$\alpha$
1	$9.9 \times 10^7$	$2.0 \times 10^4$	$9.9 \times 10^7$	$5.0 \times 10^5$	$1.9 \times 10^4$
2	$9.8 \times 10^7$	$9.0 \times 10^4$	$9.8 \times 10^7$	$1.9 \times 10^5$	$8.6 \times 10^4$

Table 3-6 Ratio of  $\alpha:\beta$  activity in final product

	Method for final purification	$\beta$ (cpm)	$\alpha$ (cpm)
1	Cation exchange	$5.0 \times 10^5$	$1.9 \times 10^4$
2	Cation exchange and solvent extraction	$1.5 \times 10^4$	$1.13 \times 10^4$
3	Cation exchange	$6.2 \times 10^5$	$6.4 \times 10^4$
4	Cation exchange	$4.0 \times 10^4$	$1.7 \times 10^4$
5	Cation exchange	$1.9 \times 10^5$	$8.6 \times 10^4$
6	Cation exchange and solvent extraction	$2.75 \times 10^4$	$2.74 \times 10^4$

**Table 3-7**  $\gamma$ -activity contaminating in  
U- and Pu-fractions

	Method	$\gamma$ -activity in original solution (cpm)	$\gamma$ -activity in U-fraction (cpm)	$\gamma$ -activity in Pu- fraction (cpm)
1	I	$2.0 \times 10^7$	$4.4 \times 10^6$	$1.1 \times 10^7$
2	I	$1.0 \times 10^7$	$2.6 \times 10^6$	$5.3 \times 10^6$
3	II	$3.8 \times 10^7$	$6.9 \times 10^5$	$1.9 \times 10^6$
4	II	$2.8 \times 10^7$	$4.9 \times 10^6$	$1.2 \times 10^7$

Table 3-8 Peak Eluate Volumes for Am, Fm and Eu  
in HDEHP and TOPO Reversed Phase Chromatography

Column	Element	Peak Eluate Volume	Conditions
HDEHP 3mm $\phi$ x 7 cm 200~400 mesh	Am	3.2 ml	Flow rate, 0.15 <sup>ml</sup> /cm <sup>2</sup> .min Eluant, 0.3 N HNO <sub>3</sub>
		3.1	
		2.8	
		3.2	
		3.0	
TOPO 3mm $\phi$ x 7 cm 100~150 mesh	Fm	15.5	Flow rate, 0.8 <sup>ml</sup> /cm <sup>2</sup> .min Eluant, 0.25 N HNO <sub>3</sub> 2.75 N NH <sub>4</sub> NO <sub>3</sub>
		16.0	
	Eu	23.5	
		24.0	
		24.5	

Table 3-9 Capacity of HDEHP-kieselguhr Columns

Column	Mesh Size	Capacity (m eq./g)	
		Found	Calculated
6mm $\phi$ x 14 cm	100 ~ 150	0.23	0.20
		0.34	0.31
		1.0	0.9
4mm $\phi$ x 11 cm	150 ~ 230	0.29	0.25
		0.61	0.53

**This is a blank page.**

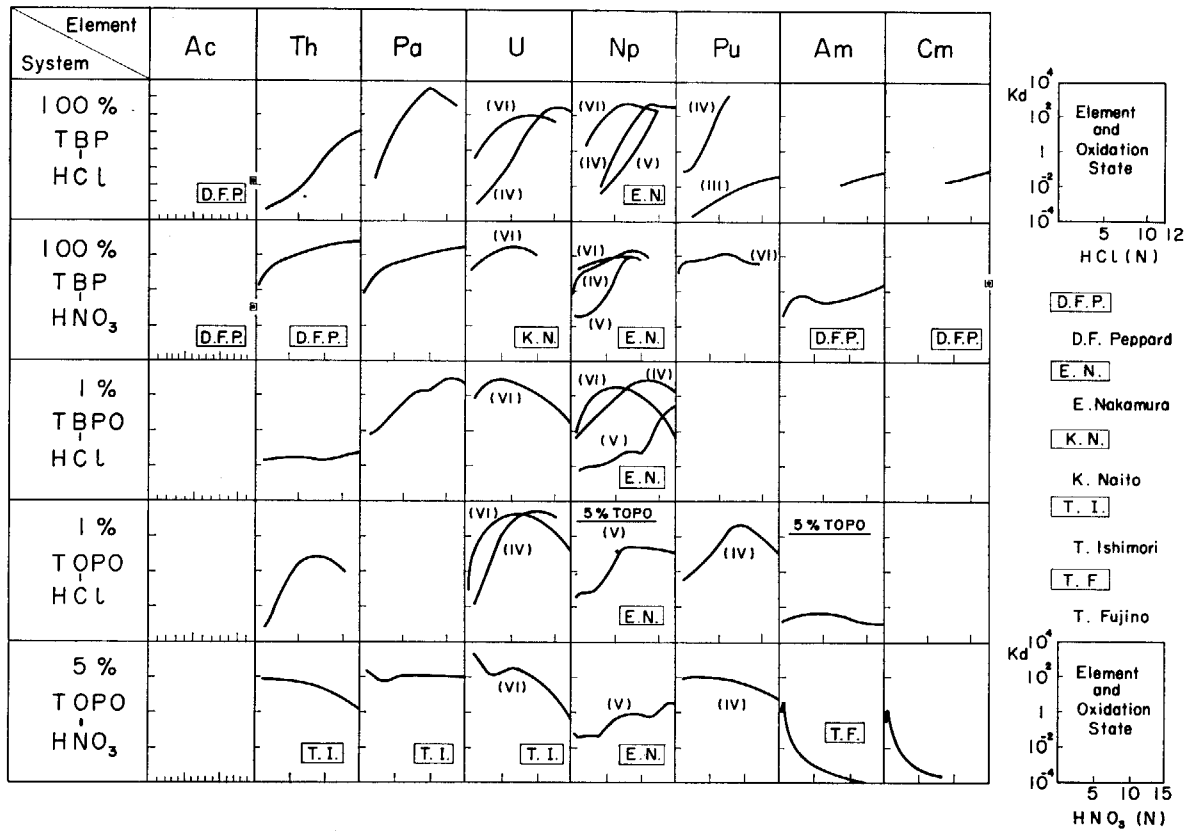


Fig. 2-1 Extraction of actinide elements from HCl and HNO<sub>3</sub> by TBP, TBPO, and TOPO

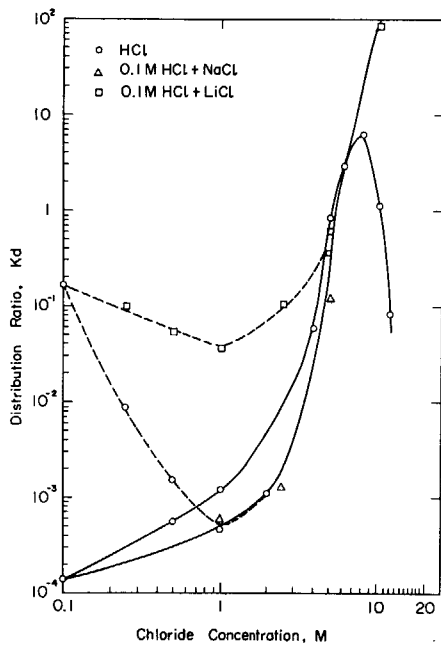


Fig. 2-2 Distribution of Th between 1% TOPO-toluene and chloride solutions

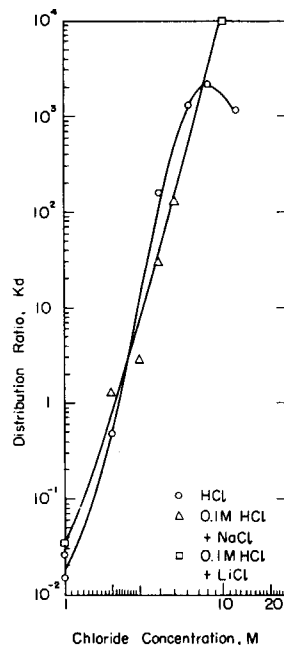


Fig. 2-3 Distribution of U(IV) between 1% TOPO-toluene and chloride solutions

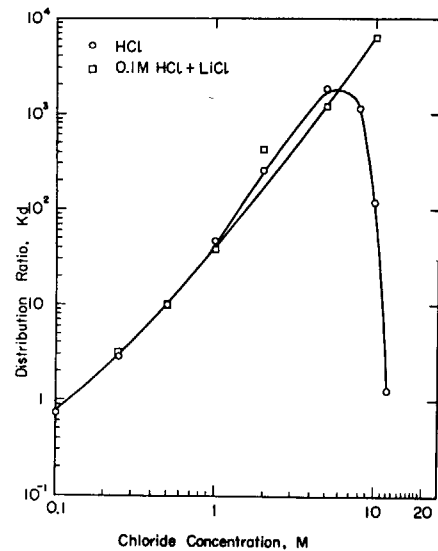


Fig. 2-4 Distribution of U(VI) between 1% TOPO-toluene and chloride solutions

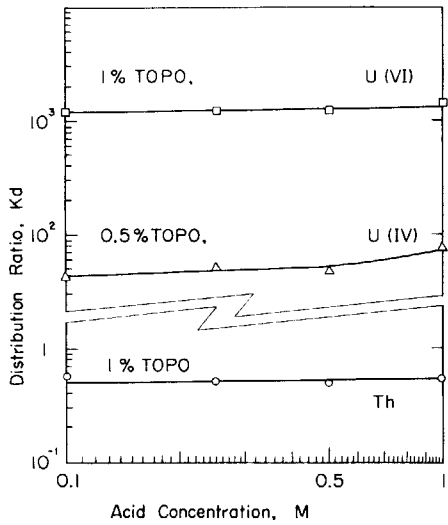


Fig. 2-5 Variation of  $K_d$  values for Th, U(IV) and (VI) with acid concentration  
Aq. soln. NaCl+HCl,  $[Cl^-]=5\text{ M}$

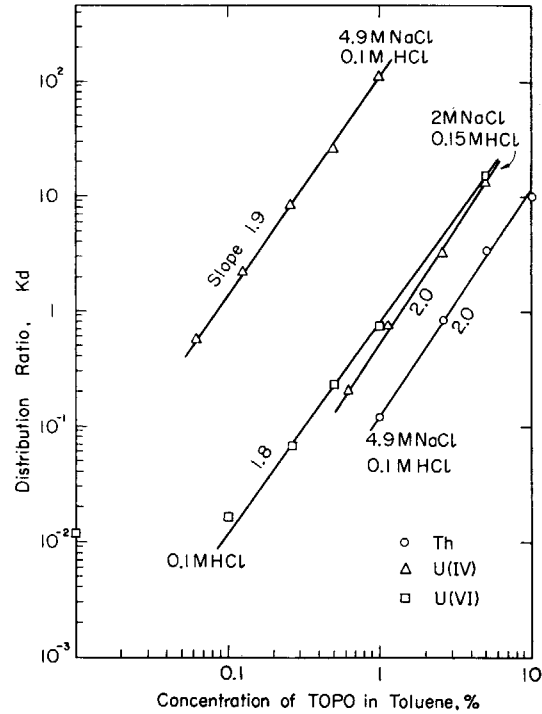


Fig. 2-6 Variation of  $K_d$  values for Th, U(IV) and (VI) with TOPO concentration

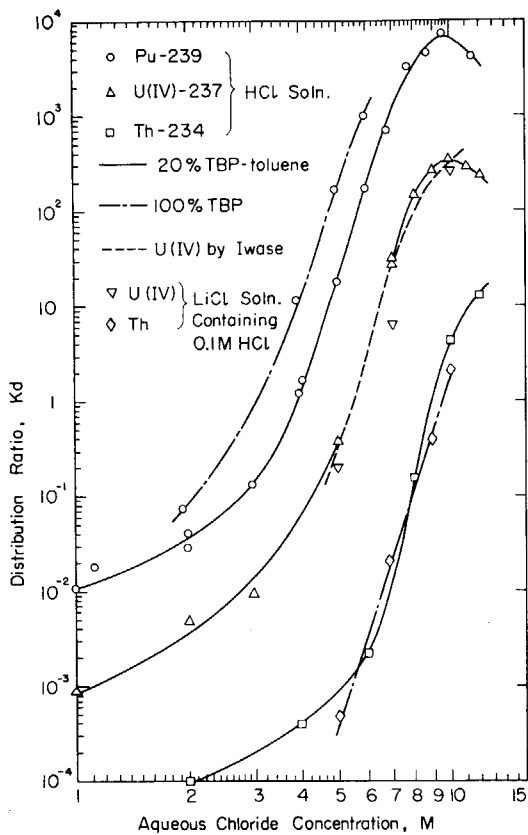


Fig. 2-7 Distribution of Th, U(IV) and Pu(IV) between TBP and HCl or LiCl solutions

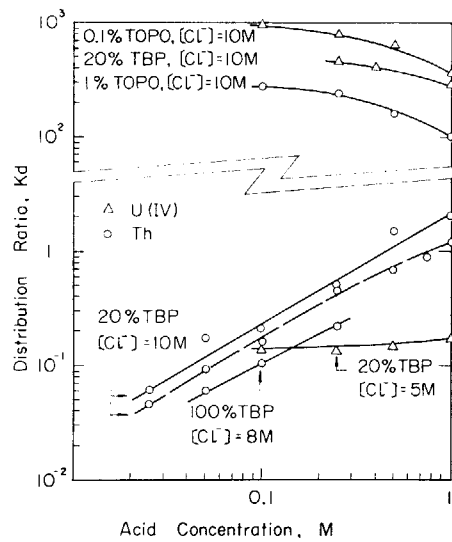


Fig. 2-8 Variation of  $K_d$  values for Th and U(IV) in extraction by TBP and TOPO

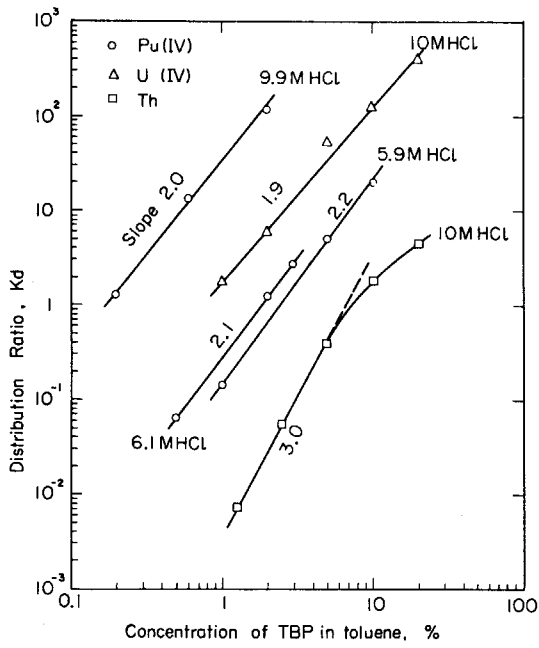


Fig. 2-9 Variation of distribution ratio of Th, U(IV) and Pu(IV) with TBP concentration

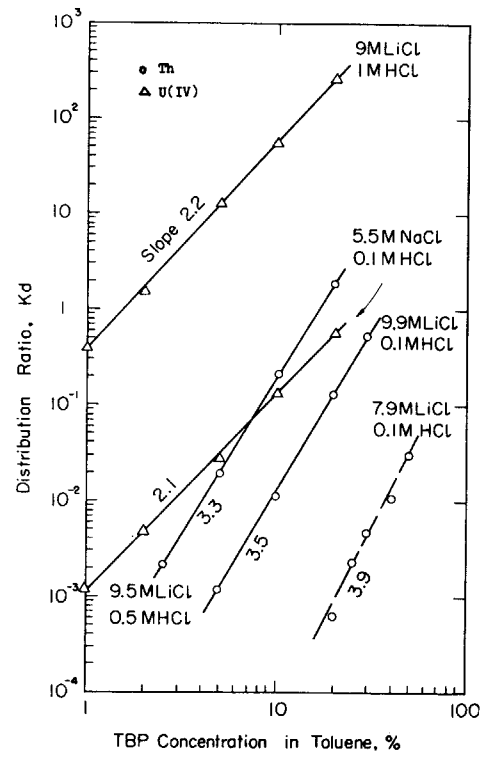


Fig. 2-10 Variation of  $K_d$  values for Th and U(IV) with TBP concentration

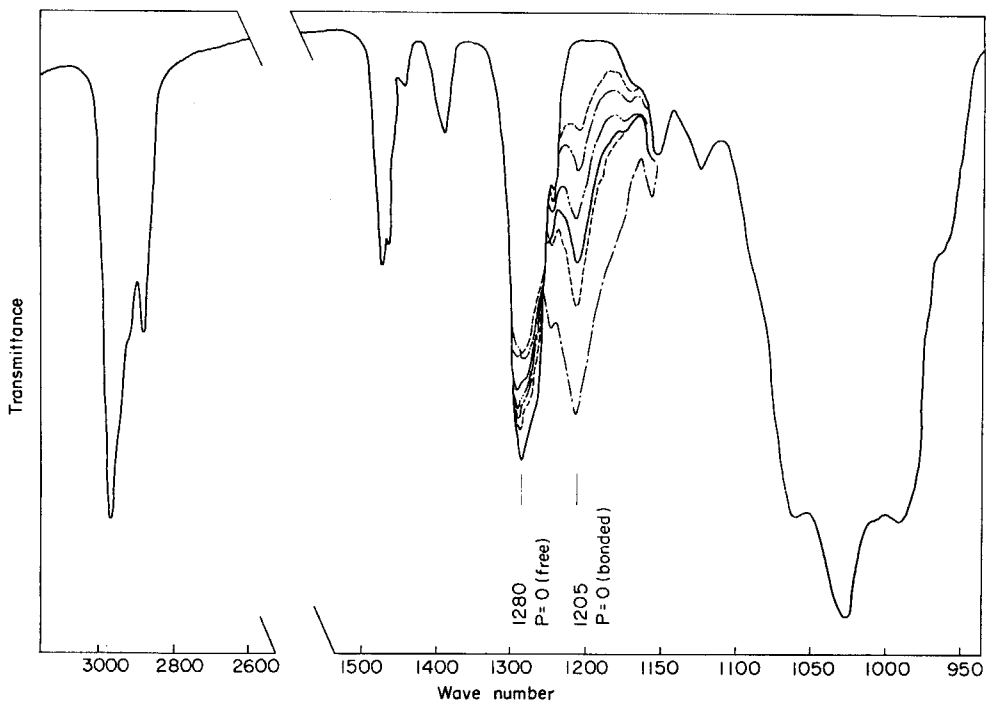


Fig. 2-11 Infrared spectra of TBP-ThCl<sub>4</sub> system

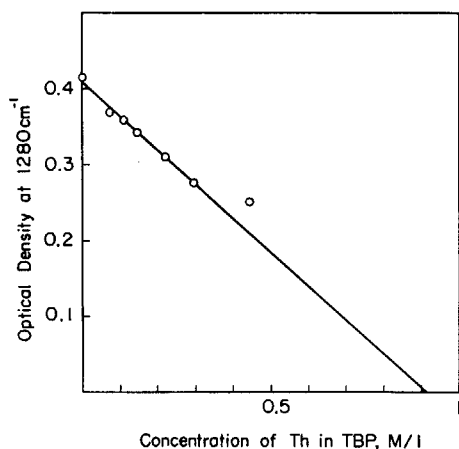


Fig. 2-12 Variation of intensity of absorption due to free TBP with Th concentration

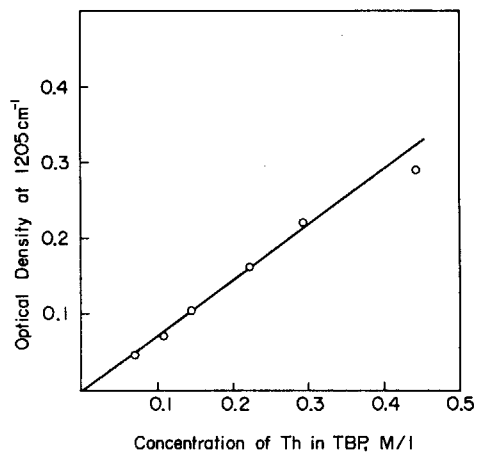


Fig. 2-13 Variation of intensity of absorption due to the complex formation of thorium chloride-TBP

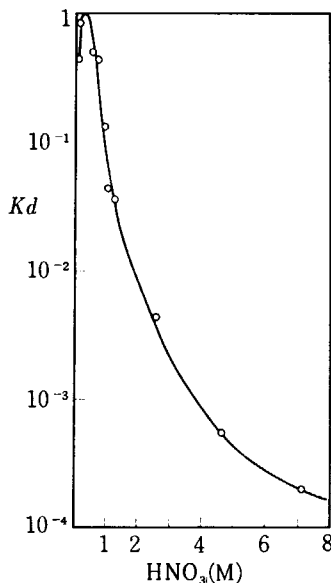


Fig. 2-14 Extraction of Cm by 5% TOPO from nitric acid solutions

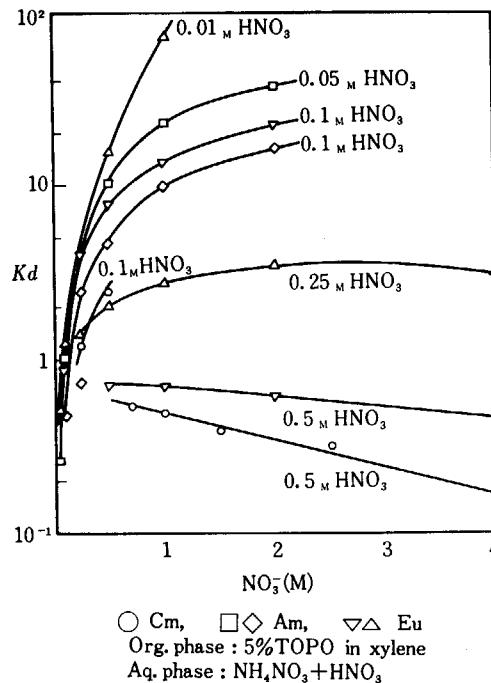


Fig. 2-16 Extraction of Cm, Am and Eu from ammonium nitrate solutions, keeping acidity constant

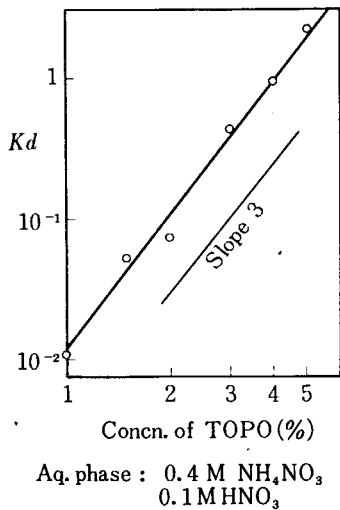


Fig. 2-15 Variation of  $K_d$  values for Cm with TOPO concentration

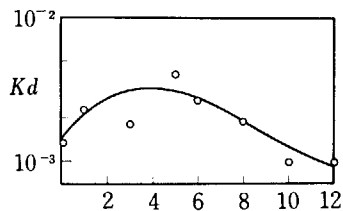


Fig. 2-17 Extraction of Am by 5% TOPO from hydrochloric acid solutions



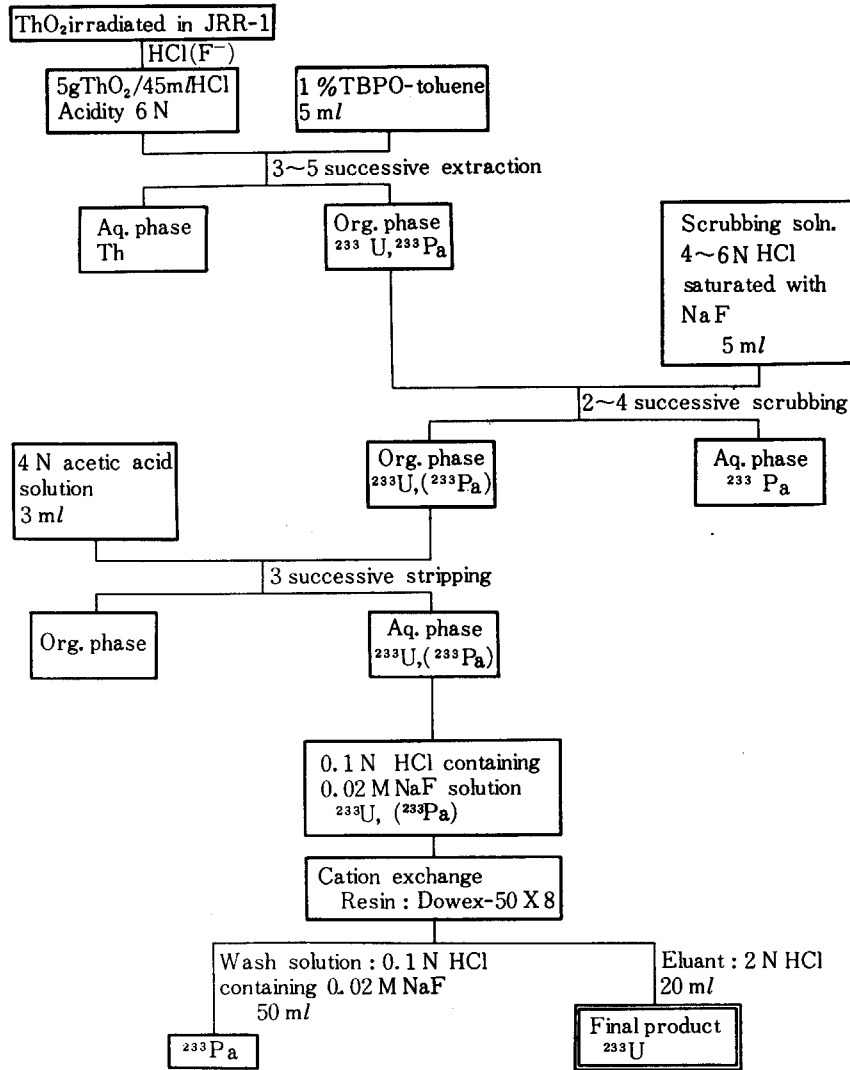
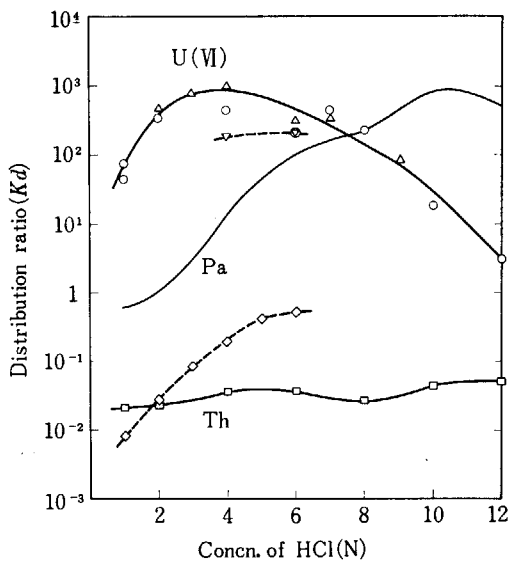


Fig. 3-1 <sup>233</sup>U separation scheme



- : Values for U obtained by activation analysis
- △ : Values for the α-emitter of final product
- ▽ : Values for U in 1%TBPO-HCl saturated with NaF
- ◇ : Values for Pa in 1%TBPO-HCl saturated with NaF
- : Values for Th in 1%TBPO-HCl (Data for Pa in 1%TBPO-HCl were taken from the work of Fujino.)

Fig. 3-2 *Kd* values for U, Pa and Th in HCl-1% TBPO system

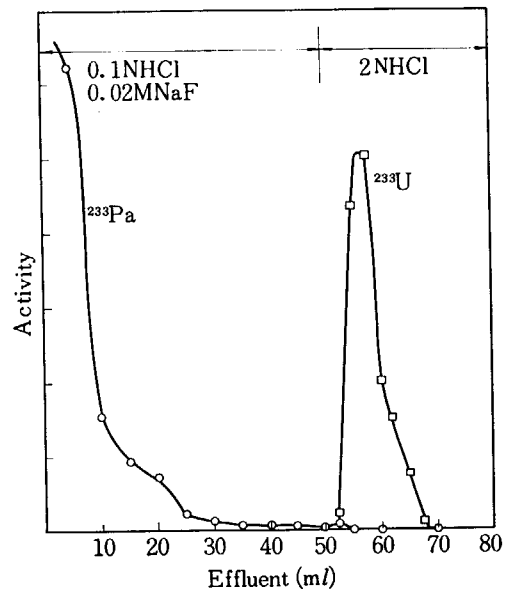


Fig. 3-3 Elution curves for <sup>233</sup>Pa and <sup>233</sup>U

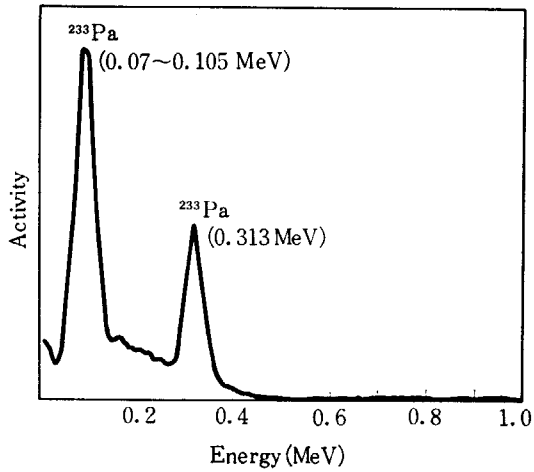


Fig. 3-4  $\gamma$ -ray spectra for irradiated thorium dioxide

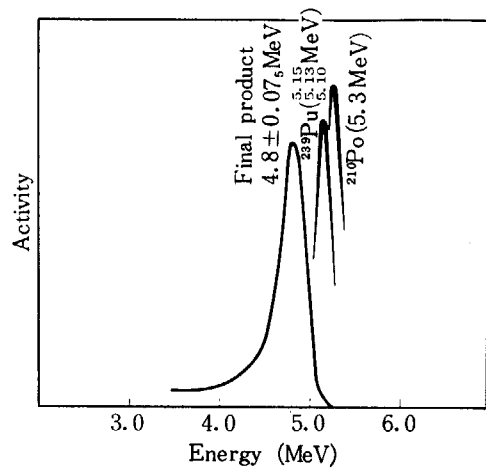


Fig. 3-5  $\alpha$ -spectrum for the final product compared with those for  $^{239}\text{Pu}$  and  $^{210}\text{Po}$

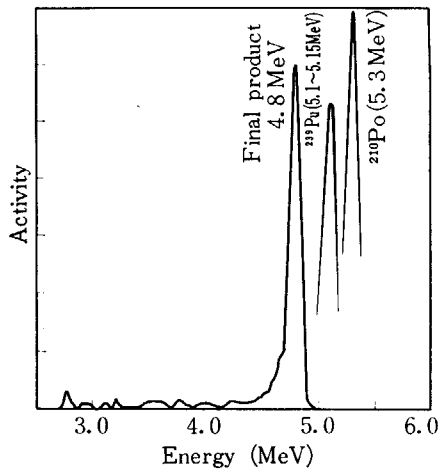


Fig. 3-6  $\alpha$ -spectrum for the final product compared with those for  $^{239}\text{Pu}$  and  $^{210}\text{Po}$

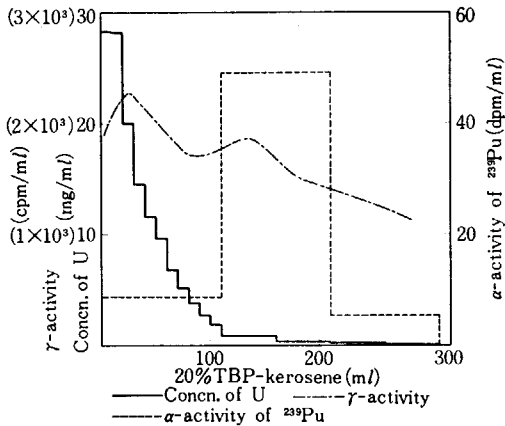
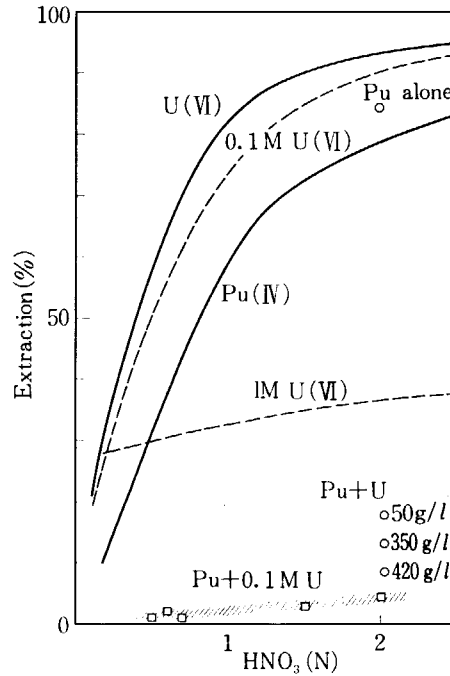


Fig. 3-7 Extraction of U and Pu with 20% TBP-kerosene from 2N nitric acid solution



- : Values based on the works of McKay, *et al.* (19% TBP-kerosene)
- - - : Values based on the works of Naito (20% TBP- $\text{CCl}_4$ )
- : Values for plutonium in presence of uranium based on the work of Goldschmidt, *et al.* (33% TBP)
- : Our data for Pu (20% TBP-kerosene)

Fig. 3-8 Extractions of U and Pu with TBP solutions from nitric acid solution

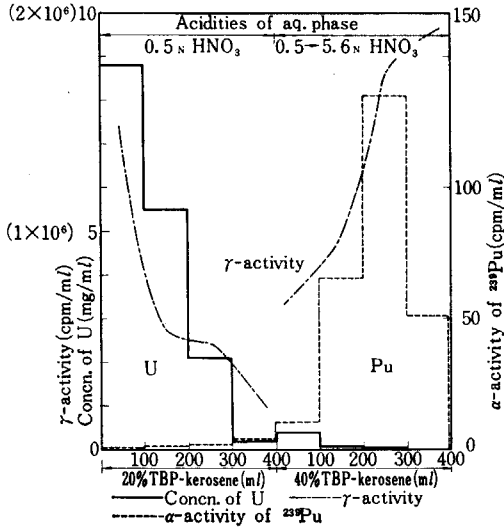


Fig. 3-9 Fractional extraction of U and Pu with 20~40% TBP-kerosene from 0.5 N nitric acid solution

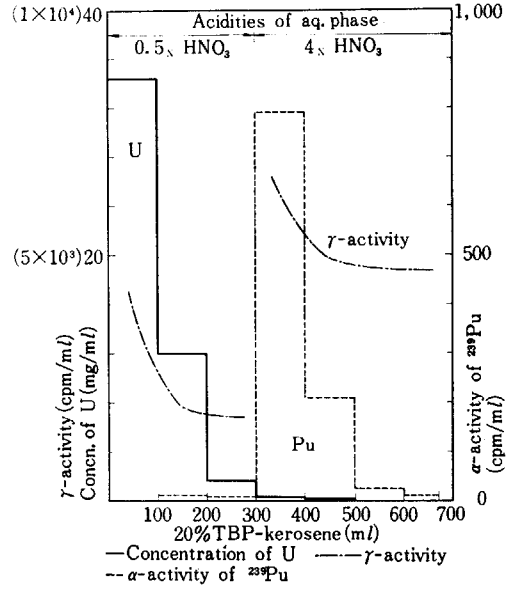


Fig. 3-10 Fractional extraction of U and Pu with 20% TBP from 0.5~4 N nitric acid solution

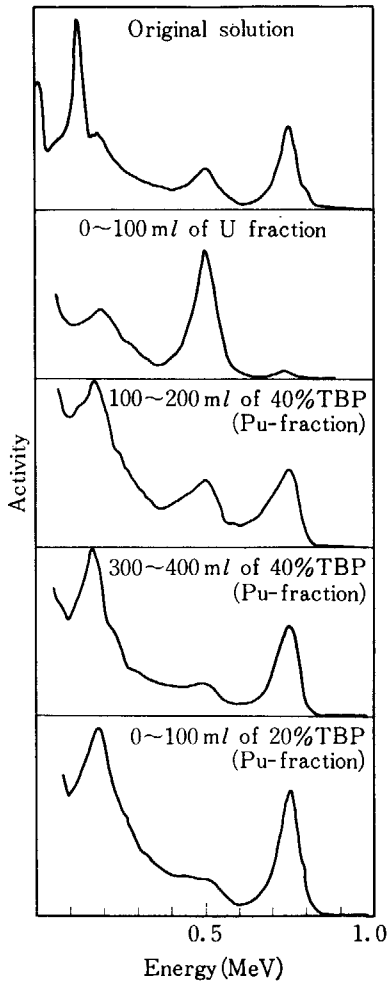
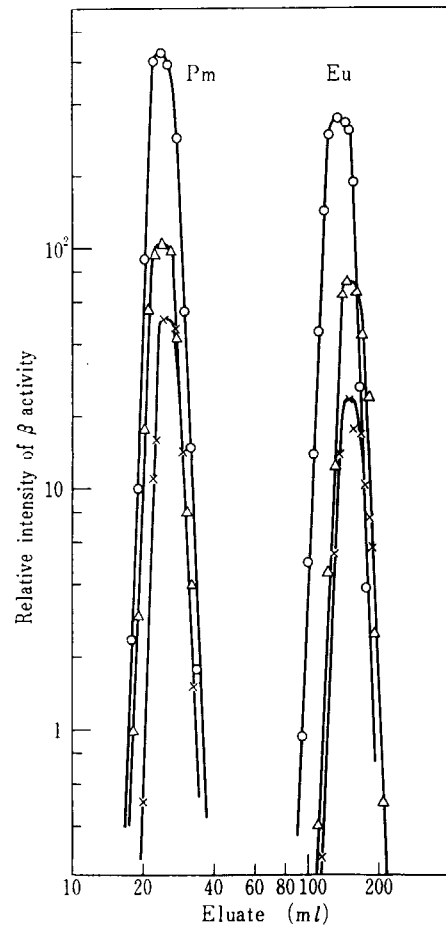


Fig. 3-11  $\gamma$ -ray spectra for U and Pu fractions



Eluants: 0.3 N, HNO<sub>3</sub> —x—, H<sub>2</sub>SO<sub>4</sub> —△—, HCl —○—  
Column: 6 mm $\phi$  × 14 cm, 50% HDEHP  
Flow rate: 0.5 ml/cm<sup>2</sup>·min

Fig. 3-12 Elution curves of Pm and Eu

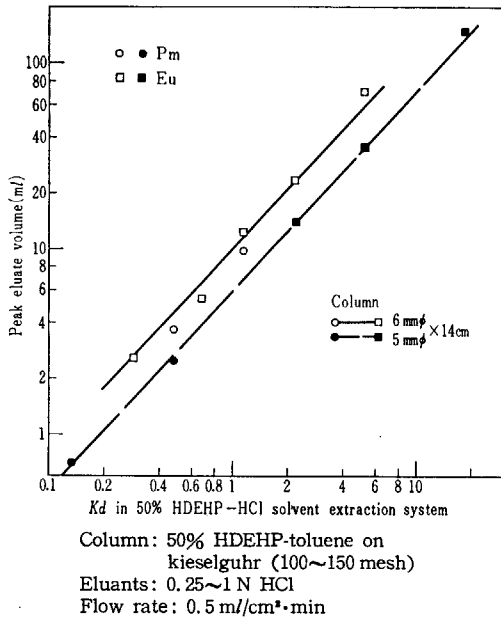


Fig. 3-13 Relationships between peak eluate volume in reversed phase chromatography and  $K_d$  values in solvent extraction systems

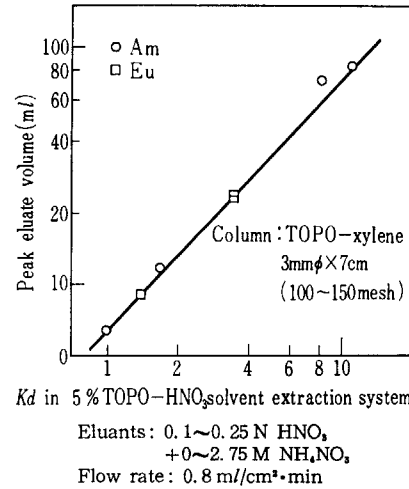


Fig. 3-14 Relationships between peak eluate volume in reversed phase chromatography and  $K_d$  values in solvent extraction systems

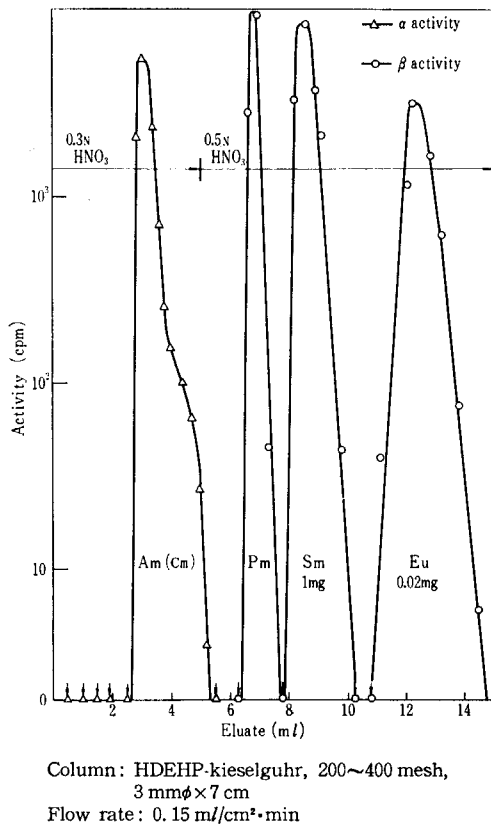


Fig. 3-15 Separation of Am from Pm, Sm and Eu

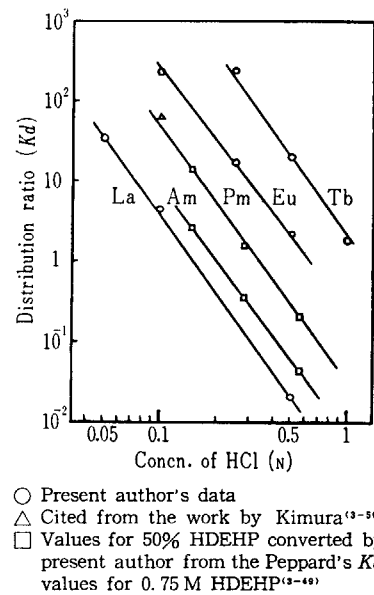
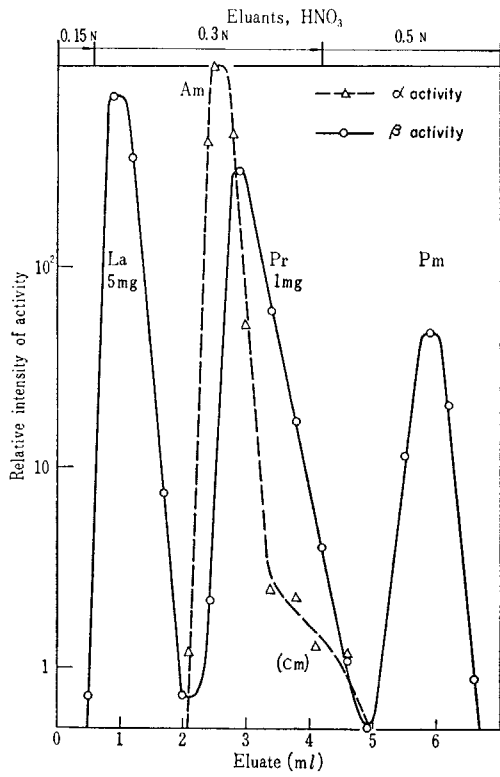
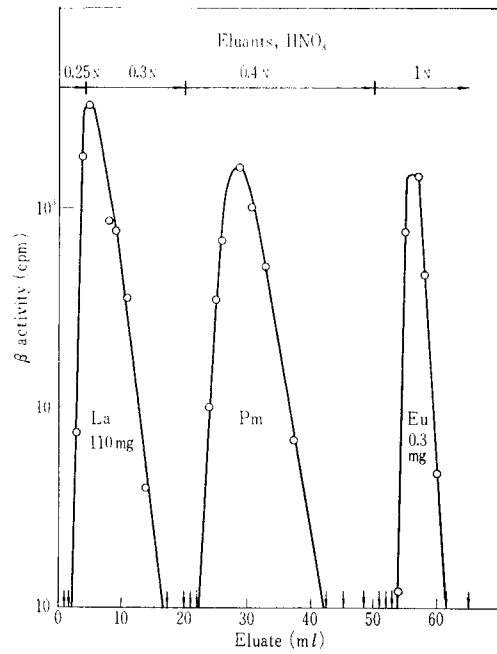


Fig. 3-16  $K_d$  values for Am, La, Pm, Eu and Tb in 50% HDEHP (toluene)-HCl system



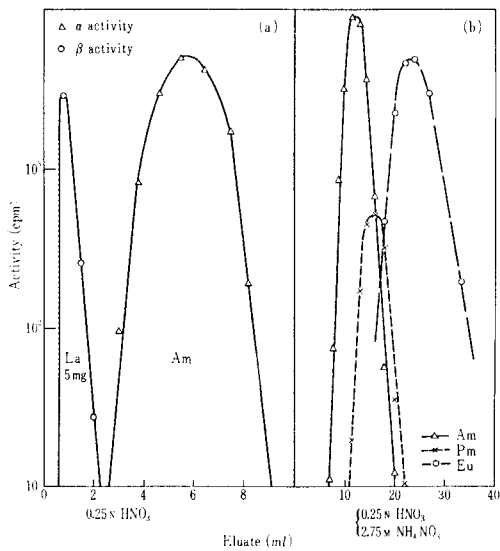
Column: HDEHP-kieselguhr, 200~400 mesh,  
3 mm  $\phi$   $\times$  7 cm  
Flow rate: 0.15 ml/cm<sup>2</sup>·min

Fig. 3-17 Separation of Am, Pr and Pm from 5 mg of La



Column: HDEHP-kieselguhr, 100~150 mesh,  
6 mm  $\phi$   $\times$  14 cm  
Flow rate: 1 ml/cm<sup>2</sup>·min

Fig. 3-18 Separation of Pm and Eu from La carrier



Column: TOPO-kieselguhr, 100~150 mesh,  
3 mm  $\phi$   $\times$  7 cm  
Flow rate: 0.8 ml/cm<sup>2</sup>·min

Fig. 3-19 Elution curves of Am, Pm and Eu from TOPO-column

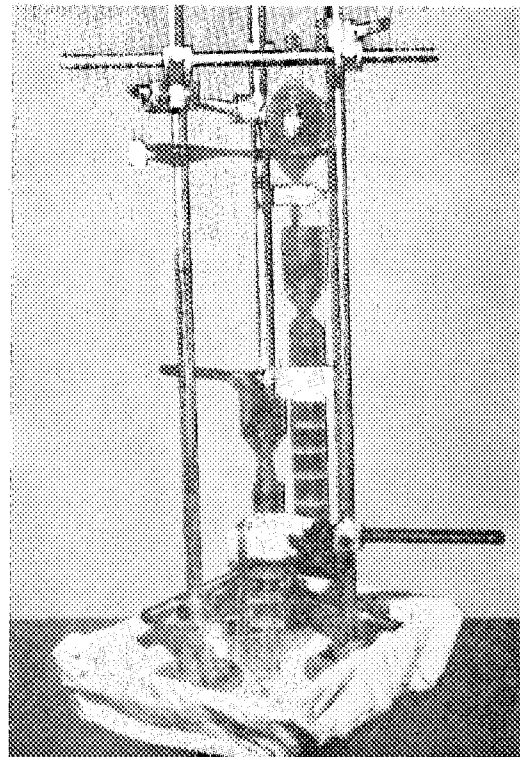


Plate 3-1 Apparatus for fractional extraction of U and Pu

**This is a blank page.**

## Acknowledgments

The author is indebted to professor Hiroshi Haseguchi, Tokyo University, for his invaluable advice and encouragement throughout this work. The author also wishes to thank Dr. Tomitaro Ishimori, Chief of Radiochemistry Laboratory, Japan Atomic Energy Research Institute, for his very kind guidance during the course of this work. He wishes to thank Dr. Keiji Haito, Japan Atomic Energy Research Institute, for his helpful counsel and discussions in this work. He is also grateful for the cooperation and advice of his coworkers; Dr. Kan Kimura, Dr. Eiko Akatsu (née Nakamura), Mr. Takeo Fujino and Miss Aiko Ono, Japan Atomic Energy Research Institute. The assistance of Mrs. Tomiko Hamano (née Izumi) in the experimental work is much appreciated.

## Appendix

Tri-n-butyl Phosphate	TBP
Tri-n-butyl Phosphine Oxide	TBPO
Tri-n-octyl Phosphine Oxide	TOPO
Di(2-ethylhexyl)phosphoric Acid	HDCHP