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Mutual Separation of Rare Earth Elements

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Mutual Separation of Rare Earth Elements

—A Gradient Extraction Method—

Summary

Behavior of some rare earth elements is studied in an eight stage discontinuous counter-current-extraction where both acid and solvent concentrations are gradually changed. Nitric acid and bis(2-ethylhexyl)-orthophosphoric acid* diluted with toluene are chosen for aqueous and organic media respectively.

The results show that this technique can be used for enrichment of a definite rare earth element from rare earth mixture of multi-components. However, it seems to be less effective for final purification of the rare earth element.

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多段勾配濃度法による希土類元素の相互分離

要　　旨

酸濃度ならびに溶媒濃度をともに，しだいに変える8段不連続カウンタカレント抽出における希土類元素の行動を研究した。水層に硝酸溶液，有機層にはビス（2-エチルヘキシル）リン酸トルエン溶液をえらんだ。

実験結果によると，本法は複雑な組成の希土類元素混合物より特定の元素を濃縮するに有効と思われる。ただ，ある希土類元素の最終的精製にはあまり役立たないであろう。

1962 年 7 月 26 日

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* Bis (2-ethyl hexyl)-orthophosphoric acid is abbreviated as HDEHP in the present paper.

Contents

Introduction

Being stimulated by the gradient elution applied in ion-exchange separations[1,2], authors try to apply graded concentrations both in acidity of aqueous fractions and in solvent concentration of organic fractions to the mutual separation of some rare earth elements.

Distribution behavior of Eu, Pm and La is studied in order to get fundamental knowledge concerning promethium isolation from the rare earth fraction of nuclear fission products. Another survey on the separation of Lu, Tm, Tb and Eu implies applications in heavy rare earths enrichment.

Experimental

Source of Materials HDEHP was purified from mono-octyl ester according to the method given by Peppard *et al.*[3] The purity was checked by measuring distribution ratio of lanthanum tracer.

40. 2 h La-140 was obtained by solvent extraction from Ba-La-140 mixture[4]. 282 d Ce-144 ; 2. 6 y Pm-147 ; 13, 16 y Eu-152, 154 ; 73 d Tb-160 ; 129 d Tm-170 and 6. 8 d Lu-177 were obtained from the stock of JAERI.

All of the chemicals used including toluene as diluent were of analytical or chemical pure grade.

Extraction Apparatus The extractor used was of conventional Craig type[5]. The number of equilibration cells was limited to eight in the present study.

Radioassay Gamma counting was carried out with NaI (Tl) well type scintillator. For beta counting, an RCL gas-flow counter with thin end window was used. Mounting of active sample solutions on stainless steel plates was carried out with the aid of a high frequency induction furnace.

As far as organic samples concern, some difficulties were encountered in making clean plates for beta counting. This was avoided by back extraction of the activity into an aqueous solution of adequate acidity.

Extraction Procedure Before beginning a real operation, the extractor was thoroughly washed with sufficient amount of acetone, nitric acid solution and finally distilled water. This is to avoid the pre-contamination of preveous works and also to prevent any possible disturbance on the distribution of the activities caused by occasional trapping droplets on the glass wall of the passage.

The gradient in the acidity of aqueous solutions was prepared in the extractor train. Namely, after filling up all equilibrating cells with predetermined nitric acid solution (0.23 or 0.5 N), two successive portions of 10 m*l* distilled water were sent through the train under usual operations of mixing, settling, overflowing. On the other hand, the gradient in the solvent concentration was obtained by mere manual dilution. The gradient conditions are summarized in **Table I.**

Table I. Operation Conditions

Condition	No. Fraction / phase	1	2	3	4	5	6	7	8	9
I	Aqueous (N HNO_3)	0.026	0.059	0.094	0.12	0.15	0.17	0.18	0.20	
	Organic (%HDEHP)	5	10	15	20	25	30	35	40	
II	Aqueous (N HNO_3)	0.055	0.13	0.20	0.27	0.32	0.37	0.40	0.43	
	Organic (%HDEHP)	2.5	3.8	5.0	7.5	8.7	10	12.4	14.8	18.0

The aqueous solution of a radioactive tracer was added to the acid solution of the first cell prior to the extraction operation. The organic fractions of a given number were supplied to the first cell one by one successively. Extraction-and transfer-cycles were repeated after the completion of the above organic supply until the last organic fraction was withdrawn from the last cell. Thus equal number of aqueous samples as the number of the equilibrating cells and solvent batches were obtained.

Results and Discussion

Behavior of La, Pm and Eu was studied in the operation condition I (**Table I**). Results are summarized in **Fig. 1** where the activity is plotted against aqueous and organic fractions. Here, the activity in each fraction is expressed as the percentage to the initial total activity. The aqueous fractions are numbered as 1A and 8A for the first and last cells respectively. The organic fractions are numbered as 1S, 2S,.....successively from the first effluent.

Fig. 1 shows that providing 1 : 1 : 1 composition of starting La-Pm-Eu mixture, more than 90% of Pm can be recovered in the fractions of 8A and 5S to 8S, and its purity is around 99%. Similarly values of recovery and purity are calculated for La and Eu assuming the above starting material. These values are summarized in **Table II.**

Similar studies undertaken with Eu, Tb, Tm and Lu under the operation condition II (**Table I**) gave results shown in **Fig. 2.** As this figure is drawn in a similar way as **Fig. 1,** the separation method can be evaluated calculating recovery and purity of products from a

Table Ⅱ. Recovery & Purity for La, Pm & Eu

Element	Fraction (taken)	% Recovery	% Contamination		
			by La	by Pm	by Eu
La	3A–6A	~90	—	<0.7	negligible
Pm	8A & 5S–8S	~90	<0.4	—	<0.3
Eu	1S–3S	~85	negligible	<0.5	—

Table Ⅲ. Recovery & Purity for Eu, Tb, Tm & Lu

Element	Fractions (taken)	% Recovery	% Contamination			
			by Eu	by Tb	by Tm	by Lu
Eu	2A—3A	~35	—	<0.4	negligible	negligible
Tb	7A—8A	~35	<0.5	—	<0.5	negligible
Tm	5S—6S	~35	negligible	<0.8	—	<0.1
Lu	1S	~40	negligible	negligible	<0.5	—

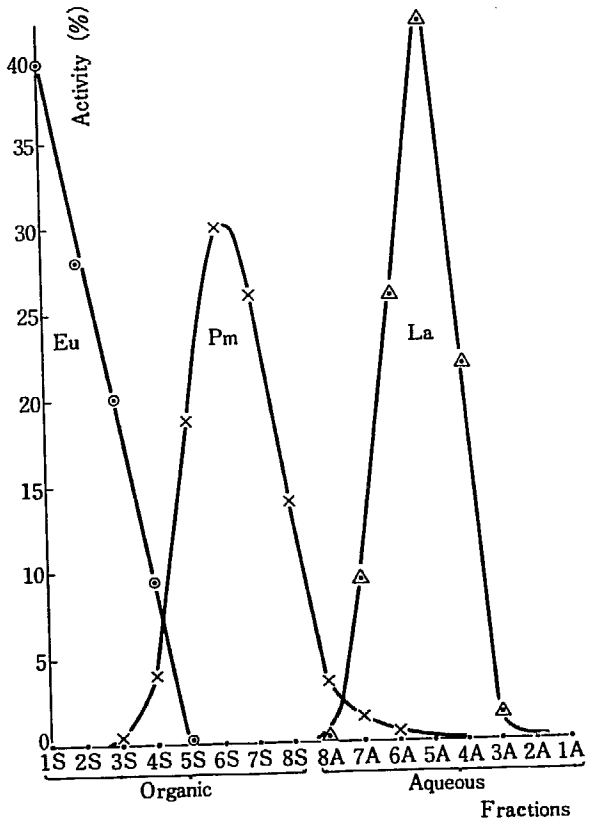

Fig. 1. Distribution of La, Pm & Eu (Operation condition I)

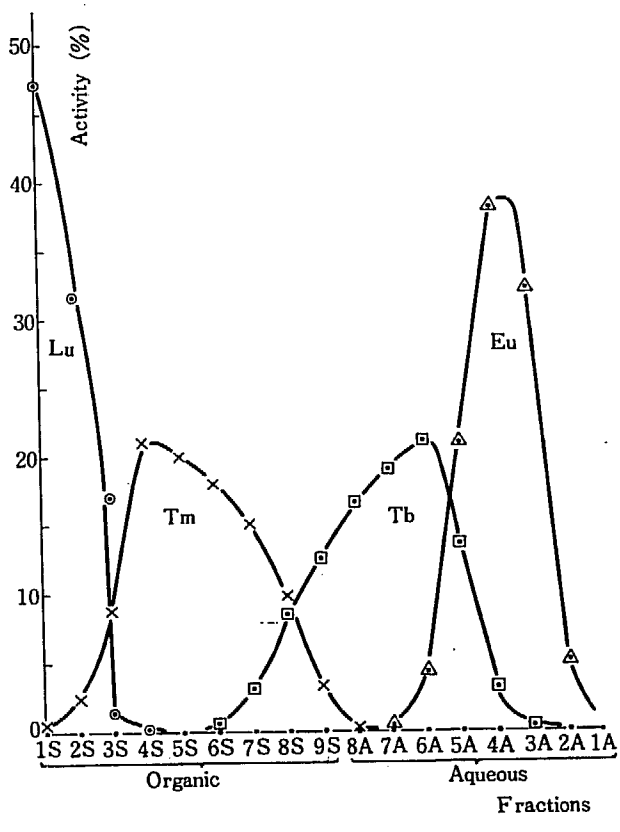

Fig. 2. Distribution of Eu, Tb, Tm & Lu (Operation condition II)

starting material of a given composition. Providing 1 : 1 : 1 : 1 composition of Eu-Tb-Tm-Lu mixture, recoveries for about 99% purity products are calculated. Values obtained are given in **Table Ⅲ.**

In **Fig. 1** rare earth elements heavier than Eu should remain in fractions 1 S to 3 S, as they are more extractable than Eu. On the other hand, rare earth clements lighter than Eu should appear in Eu fractions of **Fig. 2.**

This type of extraction is supposed to be suitable for the isolation of a desired species out of multicomponent rare earth mixture.

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