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음이온교환수지에 의한 모나자이트중 희토류원소의 분리

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Separation of Rare Earth Elements in Monazite Sand by Anion Exchange Resin

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요 약. 모나자이트 중의 Y, La, Ce, Pr 및 Nd 들을 pH 8.4에서 EDTA와 착염을 만들어 미리 음이온 교환수지에 EDTA를 흡착시킨 수지관에 용리시켜 희토류 원소들의 분리를 시도하였다. 용리액은 pH 8.4의 EDTA를 사용하였으며, 용리액의 분율에 따라 측정한 각이온의 분리도는 55~98 %이었다.

ABSTRACT. An anion exchange method for separating the individual rare earth elements in monazite into enriched fractions has been developed. The complexed rare earth ions with EDTA at pH 8.4 pass through the anion resin bed. The absorption order of the complexed ions was in accord with that of the stability constants of the complexes. The elution of a mixture of all the rare earths through an ion-exchange bed with an ammonia-buffered solution of EDTA indicated that this chelating agent is as effective for separating the light rare earths. The separation results of each ion obtained from their elution fractions are 55% to 98%.

INTRODUCTION

The monazite sand is a phosphate rock. The composition of rare earths in monazite sand, depending on original source, are generally 30 ~40 % cerium phosphate, 11~30 % neodymium phosphate, 12~24 % praseodymium phosphate, 1~7 % samarium phosphate, 1~5 % yttrium phosphate and other rare earth phosphates.[1]

Historically, the first means of separation of the rare earth elements from each other was the use of repeated fractional crystallizations.[2] A liquid extraction process has been tried by Fisher and his co-workers.[3] The methods of chromatography have been applied to the separation of the rare earths. This method was first proposed for use with the rare earths by Lange and Nagel.[4] During World War II, invaluable works of separation of rare earths were an outgrowth of the tremendous amount of research performed by Spedding and his coworkers.[5]

Since early 1945, most of ion-exchange methods for separation of rare earths have been developed which have been exceptionally efficient in producing quantities of individual rare earths in a high state of purity using commercial grace sulfonated styrene-divinyl benzene copolymer.

Schwarzenbach and his co-workers[6,7] have been determined the stability of the complexes that are formed between alkaline earth metal ions and EDTA. Vickery[8] used a modification of the above procedure to determine the rare earth EDTA stability constants. According to those reports, the rare earth-EDTA stability constants are increased with increasing atomic number of rare earth elements.

In this study, the separation of rare earth elements in domestic monazite which was decomposed with sodium hydroxide has been investigated by anion exchange chromatography. The adsorbability of rare earth elements is depends on the stability constant of complex formed between each rare earth element and chelating agent.

Separation of rare earths on anion-exchange columns depends on the ability of tervalent cations to form anionic complexes of differing stability with negatively charged ligands. Molnar *et al.*[9] reviewed previous anion-exchange separations. Dybezynski[10] initiated an investigation of the anion exchange elution behavior of rare earths in EDTA systems. They proposed that the separations observed sysstem from the varying ability of the hydrated RCh^-species to undergo the exchange;

$$2RCh^- + \overline{H_2Ch^{2-}} \rightleftharpoons \overline{2RCh^-} + H_2Ch^{2-}$$

The complexed rare earths with EDTA are poured through a anion resin bed, the complexed rare earths can be adsorbed on a resin bed and eluted with additional EDTA solution. In this elution, the lighter rare earth complexes will pass through while the heavier rare earths will be retained on the resin bed.

Separation involving anion exchange and inorganic eluents have been reported. Magnesium nitrate,[11] lithium nitrate[12] and thiocyanide[13] have been used. In the case of organic eluent, citrate[14], HEDTA, NTA, EDTA[15] and α-hydroxy-isobutyrate[16] have been used.

In this paper, rare earths-EDTA complex is used on a Dowex 1-X 400 anion exchange resin, pretreated with EDTA and eluted by 0.030~0.060 *M* EDTA solution at pH 8.4.

EXPERIMENT

Apparatus and Materials. The rare earth oxides were Merck's reagents and others were analytical grade. Anion exchange resin used in this work was Dowex 1X420 (150~200 mesh). pH meter, Electoscan 30 unit of Beckman and spectrophotometer, Perkin-Elmer 201, were used.

Glass tubes of 3.14 $cm^2 \times 120$ cm and 3.14 $cm^2 \times 60$ cm as ion exchange columns were used. The column has stopcock which adjusts flow rate. Ion exchange column is prepared as follows: Dowex 1-X400 anion exchange resin is added into water and stirred for 1~2 minutes, the mixture is standing to settle the heavy resin particle and to remove floating fine particles by decantation. This treatment is repeated three times and the water mixture of exchange resin is poured into ion exchange column to make 120 cm height of resin bed and the resin column is equilibriated with eluent solution.

Decomposition Monazite Sand. Monazite sand used in this work was collected Ansoung river. Weigh out accurately 50.0 g of sample into 500 m*l* beaker and add 200 m*l* sulfuric acid and cover with watch glass and heat on heater for 24 hours. Cool the mixture, dissolve the soluble salt with water, and then filter quantitatively into 500 m*l* volumetric flask and fill the flask to the mark with water. This solution was used as sample solution.

Analytical Methods. Rare earths in effluent are precipitated with oxalate and its precipitation was ignited to obtain oxide. Y, La and Ce elements in this oxide were determined by

X-ray fluorescene method. Sample tablet made from the mixture of 0.1 g sample oxide and 1 g cellulose powder was exited. Grating crystal used was EDDT. The spectrum of each element is shown in *Fig.* 1. The 2θ values to be used in the analysis were 33 for Ce, 35 for La and 44 for Y. Nd, Sm and Pr elements were determined by spectrophotometric method. The proper band to be used in the analysis of mixtures of these rare earths were 740 nm for Nd, 444 nm for Pr and 401 nm for Sm.[17] The determination of thorium and total rare earths is performed by gravimetic method after separating these element by anion exchange method.[18]

RESULT AND DISCUSSION

The analytical results of monazite samples used in this study are shown in the *Table* 1.

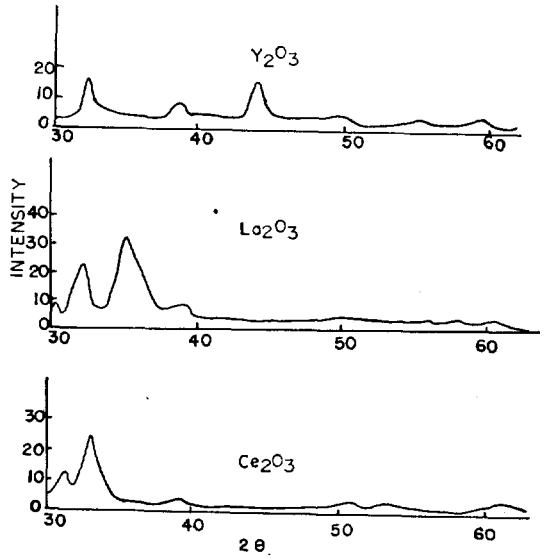

Fig. 1. X-Ray fluorescence spectrum of Y, La and Ce.

Separation Curve of Rare Earth Elements. 50 m*l* of monazite sample solution was taken and adjusted pH 1 with ammonia water. The precipitation was almost thorium in this pH range, so it was filtered and the filtrate was saturated with oxalic acid solution to precipitate rare earth element. The precipitation was ignited and the weight of the oxide obtained is 1.800 g. The oxide was dissolved by sulfuric acid.

After dissolving it 3.6 g EDTA was added into the filtrate and adjusted to pH 8.4 and the final volume was adjusted to 50 m*l*. This solution is poured into the 120 cm column. The effluent was measured from this time. After sample solution is drained into resin phase, 1 m*l* eluent of 0.0602 *M* EDTA, pH 8.4 is poured to wash the sample and then the eluent is drained. This operations are repeated 2~3 times. The flow rate is adjusted to 0.5 m*l*/min. The effluent is collected as constant volume using siphon pipette and the concentration of rare earth in each fraction is determined. The elution curve obtained from this process is shown in *Fig.* 2. The pH of eluent is adjusted to 8.4 to obtain a state of major HY^{3-} form of EDTA.

In *Fig.* 2 all the rare earths are eluted within 5 *l* effluent and those are separated almost into three parts, but it is considered as incomplete separation. In order to separate those ions completely, the concentration of eluent was changed as 0.047*M* EDTA. The ion exchange column was equilibriated with 0.047 *M* EDTA, pH 8.4 as eluent and the sample solution was loaded into resin column as a same process of *Fig.* 2

Table 1. Analytical data of monazite sand.

Composition	Total rare earth oxide	ThO_2	SiO_2	P_2O_5	U_3O_8
%	53.20	4.68	8.25	24.25	0.32

and eluted by this eluent. The results are shown in *Fig.* 3. In the result all the rare earth elements are eluted in 6 *l* effluent and separated almost into four parts, which are better results than that of *Fig.* 2, but these results are also considered as incomplete separation. Therefore the eluent concentration was reduced to 0.0301 *M* EDTA to obtain better separation. The sample was absorbed in the upper part of resin column and eluted with 0.0301 *M* EDTA of pH 8.4. The results are shown in *Fig.* 4. In this *Fig.* rare earth elements are separated into several parts within 14 *l* effluent. This result is considered as the best separation among the above results.

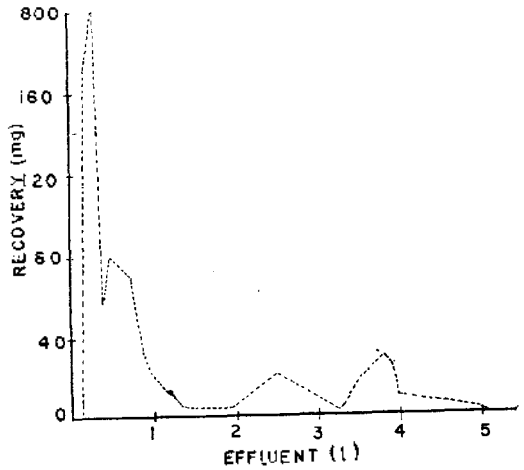

Fig. 2. Separation curve of rare earths in monazite sand. Flow rate : 0.5 m*l*/min; Eluent : 0.0602 *M* EDTA, pH=8.4; column : 3.14 cm^2×120 cm; resin : Dowex 1-X400(150~200 mesh).

Elution Curves of Each Rare Earth Element. In order to investigate the elution behavior of each element, 0.1 g each oxide of rare earths was weighed and dissolved with 10 m*l* of 1 *M* perchloric acid, 0.1 g EDTA was added into 5 m*l* of each solution and adjusted pH 8.4. Each solution was absorbed in the upper part of 60 cm resin column equilibriated with 0.031 *M* EDTA of pH 8.4 as eluent and eluted with this eluent, respectively. The results are shown in the *Fig.* 5. This *Fig.* shows that yttrium is eluted at the front and followed lanthanum, cerium, samarium, praseodymium and neodymium. Each element is not completly separated in this curve but we can see that the elution order is in the order of atomic number of rare earth element except samarium. In expressing this result, we can assume that the stabiltiy of chelate formed between EDTA and rare earth element is related with ionic size of rare earths.

Separation of Rare Earth Element in Monazite Sand. From the elution curve of *Fig.* 5, we can deduce that the elution order of rare earths shown in *Fig.* 4 will be same as

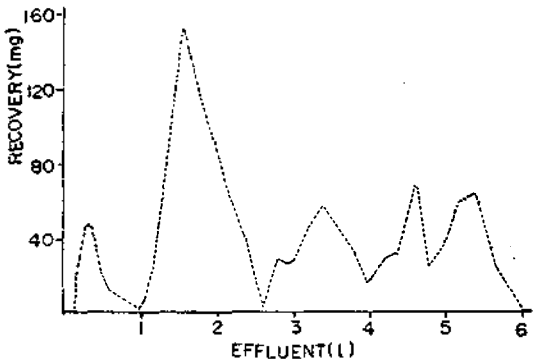

Fig. 3 Separation curveof rare earths in monazite sand. Eluent : 0.047 *M* EDTA, pH=8.4; column : 3.14 cm^2×120 cm; flow rate : 0.5 m*l*/min.

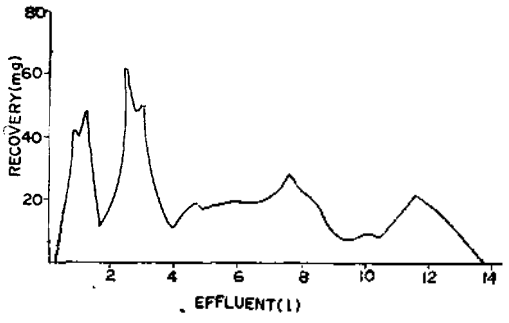

Fig. 4. Separation curve of rare earths in monazite sand. Eluent : 0.031 *M* EDTA, pH=8.4; column : 3.14 cm^2×120 cm; flow rate : 0.5 m*l*/min.

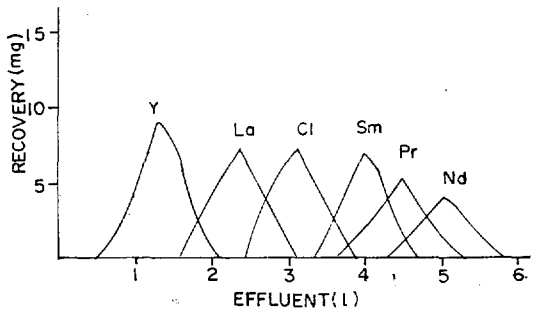

Fig. 5. Elution curve of Y, La, Ce, Sm, Pr and Nd. Eluent : 0.0301 *M* EDTA, pH=8.4; column : 3.14 $cm^2 \times 60$ cm; flow rate : 0.5 *ml*/min.

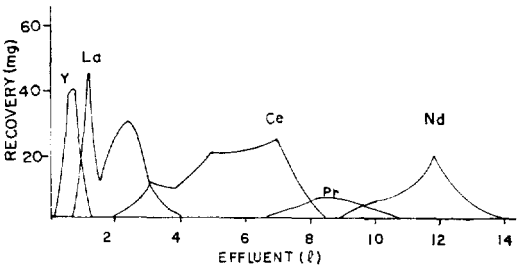

Fig. 6. Separation curve of rare earths in monazite sand. Flow rate : 0.5 *ml*/min; eluent : 0.0301 *M* EDTA, pH=8.4; column : 3.14 $cm^2 \times 120$ cm; resin : Dowex 1X 400(150~200).

that of *Fig.* 5. Actually, the oxides obtained in each fraction of *Fig.* 4 were determined. The results are *Table* 2. In the *Table* 2 all the fraction are not determined but we can see the general separation tendency. Using the data of *Table* 2, *Fig.* 6 is obtain. This *Fig.* shows that the elution order of rare earth is in the same order as that of *Fig.* 5 but samarium doesn't appear, so we can think that the monazite sample collected around Ansoung river contains no samarium and it also shows that each element isn't completely separated because the adjacent elements are overlapped some parts, but the overlapped part can be separated into each element by the process of a repeating treatment.

CONCLUSION

1. The separation order of these element is yttrium, lanthanum, cerium, praseodymium and neodymium and this sequence is the same as that of these atomic number.

2. Sufficient difference in the distribution coefficients is able to separate rare earths by

Table 2. Analytical data of the oxides obtained in each fraction of *Fig.* 4.

Effluent (*l*)	Wt of Oxide (mg)	Analytical Data (%)				
		Y_2O_3	La_2O_3	CeO_2	Pr_2O_3	Nd_2O_3
0.3~0.5	13.2	98	2	—	—	—
0.7~0.9	42.3	95	2	—	—	—
1.1~1.3	49.3	2	98	—	—	—
1.5~1.9	48.2	—	90	6	—	—
2.3~2.5	49.7	—	80	15	—	—
2.9~3.1	80.4	—	40	55	—	—
4.7~4.9	36.8	—	5	90	—	—
5.7~5.9	39.1	—	—	85	7	—
7.1~7.3	51.0	—	—	40	55	—
8.1~8.3	38.6	—	—	10	70	10
9.1~9.7	28.1	—	—	—	35	60
10.3~10.9	33.8	—	—	—	20	75
11.3~11.5	58.5	—	—	—	10	85
11.9~12.3	42.2	—	—	—	—	98

g unit, using the ion exchange column of 3.14 $cm^2 \times 120$ cm.

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