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The Separation of the Cerium-group Rare Earth Elements by Ion Exchange using a Citrate-acetate Mixed Solution as Eluting Agent[*1]

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The separation of rare earth elements by ion exchange was studied. The new eluting agent consists of an aqueous solution of diammonium hydrogencitrate and an aqueous ammonia-acetic acid mixture; the two solutions were mixed in definite ratios. Using a column of Dowex 50 W resin, the separation of Sm, Nd, Pr, Ce and La was successfully achieved. As practical samples, mixed chlorides obtained from monazite concentrates were used. Both the purities and the yields of the recovered rare earths were greater than 99%. This eluting agent was applied to the separation of yttrium-group rare earths such as Dy, Er, Yb and Y, but the attempt was not successful.

During the past twenty years, a great number of papers have been published on the separation of rare earths by ion-exchangers. In the earlier papers, citric acid solution buffered with ammonia was widely used as eluting agent. Initially, 5% citrate at pH 2.5—3.0 was used, but this concentration was found costly in large scale operations.[1,2] Subsequently, 0.5% citrate at pH 3.9 was applied to pilot plant scale separations of the cerium-group rare earths.[3] Systematic studies on the effects of such variables as temperature, pH, size of resin particles and flow rate were also made with the same concentration of eluting agent.[4] Furthermore, certain workers used 0.1% citrate at pH 5.0—8.0 and found that the eluting agent was useful for macro separations of the cerium-group in kilogram quantities.[5] Shiokawa *et al.*[6-9] used 0.1% citric acid at pH 6.0 to separate cerium-group rare earths. Their experiments indicated yields of La, Pr, Nd and Sm at 96.2, 70.3, 90.0 and 77.2%, respectively.

A number of complexing agents beside citrate have also been used for analytical purposes. These are lactate, glycolate, malate, α-hydroxyisobutylate, *etc.* For commercial separation, aminopolycarboxylates such as ethylenediaminetetraacetate and nitrilotriacetate have now been used in conjunction with Cu(II)- or Zn(II)-resin retaining beds. Detailed reviews of such developments of ion exchange methods are described in a book edited by Spedding and Danne.[10]

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The present paper deals with a new eluting agent. The eluting agent consists of a mixed system of citrate and acetate solutions. The minor component, acetate, greatly affects the rapid and sharp separation of the cerium-group elements (La, Ce, Pr, Nd and Sm). Successful separations on an analytical scale were provided with practical samples from monazite concentrates.

Experimental

The Eluting Agent. Two hundred grams of citric acid monohydrate and 50 g of diammonium hydrogencitrate were dissolved in water and diluted to 4000 m*l*. Hereafter, this solution is called the "A" solution for convenience. On the other hand, aqueous ammonia (40 m*l* of 28% ammonia diluted to 160 m*l*) was mixed with aqueous acetic acid (100 m*l* of glacial acetic acid diluted to 300 m*l*). This solution is called the "B" solution. Both the "A" and "B" solutions were mixed in definite ratios and used as eluting agents.

The Samples. Stocks of rare earths of 99% or higher purity were available for La, Pr, Nd and Sm as oxides. These were weighed in amounts to produce 10 mg per m*l* of solution. The calculated amount of nitric acid necessary to dissolve the oxide and to produce a final excess of 0.1 M acid was added, and each stock solution was brought to a definite volume with water. For cerium stock solution, cerium(III) nitrate hexahydrate was used. These solutions were used individually or as mixtures for determining optimum conditions for the separation of cerium-group rare earths.

For practical separation of the cerium-group, concentrates from monazite sand were obtained from our company. The concentrates were mixed chloride hydrates of the cerium-group rare earths. Furthermore, mixed oxides prepared from the mixed chlorides were also available for analytical separation. Further details of these separations will be described for each experimental result.

Some of yttrium-group rare earths were used: Stock solutions of Dy, Er and Yb were made from their oxides and that of Y, from the nitrate.

General Procedure. A few preliminary experiments comparing Dowex 50 W X8 resin with Amberlite IR-120 indicated the former to be superior. Therefore, unless otherwise noted, the Dowex resin of 100—200 mesh was used. Prior to elution, the column was washed with the "B" solution and then regenerated to hydrogen-form with 2 N hydrochloric acid. After removing excess acid with water, a sample solution was introduced into the column, the column was again rinsed with water and then eluted with a mixture of the "A" and "B" solutions. Other conditions, such as column dimensions, resin-bed length, flow rate and composition of rare earths are given in each experimental result.

The rare earths were recovered from the eluate as oxalates by adding 5% oxalic acid. The oxalates were ignited to oxides for weighing. Fractions which seemed to be contaminated with adjacent elements were spectrophotometrically analyzed according to the method described by Spedding *et al.*[4] Sm was measured at 401 mμ, Nd at 740 mμ and Pr at 444 mμ. The values for the molar extinction coefficients of Sm, Nd and Pr at the above wavelengths were 3.09, 6.53 and 10.07, respectively. For portions which seemed to be recovered in pure states, characteristic absorption spectra were taken by means of a recording spectrophotometer over the visible range (350—700 mμ).

Results and Discussion

Optimum Composition of the Eluting Agent. In the beginning of the present work, it was found that the "B" solutions show much greater effects on the elution of the rare earth ions than the "A" solutions. When "A" solution was applied alone to a column ($\phi = 1.6$ cm, 10 g the Amberlite resin) which was charged with *ca.* 10 mg of Sm, the elution of Sm ranged from 300 to 700 m*l* of the eluate. In the case of "B" solution, the corresponding elution completed within 50 m*l* of the eluate. This fact suggested that mixing solutions "A" and "B" would be favorable. Then, a few experiments on the elution of Sm-Nd mixtures were made in order to find a suitable composition for the mixed solution. The results indicated that a solution consisting of one volume of "B" and forty volumes of "A" is effective. From this, a set of experiments was made to determine the optimum composition of the eluting agent for the separation of Sm, Nd and Pr. The parts of "A" to be mixed with one part of "B" were varied, maintaining other conditions constant. The results are shown in Figs. 1—3. It is clear from these figures that the best separation of Sm, Pr and Nd was achieved with an eluting agent having a 50 : 1 ("A" : "B") ratio by volume.

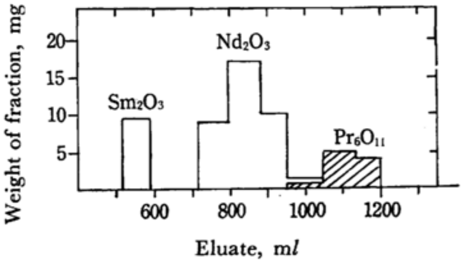

Fig. 1. Elution of Sm, Nd and Pr mixture with 40 : 1 eluting agent.
Weight of sample: Sm_2O_3 10 mg, Nd_2O_3 40 mg, Pr_6O_{11} 10 mg; column diameter 1.6 cm; resin height 19.3 cm (20 g); 1 fraction of eluate 20 m*l*.

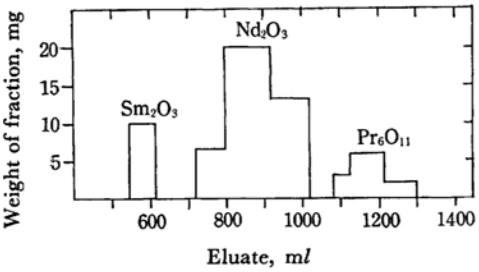

Fig. 2. Elution of Sm, Nd and Pr mixture with 45 : 1 eluting agent.
All the other conditions are the same as in Fig. 1.

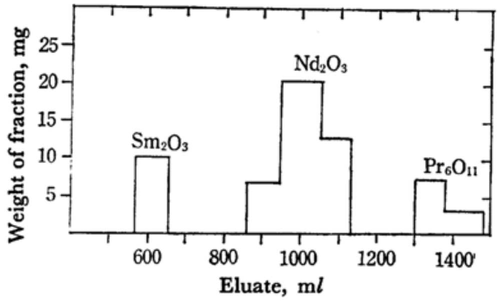

Fig. 3. Elution of Sm, Nd and Pr mixture with 50 : 1 eluting agent.
All the other conditions are the same as in Fig. 1.

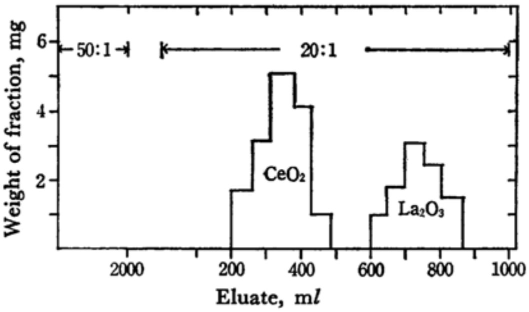

Fig. 4. Elution of Ce and La with 20 : 1 eluting agent.
Weight of sample: CeO_2 20 mg, La_2O_3 20 mg; The other conditions are the same as in Fig. 1.

Similar experiments were made with a mixture of Ce and La. When eluting agent consisting of a 50 : 1 ratio was applied, neither species of Ce nor La appeared in the eluate even when the eluate was 2000 m*l*. With decreasing the "A" component, each breakthrough volume of both elements was more and more reduced, and complete separation was obtained by using 20 : 1 eluting agent (Fig. 4).

The Elution of Mixed Chlorides of the Cerium-group Rare Earths. Conditions for this separation, based on the above results using Dowex 50W X8 (100—200 mesh), are;

Diameter of column: 2.2 cm
Height of bed: About 22.5 cm
Sample: Two kinds of $LnCl_3 \cdot nH_2O$ (Ln represents rare earths) were available and denoted as sample A and sample B for convenience; two grams of each sample was dissolved in 50 m*l* of 1 N HCl.
Flow rate: 0.7 cm/min.

The column in hydrogen-form was loaded with sample and washed with water (500 m*l*). Elution was started with 50:1 eluting agent. With progress in the elution process, movements of colored Nd and Pr bands were clearly observed visually. When the pale greenish band of Pr disappeared from the column, the eluting agent was changed to a 20 : 1 mixture for the elution of Ce and finally to 5 : 1 for the effective removal of La. Typical elution curves are shown in Figs. 5 and 6 and approximate compositions obtained by weighing as oxides are given in Table 1.

TABLE 1. ELUTION RESULTS OF MIXED CHLORIDES

	Sample A		Sample B	
	Ln_2O_3 recovered mg	Composition as oxides %	Ln_2O_3 recovered mg	Composition as oxide %
Sm	42.6	6.1	67.0	7.6
Nd	135.1	19.3	184.3	20.8
Pr	42.4*	5.8	40.4*	4.6
Ce	327.4**	44.5	404.7**	45.6
La	170.5	24.3	189.3	21.4

* as Pr_6O_{11} ** as CeO_2

As is shown in Fig. 5, complete separation of Sm, Nd, Pr, Ce and La is obtained for sample A, while a little overlapping of the Nd fraction with Pr is observed in Fig. 6 for sample B. This somewhat poorer separation arises from the higher content of Nd in sample B as compared with that in sample A.

Our elution method was developed for larger scale separation; the sample A absorbed corresponded to 10 g of $LnCl_3 \cdot nH_2O$. The resin was 50—100 mesh in size, and its 540 m*l* was put into a column 3.0 cm in diameter; the flow rate was 1.5 cm/min, and the results are shown in Fig. 7.

Analyses of Rare Earth Oxides. Samples "C" and "D" were obtained from our company in the form of mixed chlorides after removing almost all the Ce from the other rare earths; these mixed chloride hydrates were first converted to mixed oxides and the oxides were treated with dilute nitric acid to remove the remaining cerium as an insoluble residue. The other rare earths in the solution were precipitated as oxalates and converted to oxides by ignition. The experimental conditions employed were: sample, about 1 g; column, 2.0×50 cm; Dowex 50W X8 (100—200 mesh), 40 g; bed length, about 22 cm; flow rate, 1.0 cm/min.

Elution was started with 50 : 1 eluting agent for Sm. Then the eluting agent was changed to 30 : 1 solution for the effective elution of Nd, where contamination of the Nd fraction with Pr was not observed. The elutions of Pr and Ce were carried out with 20 : 1 and 10 : 1 solutions in turn. Finally, 5 : 1 eluting agent was used for La. The eluates were collected for each fraction and tested for the presence of rare earth species by adding oxalic acid to the fractions placed at intervals of five fractions. The portions containing each species were brought together and evaporated to

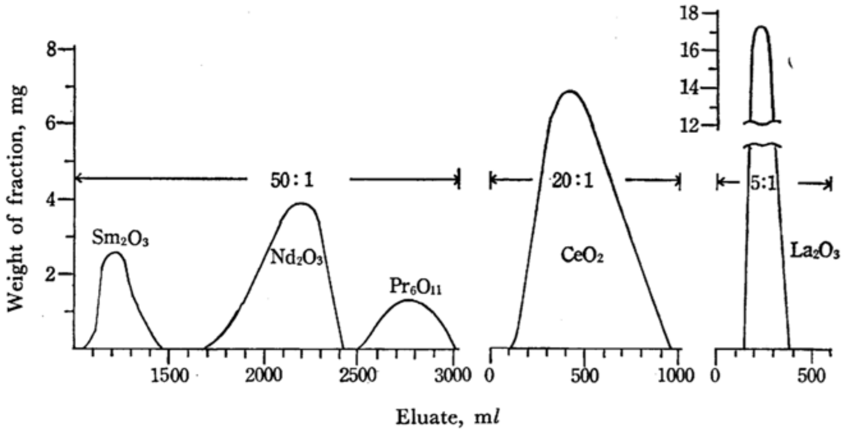

Fig. 5. Elution of the sample "A" in 2 g scale. One fraction of eluate. 50 ml

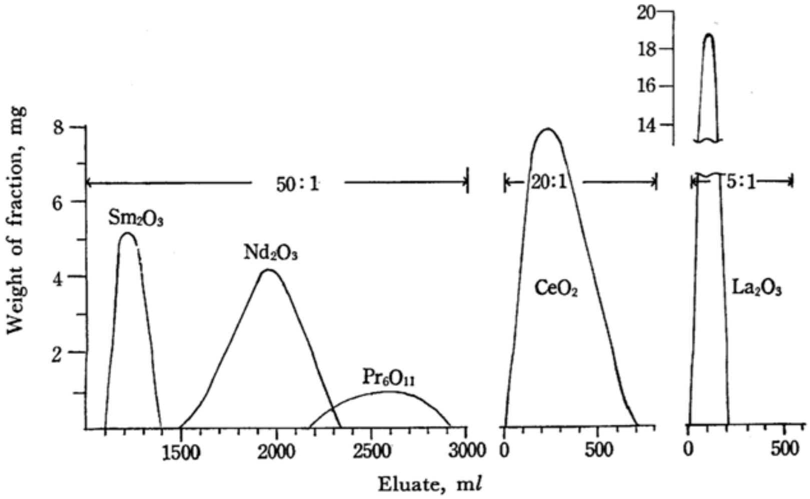

Fig. 6. Elution of the sample "B" in 2 g scale. One fraction of eluate, 50 ml

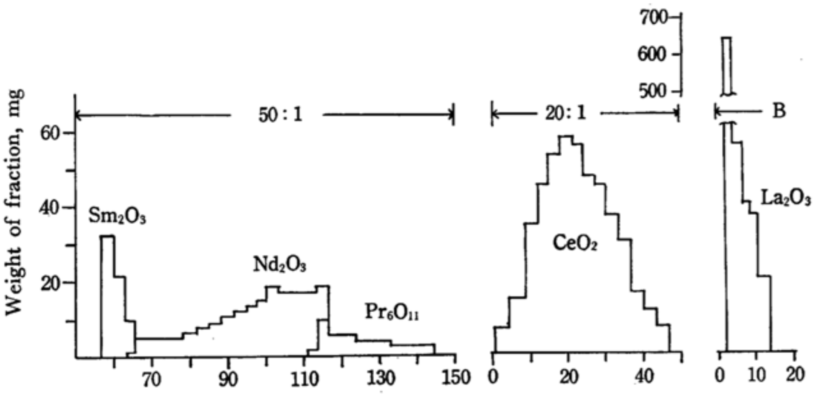

Fig. 7. Elution of the sample "A" in 10 g scale. One fraction of eluate, 120 ml

a suitable volume. A large excess of oxalic acid was added to the concentrated solution and its pH adjusted to about 1.5 with ammonia. After heating for about 20 min, the whole was allowed to stand overnight. The precipitated oxalate was converted to oxide at 900°C. Typical results are given in Table 2.

TABLE 2. ELUTION RESULTS FOR MIXED OXIDES

Sample	C		D	
Sample taken, mg	1054.0		828.8	
	Recovered mg	Recovered %	Recovered mg	Recovered %
Sm_2O_3	129.1	12.25	74.0	8.93
Nd_2O_3	373.0	35.39	291.6	35.18
Pr_6O_{11}	98.3	9.33	81.1	9.79
CeO_2	0*	0	6.2	0.75
La_2O_3	450.6	42.75	371.6	44.84
Total	1051.0	99.72	824.5	99.48

* Qualitative test for its presence was also negative.

Behavior of the Yttrium-group Rare Earths. The utility of the new eluting agent for the cerium-group directed our attention to the separation of the yttrium-group rare earths, and some experiments were carried out in order to investigate the possibility. The individual elutions of Dy, Er, Yb and Y with 50 : 1 eluting agent are presented for comparison (Fig. 8). It is seen from the results that these elements show similar behavior. When 70 : 1 eluting agent was used, the nature of the elution was slightly improved, but it was still hopeless to separate these elements.

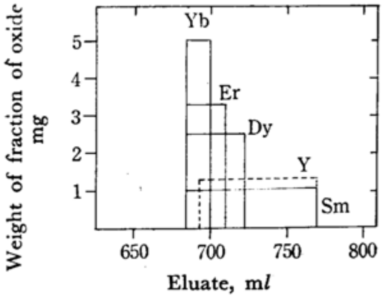

Fig. 8. Individual elution for the yttrium-group rare earths.
Weight of each sample, 10 mg as oxide; column diameter, 1.8 cm; bed height, 18 cm; flow rate 1.0 cm/min; eluting agent, 50 : 1; 1 fraction of eluate, 20 m*l*

On the Eluting Agent. A distinctive feature of our eluting agent is that the solution contains acetate anions in addition to citrate anions. Both anions may be responsible for the separation of the rare earths in the manner of complex formation. Tompkins and Mayer(11) mentioned that three H_2Cit^- ions are predominantly complexed with a rare earth ion under the condition of 0.25 M (5%) citrate at a pH lower than 3.2. In our eluting agent, the citrate concentration is about 6% and the pH values are 2.9 in 50 : 1 and 3.0 in 30 : 1 eluting agents. Therefore, formation of such complex species as $R(H_2Cit)_3$ should be considered in the elution process. On the other hand, the effect of the "B" component on the separation also suggests the formation of acetate-complex species. Kolat and Powell(12) reported the first two formation constants of acetate anions with rare earths. According to their data, a regular increase in stability is observed in the La-Sm region, while a decrease appears for the heavier elements. This decrease in stability reflects the failure to separate the yittrium-group rare earths.

Summary

A mixed system consisting of citric acid - ammonium citrate and acetic acid - ammonia was found to be a new eluting agent for the separation of La, Ce, Pr, Nd and Sm. The essential feature of this eluting agent is that the solution contains acetate anions in addition to citrate anions, and the former greatly affects the separation. As examples of separation, mixed chlorides obtained from monazite concentrates were eluted on an analytical scale. Mixed oxide samples were also analyzed successfully by this elution method.

Application of this eluting agent to heavier rare earths (yttrium-group) was unsuccessful.

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12) R. S. Kolat and J. E. Powell, *Inorg. Chem.*, **1**, 293 (1962).