Ion-Exchange Separation of Cerium and Thorium with Lead-EDTA Complex as Eluting Agent

By Tomitsugu TAKETATSU

(Received October 11, 1958)

Vickery¹⁾ reported that when EDTA was used as eluant, separation of two metal ions by ion-exchange resin became more effective by introducing a third metal ion having a peak position of elution between those of the two ions, than the separation without the third metal ion. The method, using a third metal-EDTA complex solution as eluant was studied in this paper, instead of adding the third metal ion to the sample solution. Schwarzenbach et al.²⁾ determined the formation constants of cerium(III)-, lead(II)- and thorium(IV)-EDTA complexes and gave values $10^{16.0}$, $10^{18.0}$ and $10^{23.2}$, respectively. The separation of cerium and thorium ions was tried here by cation exchange resin with lead-EDTA.

Experimental

Reagents and apparatus.—Solution of lead-EDTA complex in various concentrations was prepared by adding a measured volume of a 0.1 mole solution of disodium salt of ethylenediaminetetraacetic acid to a 0.1 mole lead nitrate solution of the same volume, the pH controlled with aqueous ammonia and nitric acid and filled up to 1000 ml. with distilled water. Thorium or cerium standard solutions were prepared by dissolving their nitrate in distilled water and the concentrations were determined gravimetrically as their oxides. The results were 5.38 mg./ml. (ThO_2) and 12.00 mg./ml. (CeO_2).

The cation exchange resin Dowex 50 of ammonium form and of 50×100 mesh was used in a column of 5 cm.×0.6 cm².

General procedure.—The following procedure was recommended. A slightly acidic mixed solution of cerium and thorium ions was poured over the top of the column and the ions were adsorbed on the resin bed. After the resin bed was washed with 100 ml. of water, 250 ml. of a 0.015 M solution of lead-EDTA complex (pH 3.0) was passed through the column at a flow rate of 1.0~1.5 ml./min. in order to elute thorium ions. It was again washed with 100 ml. of water and cerium ions were eluted with 3 N hydrochloric acid. Lead ions remaining in the column were

---

1) R. C. Vickery, *J. Chem. Soc.*, **1952**, 4357.

2) G. Schwarzenbach, R. Gut and G. Anderegg, *Helv. Chim. Acta*, **37**, 937 (1954).

precipitated as lead chloride but gradually redissolved in hydrochloric acid and eluted from the resin bed.

Analytical method.—The first effluent containing thorium and lead ions was dried up, and treated with concentrated sulfuric and nitric acid to decompose EDTA[3]. Lead ions were thus removed as lead sulfate. The second effluent containing cerium and lead ions was similarly treated. Cerium and thorium ions were precipitated with aqueous ammonia and their concentrations determined gravimetrically as oxides.

Results and Discussion

The quantities of thorium and cerium used were 26.9 mg. (ThO_2) and 44.1 mg. (CeO_2), respectively. The effects of various conditions of the eluant on the rate of separation were examined, i.e., the concentration of lead-EDTA complex solution, the pH and the flow rate.

Effect of the concentration.—Lead-EDTA complex solution with concentrations varying from 0.010 to 0.020 mole was used as eluants. The pH value was fixed at 3.0 and the flow rate at 1.5 ml./min. Each 100 ml. of the effluents was collected and the concentration of thorium or cerium ions was determined. The data obtained are given in Fig. 1.

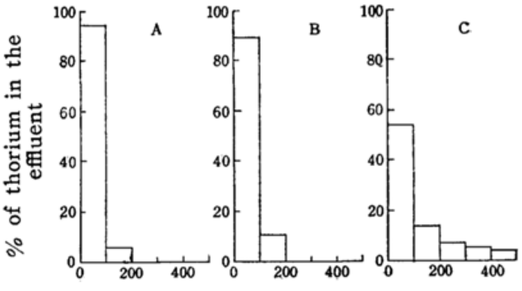

Fig. 1. Elution of thorium ion at different concentrations of eluants.
A: 0.020 mol. lead-EDTA complex solution.
B: 0.015 mol. lead-EDTA complex solution.
C: 0.010 mol. lead-EDTA complex solution.

It can be seen that thorium ions were completely eluted with 200 ml. of 0.020 and 0.015 mole eluants but incompletely with 500 ml. of 0.010 mole eluants. On the other hand, cerium ions were not eluted with the eluants under the same conditions.

Effect of pH.—In order to determine the optimum pH, 0.015 mole eluants of pH 2.4, 3.0 and 4.7 were used. The elution graphs for thorium ions are shown in Fig. 2.

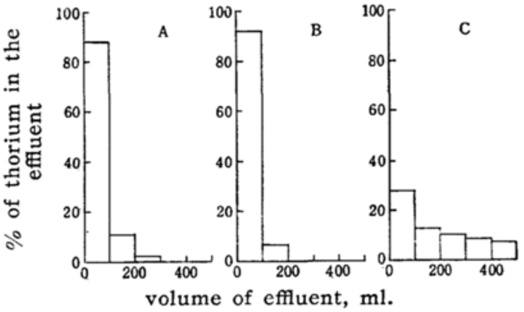

Fig. 2. Elution of thorium ion at different pH values of eluants.
A: pH 2.4 B: pH 3.0 C: pH 4.7

The data indicate that thorium ions were most effectively eluted at pH 3.0, whereas cerium ions were not eluted in the range of pH between 2.4 and 4.7.

Effect of flow rate.—The flow rate studied was 0.6, 1.2 and 2.0 ml./min. Each 50 ml. of the effluent was collected and the concentration of thorium ions was determined. The results are shown in Fig. 3.

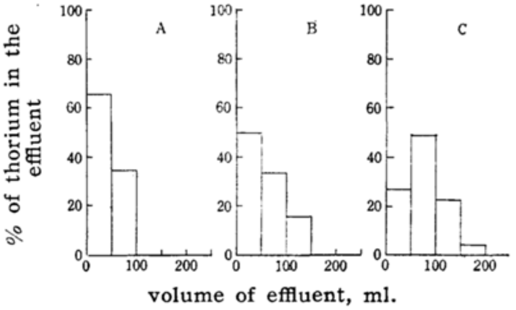

Fig. 3. Elution of thorium ion at different flow rates.
A: 0.6 ml./min. B: 1.5 ml./min.
C: 2.0 ml./min.

From the elution graphs it can be seen that the amount of thorium ions in the effluent increases with decrease of the flow rate. However, a flow rate of 1.0~1.5 ml./min. was employed to make the time taken for an experiment reasonable. Cerium ions were not eluted at any flow rate of the eluant.

The optimum conditions for the separation were as follows: the concentration of the lead-EDTA complex solution was 0.015 mole, pH 3.0 and the flow rate 1.0~1.5 ml./min. Fig. 4 shows that cerium ions

---

[3] W. F. Hillebrand and G. E. F. Lundell, "Applied Inorganic Analysis" (1929), John Wiley & Sons, Inc., New York, p. 61.

were not eluted even with 1000 ml. of the lead-EDTA solution at the optimum conditions.

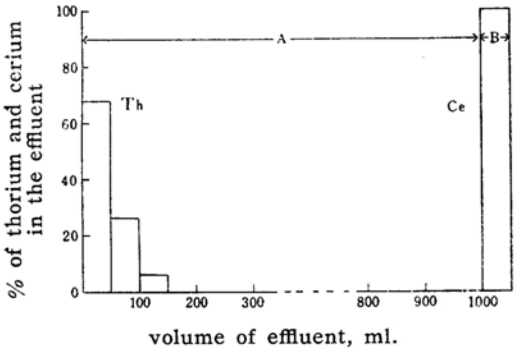

Fig. 4. Elution graph of thorium and cerium.

eluant { A: 0.015 ml. lead-EDTA complex solution.
B: 3 N HCl solution.

On the other hand, when only an EDTA solution of the concentration of 0.015 mole was used as eluant at pH 3.0 and at a flow rate 1.0∼1.5 ml./min. instead of the lead-EDTA complex solution, cerium ions began to flow out even in the first fraction of the volume of 50 ml. This shows that lead ions as the third element in the lead-EDTA complex gave a remarkable effect on the efficiency of the separation.

The results of analyses for various quantities of the two ions by this procedure are shown in Table 1.

TABLE I

SEPARATION OF CERIUM AND THORIUM IONS

Taken. (mg.)		Found. (mg.)			
ThO_2	CeO_2	ThO_2	Error	CeO_2	Error
39.5	19.6	39.7	+0.2	19.6	±0.0
26.9	12.0	26.9	±0.0	11.7	−0.3
53.8	12.0	53.6	−0.2	11.9	−0.1

A qualitative detection by the fluorescent X-ray spectrometer "Norelco" showed that there was neither cerium in the thorium oxide fraction nor thorium in the cerium fraction. Thus, it was concluded that the separation of cerium and thorium ions was quantitatively carried out.

At the optimum conditions of the separation of cerium and thorium ions, the behavior of other rare earth ions was examined. Rare earth ions, i.e., lanthanum, cerium, praseodymium, neodymium, dysprosium and yttrium and a trace of thorium were extracted from allanite and adsorbed on the resin bed. The total weight of their oxides was about 123.2 mg. After 250 ml. of the 0.015 mole lead-EDTA solution (pH 3.0) was passed through the resin bed, the rare earth and thorium ions in the effluent and in the resin bed were separately determined gravimetrically as oxides. Each rare earth oxide was qualitatively detected by the fluorescent X-ray spectrometer. Heavy lanthanons, gadolinium, dysprosium and yttrium and thorium (total oxides 11.1 mg.) were detected in the effluent; on the other hand, light lanthanons, lanthanum, cerium, praseodymium, neodymium, samarium and gadolinium (total oxides 112.0 mg.) were found to remain in the resin bed.

Further studies are under way on the separation of the rare earths with the lead- and other-EDTA complex solutions as eluants.

Summary

The separation of cerium and thorium ions was studied with a lead-EDTA complex solution as eluant. The optimum conditions were determined as the following: the concentration of the lead-EDTA solution was 0.015 mole, pH 3.0 and the flow rate 1.0∼1.5 ml./min. Thorium ions were completely eluted with 200 ml. of the eluant at the optimum conditions, while no cerium ions were detected in the effluent with 1000 ml. of the eluant. Thus the use of a lead-EDTA complex solution as eluant was concluded to be effective for separation of cerium and thorium ions.

The author wishes to express his gratitude to Professor S. Misumi for his valuable discussion and encouragement.

Department of Chemistry
Faculty of Science
Kyushu University
Hakozaki, Fukuoka