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MASTER

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CATION EXCHANGE SEPARATION OF DIVALENT METAL IONS
FROM RARE EARTHS*

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Abstract-The divalent metal ions of calcium, magnesium, nickel, and strontium are eluted from a cation exchange column with 1.5M nitric acid and separated from trivalent rare earths, aluminum and yttrium. Prior sequential elution of other metal ions with hydrochloric acid in acetone-water or with dilute hydrofluoric acid does not interfere with the present separation method.

INTRODUCTION

Several excellent ion exchange methods for the separation of metal ions into groups have been developed in the last few years. Many elements are taken up by an anion exchange column from aqueous or nonaqueous hydrochloric acid^{7, 9} or from hydrofluoric acid solutions.^{2, 10} Likewise, many metal cations can be eluted from a cation exchange column with dilute aqueous hydrobromic acid,⁴ hydrofluoric acid,⁵ hydrogen peroxide,³ or hydrochloric acid in acetone-water solution.⁸ In these separations, aluminum(III), chromium(III), rare earths(III), yttrium(III), alkaline earths(II), magnesium(II), and nickel(II) may remain as a group because they pass through an anion exchange column and are not eluted from a cation exchange column by the method listed above.

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Fritz and Karraker⁶ separated metal cations of different charge type by elution from an ethylenediammonium-form cation exchange column. For sequential separations, elution of metal ions with a volatile acid from a hydrogen-form cation exchange column is advantageous. Strelow¹¹ eluted beryllium(II) from a cation exchange column with 1M hydrochloric or 1.2M nitric acid and thus separated it from aluminium, iron, rare earths, and yttrium. Edge and Ahrens¹ concentrated rare earths from silicate rock samples by prior elution of the bulk of other metal ions with 3M hydrochloric acid.

In the present work, a scheme is presented for the ion exchange separation of calcium(II), strontium(II), magnesium(II), and nickel(II) from the trivalent ions, aluminum(III), rare earths(III), and yttrium(III). These divalent metal ions are eluted as a group from a hydrogen form cation exchange column using 1.5M nitric acid as the eluent. Following this separation, the trivalent metal ions are stripped from the column and titrated with EDTA.

EXPERIMENTAL

Ion Exchange Column

Conventional glass ion exchange columns (i. D. 1.2 cm) were filled to a bed height of 16 cm with a slurry of water and resin. Eluent was added to the column from a cylindrical separatory funnel which was inserted in the top of the column through a one-holed rubber stopper. This method allowed dropwise addition of eluent so that the top of the resin bed was not disturbed.

Ion Exchange Resin

Dowex 50W X8, 100-200 mesh, hydrogen-form cation exchange resin was used. Before use, the resin was cleaned by back-washing to remove the fine particles. The resin was then washed with 10% ammonium citrate (pH 3.0-3.5), 3M hydrochloric acid, and finally with water until a negative chloride test was obtained with silver chloride. The resin was then air dried.

Procedure for Separation

An aliquot of 0.05M solution of the nitrate or perchlorate salts of the metal ions containing the desired amount of metal was diluted to 25 ml with water and added to the column. The metal ion was then eluted at a flow rate of 2 ml/min. In single ion elutions, 10-ml fractions were collected and tested for presence of the metal ion. In the separation of mixtures, a single, large fraction was used of a volume slightly larger than the amount needed for complete removal of the ion. If subsequent ions were removed with a different eluent, the column was rinsed with 20 ml of water between elutions.

When a nonaqueous media was used for elution of some mixture components, the solution of metal salts was evaporated to a volume of 1 to 2 ml. Concentrated nitric acid was added during evaporation to prevent hydrolysis. Prior to loading this mixture onto the column, the column was equilibrated by passing 15 ml of 60% acetone-0.1M hydrochloric acid through at maximum flow rate. After quantitatively transferring the mixture to the column, the flow rate was adjusted to

approximately 0.5 ml/min for all nonaqueous separations.

Analysis

After elution, the collected fractions were evaporated nearly to dryness and analyzed for the metal by titration with 0.05M EDTA.⁴

RESULTS

A study was made of the elution of individual metal ions from a 16 x 1.2 cm column with hydrochloric and nitric acids. The best eluent appears to be 1.5M nitric acid (see Tables I and II). With lower concentrations, the elution is too slow; 2M nitric acid causes some of the rare-earth elements to break through too early. Hydrochloric acid, 1.5 to 2M, is promising for the separation of divalent metal ions from rare earths and yttrium but aluminum breaks through very early.

Chromium(III) splits into two bands upon elution with 1.5M nitric acid. One band is eluted and the other remains on the column. The first chromium(III) appears in the effluent in the 120- to 130-ml fraction. Chromium(III) is an interference in the proposed separation.

The effect of load was next studied. The normal 0.25mmole load used for single ion elutions was increased to 1 mmole. This increase had no effect on the volume of 1.5M nitric acid required for elution of divalent metal ions. However, increasing the load of the trivalent metal ion caused it to break through earlier. Figure 1 shows the significant decrease in the distribution coefficients of trivalent metal ions with increasing load. It appears that 1 mmole is the maximum load for a trivalent metal ion with a column of the dimensions used. The load

TABLE I. ELUTION OF INDIVIDUAL METAL IONS FROM A
1.2 X CM CATION-EXCHANGE COLUMN WITH NITRIC ACID

| Ion | Nitric Acid Eluent | Break-Through, ml | | |
|------------------|-----------------------|-------------------|-----------|-----------|
| | | 0.25 mmole | 0.5 mmole | 1.0 mmole |
| Al ⁺³ | 1.5M | >300 | >300 | 130 |
| | 2.0M | 150 | -- | -- |
| Cr ⁺³ | 1.5M | 120 | -- | -- |
| Dy ⁺³ | 1.5M | >500 | >300 | 220 |
| | 2.0M | 130 | -- | -- |
| Lu ⁺³ | 1.5M | >500 | >300 | -- |
| | 2.0M | 130 | -- | -- |
| Y ⁺³ | 1.5M | >500 | >350 | 240 |
| | 2.0M | 170 | -- | -- |
| Yb ⁺³ | 1.5M | >500 | >350 | -- |
| | 2.0M | 130 | -- | -- |

TABLE II. ELUTION OF 0.25 MMOLE OF INDIVIDUAL METAL
IONS WITH 1.5 M NITRIC ACID (COLUMN 1.2 X 16 CM)

| Ion | Break-Through, ml | Elution Complete, ml |
|------------------|-------------------|----------------------|
| Ca ⁺² | 60 | 160 |
| Mg ⁺² | 70 | 130 |
| Ni ⁺² | 70 | 130 |
| Sr ⁺² | 40 | 170 |

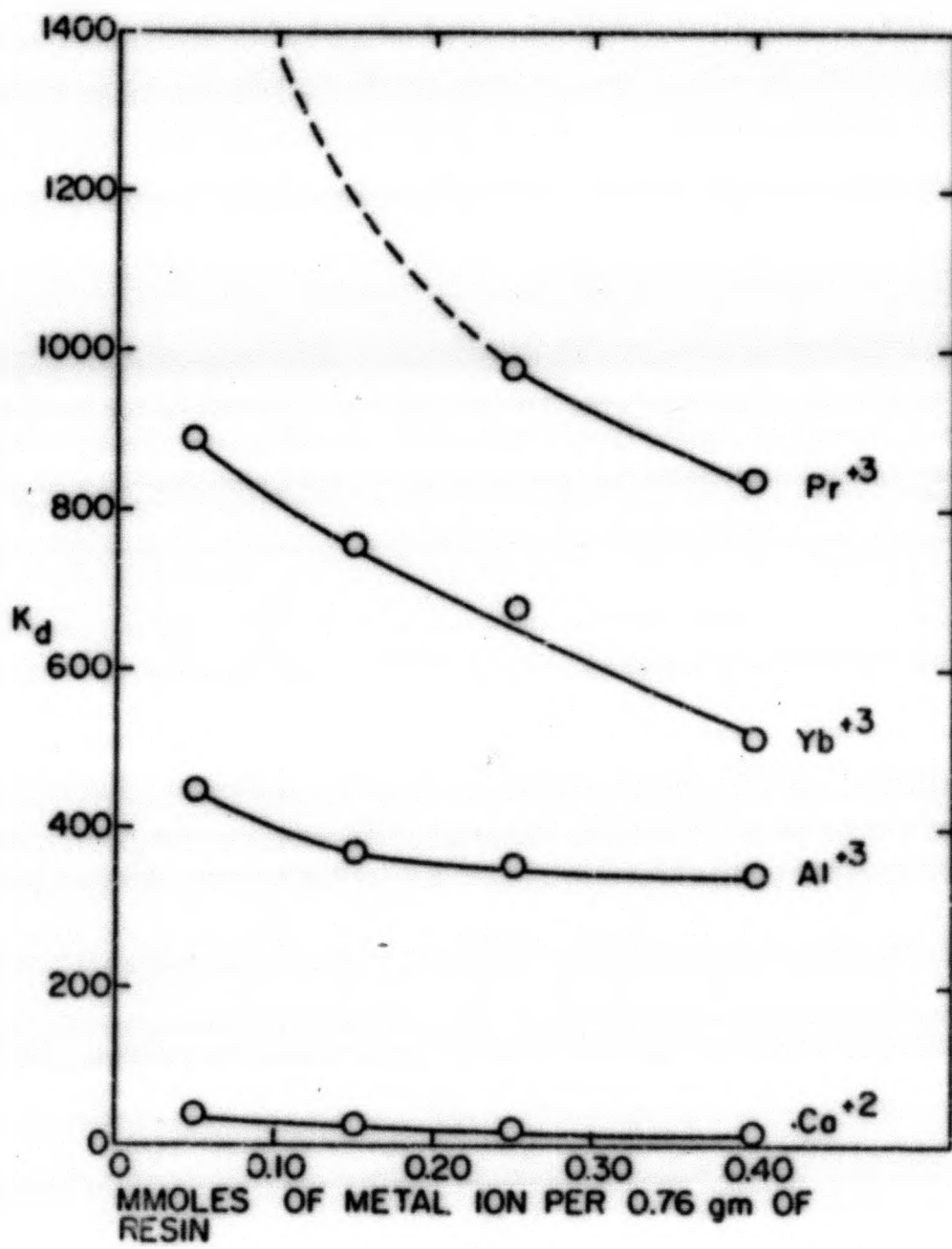


Fig. 1

recommended for separation of mixtures is 0.5 mmole or less of total trivalent metal ion and 0.5 mmole or less of total divalent metal ion. Larger loads can, of course, be employed with columns of larger dimensions.

Mixtures containing 0.25 or 0.5 mmole of a divalent metal ion and 0.25 or 0.5 mmole of the trivalent metal ion were added to a cation exchange column in dilute acid and the divalent metal ion was eluted with 200 ml of 1.5M nitric acid. Then the trivalent metal ion was stripped from the column with 200 ml of 3M nitric acid. Each fraction was evaporated to remove excess acid and the metal ion present was titrated with EDTA. The following two-component mixtures were all separated successfully.

Ca^{+2} from Al^{+3} , Dy^{+3} , Lu^{+3} , Nd^{+3} , Y^{+3} , and Yb^{+3}

Mg^{+2} from Al^{+3} , Dy^{+3} , Lu^{+3} , Nd^{+3} , Y^{+3} , and Yb^{+3}

Ni^{+2} from Al^{+3} , Dy^{+3} , Lu^{+3} , Nd^{+3} , Y^{+3} , and Yb^{+3}

Sr^{+2} from Al^{+3} , Dy^{+3} , Lu^{+3} , Nd^{+3} , Y^{+3} , and Yb^{+3}

Mixtures containing 1.00 mmole of yttrium(III) and 0.10 mmole of nickel(II) or magnesium(II) were separated successfully. A mixture of 1.0 mmole magnesium(II) plus 0.25 mmole of lutetium(III), and a mixture of 0.25 mmole strontium(II) plus 1.0 mmole of dysprosium(III) were also separated quantitatively. Analysis of all data obtained (65 individual determinations) shows an average recovery of 100.0% with a standard deviation of 0.2%.

It is interesting to know whether prior separations performed on the same column with other eluting agents would effect the separation of di- and trivalent metal ions with 1.5M nitric acid. To check this, a mixture containing six different metal ions was resolved completely by sequential elutions with 0.12 hydrobromic acid, 0.5 M hydrobromic acid, 0.1 M hydrochloric acid, 1M hydrochloric acid, and 1.5M nitric acid. Another more complicated mixture was separated by sequential elutions with various concentrations of hydrochloric acid in acetone, 0.3% hydrogen peroxide-0.01M perchloric acid, 0.1M hydrofluoric acid, and 1.5M nitric acid. The results given in Table III show excellent recovery of all of the sample components. Thus it appears that these prior elutions have a negligible effect on the separations using 1.5M nitric acid as the eluent.

TABLE III. SEPARATIONS ON A 16 X 1.2 CM CATION-EXCHANGE COLUMN

| Ion Mixtures | Load (m moles) | Eluent | EDTA Titrations | | |
|------------------|----------------|--|-----------------|-------------|------------|
| | | | Theory (ml) | Actual (ml) | Dif. in ml |
| Bi ⁺³ | 0.10 | 35 ml 60% Acetone - 0.1M HCl | 2.05 | 2.04 | -0.01 |
| Cd ⁺² | 0.10 | 30 ml 40% Acetone - 0.5M HCl | 2.05 | 2.05 | +0.00 |
| Zn ⁺² | 0.10 | 25 ml 60% Acetone - 0.5M HCl | 2.02 | 2.02 | +0.00 |
| Fe ⁺³ | 0.10 | 20 ml 70% Acetone - 0.5M HCl | | | |
| | | 20 ml 80% Acetone - 0.5M HCl | 2.04 | 2.05 | +0.01 |
| Cu ⁺² | 0.10 | 35 ml 80% Acetone - 0.5M HCl | 2.06 | 2.06 | +0.00 |
| VO ⁺² | 0.10 | 70 ml 0.3% H ₂ O ₂ - 0.01M HClO ₄ | 2.03 | 2.03 | +0.00 |
| Mn ⁺² | 0.10 | 50 ml 92% Acetone - 1.0M HCl | 2.05 | 2.04 | -0.01 |
| Al ⁺³ | 0.10 | 200 ml 0.1M HF | 2.05 | 2.04 | -0.01 |
| Ni ⁺² | 0.10 | 200 ml 1.5M HNO ₃ | 2.07 | 2.08 | -0.01 |
| Y ⁺³ | 0.10 | 250 ml 2.0M HNO ₃ | 2.04 | 2.04 | +0.00 |
| Hg ⁺² | 0.25 | 120 ml 0.12M HBr | 4.98 | 4.99 | +0.01 |
| Bi ⁺³ | 0.25 | 60 ml 0.5M HBr | 5.06 | 5.07 | +0.01 |
| Cd ⁺² | 0.25 | 150 ml 0.1M HF | 5.11 | 5.10 | -0.01 |
| Fe ⁺³ | 0.25 | 200 ml 1.0M HF | 5.13 | 5.11 | -0.02 |
| Ni ⁺² | 0.25 | 200 ml 1.5M HNO ₃ | 5.04 | 5.05 | +0.01 |
| Y ⁺³ | 0.25 | 250 ml 2.0M HNO ₃ | 5.02 | 5.03 | +0.01 |

REFERENCES

- 1 R. A. Edge and L. H. Ahrens, Anal. Chim. Acta, 1962, 26, 355.
- 2 J. P. Faris, Anal. Chem., 1960, 32, 520.
- 3 J. S. Fritz and Janet E. Abbink, Anal. Chem. (in press).
- 4 J. S. Fritz and Barbara B. Garralda, Ibid., 1962, 34, 102.
- 5 J. S. Fritz, Barbara B. Garralda and Shirley K. Karraker, Ibid., 1961, 33, 882.
- 6 J. S. Fritz and Shirley K. Karraker, Ibid., 1959, 31, 921.
- 7 J. S. Fritz and D. J. Pietrzyk, Talanta, 1961, 8, 143.
- 8 J. S. Fritz and T. Rettig, Anal. Chem. (submitted).
- 9 K. A. Kraus and F. Nelson, "Symposium on Ion Exchange and Chromatography in Analytical Chemistry", Am. Soc. Testing Materials, Philadelphia, 1956, pp. 27-57.
- 10 F. Nelson, R. M. Rush, and K. A. Kraus, J. Am. Chem. Soc., 1960, 82, 339.
- 11 F. W. E. Strelow, Anal. Chem., 1961, 33, 542.

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