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Synthetic Inorganic Ion-Exchange Materials. XIX. Ion-Exchange Behavior and Separation of Alkaline Earth Metals on Crystalline Antimonic(V) Acid as a Cation Exchanger

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Synthetic Inorganic Ion-Exchange Materials. XIX. Ion-Exchange Behavior and Separation of Alkaline Earth Metals on Crystalline Antimonic(V) Acid as a Cation Exchanger

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Abstract

A study of the distribution coefficients on crystalline antimonic(V) acid (C-SbA) as a cation exchanger shows an unusual affinity series (Mg < Ba < Ca <Sr) for microamounts of alkaline earth metals in a nitric acid solution. An extremely slow rate of adsorption was observed for calcium and strontium ions on the exchanger. On the basis of the distribution coefficients, the effective separation of Mg^{2+}–Ba^{2+}, Mg^{2+}–Cs^{+}–Ba^{2+}, and Mg^{2+}–Cs^{+}–Ca^{2+}, Sr^{2+} has been achieved with a small column (1.0 or 2.0×0.4 cm i.d.) of C-SbA.

INTRODUCTION

A great deal of work has been carried out on synthetic inorganic ion-exchangers (*1*, *2*). The analytical applications of inorganic ion-exchangers have received considerable attention owing to their high selectivities with respect to certain elements (*3*, *4*). The adsorption properties of the hydrous oxides of multivalent metals have been studied systematically for their use as ion exchangers (*5*, *6*). Among them, the hydrous antimony pentoxide (so-called antimonic acid) exhibits a relatively high adsorption capacity

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with a reasonable rate of adsorption and desorption for alkali metal ions when used in the usual column operations (*7*, *8*). Various antimonic acid materials have been obtained with different chemical composition and ion-exchange properties, depending on the method of preparation as well as on aging (*9*). The species can be divided into three groups—crystalline, amorphous, and glassy. Among the three different antimonic acids, crystalline antimonic acid (C-SbA) showed an unusual selectivity for alkali metal ions as compared with the strong acid-type cation exchange resins and other inorganic ion-exchangers (*8*, *10*). The increasing order of selectivity was Li < K < Cs < Rb < Na for microquantities of alkali metals in nitric acid solution. The selectivity sequence for C-SbA depends on the loading of the exchanging metal ions as well as on the sorption media (*11*). The effective separation of alkali metals can be achieved by using a relatively short column (6 × 0.8 cm i.d.) of C-SbA (*8*, *10*, *12*). Compounds similar to C-SbA have been reported by several authors (*13*–*17*). Slightly different selectivity has been found for polyantimonic acid: $Mg^{2+} < Ca^{2+} < Sr^{2+} < Ba^{2+}$ (*13*) and $Ra^{2+} < Ba^{2+} < Ca^{2+} < Sr^{2+}$ (*14*). The separation of ^{90}Sr from fission waste in a HNO_3 solution can be achieved with polyantimonic acid (*18*).

This paper describes the measurement of the distribution coefficients of alkaline earth metals and their possible separation by using a C-SbA column.

EXPERIMENTAL

Reagents

Antimony pentachloride (Yotsuhata Chemical Co. Ltd., Japan) was used without further purification. The other reagents used were all of analytical grade.

Preparation of C-SbA as an Ion-Exchange Material

The C-SbA was prepared as described previously (*9*); the aqueous solution of antimony pentachloride (75 ml $SbCl_5$ + 75 ml H_2O) was hydrolyzed in 5 liters of demineralized water at 25°C. The precipitate was kept in the mother liquor at 30°C for 7 days and then washed with cold demineralized water with the aid of a centrifuge (about 10,000 rpm) until it was free of chloride ions. After drying, the product was ground and sieved to 100–200 mesh size. The collected sample was rewashed with water in order to eliminate small quantities of adherent C-SbA dust to improve the elution flow rate.

Distribution Coefficients

The distribution coefficients (K_d) of the metal ions were determined by batch operation as follows. C-SbA (0.250 g) was immersed in 25 ml of the nitric acid solution containing the metal ions at 30 ± 0.1°C with intermittent shaking. The concentration of metal ions in the solid and in the solution phase was deduced from the concentration relative to the initial concentration in the solution. The K_d values of metal ions were calculated after attainment of equilibrium by using the following expression:

$$K_d = \frac{\text{amount of metal ions in exchanger}}{\text{amount of metal ions in solution}} \times \frac{\text{ml of solution}}{\text{g of exchanger}}$$

A Varian Techtron 1100 atomic absorption spectrometer was employed to determine the concentration of alkaline earth metals.

RESULTS AND DISCUSSION

Adsorption of Alkaline Earth Metals

The time dependence on adsorption of the different metals was measured qualitatively in order to determine the equilibrium distribution coefficients (Fig. 1). The equilibrium of Ba^{2+}–H^+ exchange was attained within 24 hr as observed for the system of alkali metal ions–H^+ on C-SbA (except Cs^+–H^+). The ion-exchange reactions of Mg^{2+} and Cs^+ are slow, about 14 days being required for attainment of equilibrium in batch operation. The reactions of Sr^{2+} and Ca^{2+} are extremely slow, about several months being required.

Our earlier study indicated that the selectivity of the elements alters with the degree of crystallinity of antimonic acid by aging in a strong acid solution (*9*). It may be that this slow adsorption behavior occurs if the K_d values of Ca^{2+} and Sr^{2+} increase with an increasing degree of the crystallinity during the adsorption process. However, the rate of adsorption of the above metal ions remains fairly constant even though the C-SbA was immersed in a 10 *M* nitric acid solution for 1 month before the adsorption step of the alkaline earth metals. The ion-exchange reaction is usually quite rapid, and equilibrium may be reached almost instantane-

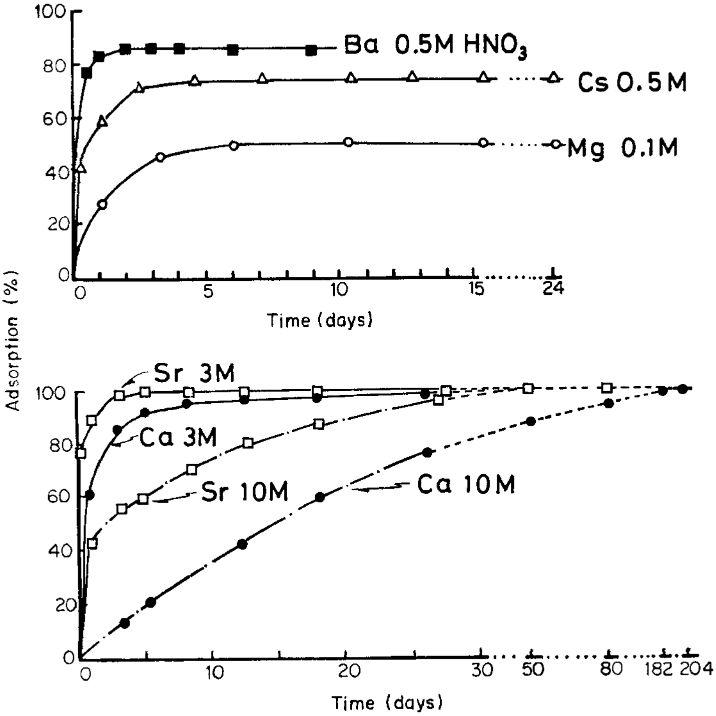

FIG. 1. Time dependence of the adsorption of alkaline earth metal and cesium ions on C-SbA in various nitric acid solutions. Initial concentration of metal ions, 1×10^{-3} *M*. C-SbA, 0.250 g. Total volume, 25.0 ml. Temperature, 30 ± 0.1 °C. 0.1 to 10 *M* represents the concentration of nitric acid solution.

ously in certain cases. On the other hand, an ion exchanger having the site accessible only through a very tight network structure exhibits a low rate of exchange.

Distribution Coefficients

The equilibrium distribution coefficients of alkaline earth metals and cesium on C-SbA are shown in Fig. 2 as log-log plots of K_d vs $[HNO_3]$. The slopes, $d \log K_d / d \log [HNO_3]$, are about 2 for all alkaline earth metals, as expected for an "ideal" 2:1 ion-exchange reaction. The following affinity series was observed for C-SbA selectivity: $Mg^{2+} < Ba^{2+} < Ca^{2+} < Sr^{2+}$. The K_d values of cesium showed good agreement with our earlier report (*10*). Thus C-SbA showed an unusual selectivity for alkaline

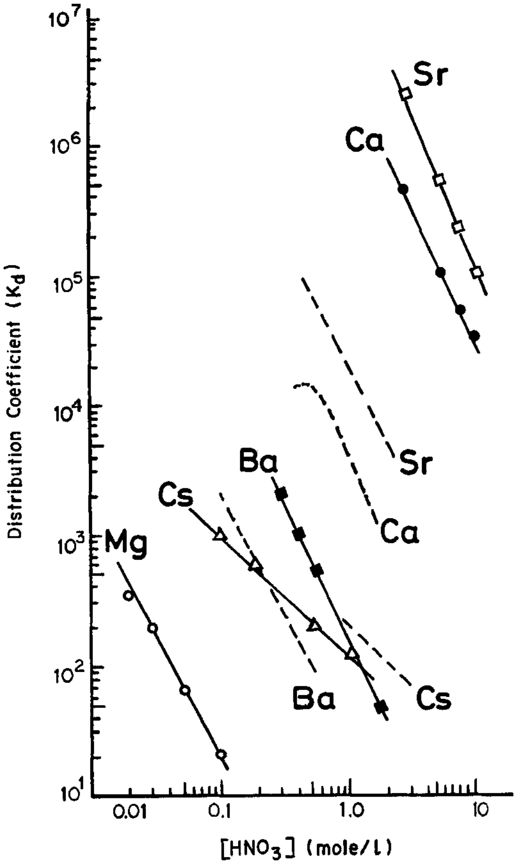

FIG. 2. Distribution coefficients of alkaline earth metal and cesium ions on C-SbA at different concentrations of nitric acid solution. Initial concentration of metal ions, 1×10^{-3} *M* (except Mg^{2+}, 1×10^{-5} *M*). C-SbA, 0.250 g. Total volume, 25.0 ml. Temperature, 30 ± 0.1 °C. Dashed line: data from Ref. *14*.

TABLE 1

Selectivity Quotients of Metal–Hydrogen Ion Exchange Equilibria on C-SbA in Nitric Acid Solution[a]

Ion exchanger	Temperature (°C)	Mg^{2+}–H^+	Ca^{2+}–H^+	Sr^{2+}–H^+	Ba^{2+}–H^+
C-SbA	30	7×10^{-3}	1.6×10^5	8.4×10^5	4.1
Polyantimonic acid[b]	20–25	—	2.0×10^2	8.0×10^2	1.0[c]
AG 50W-X8[d]	Room temp	6.0	9.9	12.0	17.1

[a] Initial metal concentration: 1×10^{-3} *M*, 1 *M* nitric acid solution.

[b] Data from Ref. *14*.

[c] They gave a value of 10, but correct value might be 1.0 from recalculation based on Fig. 3 in Ref. *14*.

[d] Calculated values are from the data of Table 2 in Ref. *19*.

earth metals as well as for alkali metals. The strong acid-type exchange resin AG 50W-8 exhibits the selectivity series $Mg^{2+} < Ca^{2+} < Sr^{2+} < Ba^{2+}$, which is qualitatively parallel to the crystal ionic radii of the alkaline earth metals.

The selectivity quotient is given by the general expression

$$K_{\mathrm{H}}^{\mathrm{M}^{2+}} = \frac{[\mathrm{H}^+]^2[\overline{\mathrm{M}^{2+}}]}{[\overline{\mathrm{H}^+}]^2[\mathrm{M}^{2+}]}$$

where the bars denote a species within the C-SbA, and the equilibrium concentrations of a species in the exchanger are represented in meq/g. The selectivity quotients of the various exchangers are summarized in Table 1.

The affinity series $Mg^{2+} < Ba^{2+} < Ca^{2+} < Sr^{2+}$ agrees well qualitatively with that reported for polyantimonic acid as reported by Baetsle and Huys (*14*). However, the numerical values of the selectivity quotients of Ca^{2+}–H^+ and Sr^{2+}–H^+ on C-SbA are much higher than those reported above. A different selectivity series, $Mg^{2+} < Ca^{2+} < Sr^{2+} < Ba^{2+}$, has been reported by Lefebre and Gaymard (*13*). These differences may be due to the different degrees of crystallinity of the antimonic acid, as mentioned earlier (*9*).

Dependence on the Concentration of the Metal Ions for the Distribution Coefficients

The distribution coefficient generally differs as a function of the concentration of the metal ions in the inorganic ion-exchangers which have

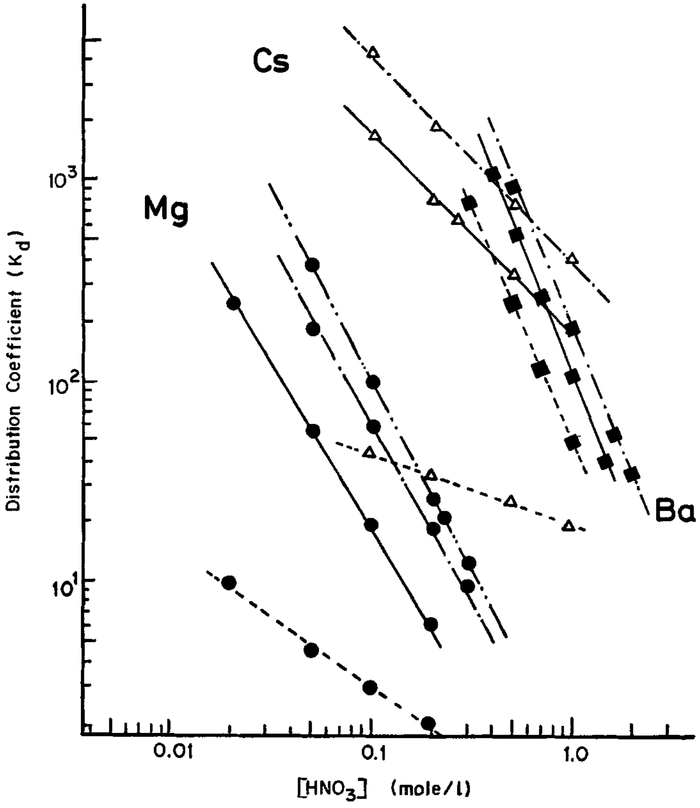

FIG. 3. The dependence upon the initial concentration of the metals for the distribution coefficients (K_d) of Mg^{2+}, Ba^{2+}, and Cs^+ on C–SbA. Initial concentration of metals: Mg^{2+} (●), (- -) 10^{-2} *M*, (——) 10^{-3} *M*, (- ·) 10^{-4} *M*, (- · ·) 10^{-5} *M*; Ba^{2+} (■), (- -) 10^{-2} *M*, (——) 10^{-3} *M*, (- ·) 10^{-4} *M*; Cs^+ (△), (- -) 10^{-2} *M*, (——) 10^{-3} *M*, (- ·) 10^{-4} M.

rigid structure. The K_d values on C-SbA are strongly dependent on the initial concentration of metal ions, even at the same concentration of nitric acid, especially for cesium ions (Fig. 3). This may be due to the existence of small amounts of an adsorption site capable of interacting with the sorbed cation, as pointed out by Ahrland et al. (*20*).

Ion-Exchange Separation

It is evident from studies of the distribution coefficients on C-SbA that some selective separations are feasible for alkaline earth metals.

Separation of Magnesium and Barium

Separation has been achieved by using a small column (1.0 × 0.4 cm i.d.) containing 0.12 g of C-SbA. The exchange column was pretreated with a few milliliters of 0.2 *M* HNO_3. The mixed solution of magnesium and barium to be separated contained 0.2 *M* HNO_3 to prevent tailing on the elution of magnesium ions. The mixed solution was added to the top of the C-SbA column. The column was washed with 0.2 *M* HNO_3 and then with 3 *M* HNO_3. The quantitative separation was performed with 99 to 100% recovery of pure magnesium and barium in a relatively short time (Fig. 4, top).

Separation of Magnesium, Cesium, and Barium

Separation of Mg^{2+}-Cs^{+}-Ba^{2+} was achieved with the column (2.0 × 0.4 cm i.d.) by using the nitric acid solutions at different concentrations (Fig. 4, bottom). An individual elution peak with a sharp front and a tailing rear was observed on the elution of magnesium and cesium ions. As is evident from studies of the dependence on the concentration of the metal ions for the distribution coefficients (Fig. 3), such an elution curve is caused by the main portion of the solute band being eluted more rapidly than the leading front edge due to the limited number of sites available for adsorption as a function of the concentration of the solute (*21*). Thus cesium ions of 4% were eluted with barium ions when 3 *M* HNO_3 was used as the eluant.

The elution curve for barium ions resembles the symmetrical bell-shaped peak of the normal Gaussian function without tailing effect with 1.0 to 3.0 *M* HNO_3, as expected from Fig. 3.

Separation of Cesium, Calcium, and Strontium

A satisfactory separation of cesium from strontium was achieved with the usual column operation conditions (Fig. 5, top), while calcium ions of about 33% were eluted with the elution of cesium ions. Further elution of the adsorbed calcium and strontium ions was obtained with 11 and 6% recovery up to 100 ml with 6 *M* HNO_3 as the eluant. Overlapping on the elution curve of calcium ions is thought to be due to the slow rate of adsorption of the calcium ion, as expected from Fig. 1.

When the elution was started after keeping the adsorbed metal ions on

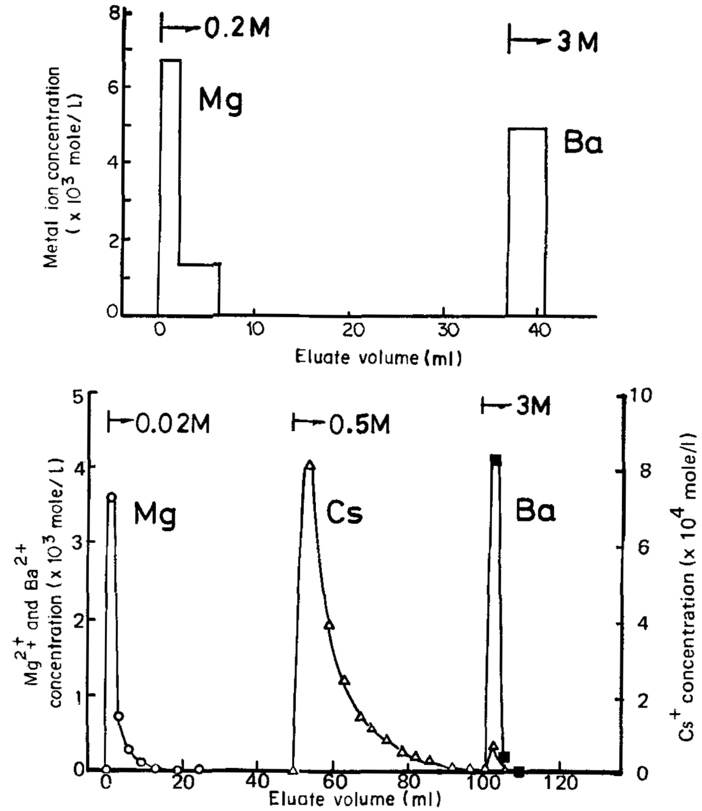

FIG. 4. Separation of Mg^{2+}–Ba^{2+} and Mg^{2+}–Cs^+–Ba^{2+} with C-SbA by various nitric acid solutions as the eluants. Top: C-SbA column, 1.0 × 0.4 cm i.d.; flow rate, 0.6 ml/min. Bottom: C-SbA column, 2.0 × 0.4 cm i.d.; flow rate, 0.4 ml/min. Adsorption on the column; 0.01 mmole of each of the metal ions.

the top of the column for about 15 hr, the cesium ions were separated without the elution of calcium ions with 0.5 *M* HNO_3 (Fig. 5, bottom). The adsorbed calcium and strontium ions were eluted with the recovery of several percent by using 6 *M* HNO_3 up to 100 ml. They were extremely difficult to remove completely, even by generation with concentrated nitric acid. It was thought that the calcium and strontium ions might have had time to diffuse deeply into the very narrow sites and difficultly approachable parts of C-SbA.

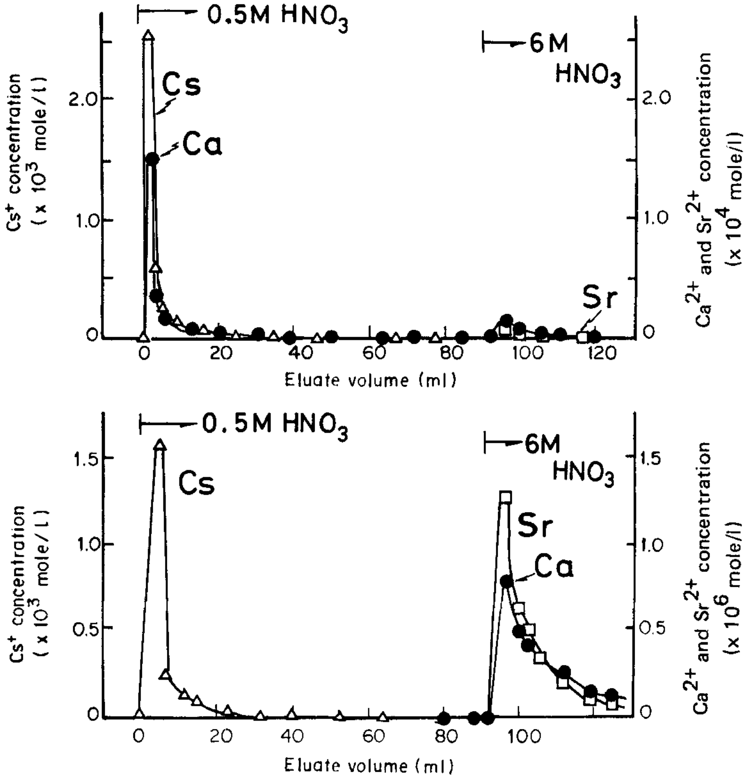

FIG. 5. Separation of Cs^+–Ca^{2+} and Sr^{2+} with C-SbA by various nitric acid solutions as the eluants. C-SbA column: 1.0 × 0.4 cm i.d.; Ca^{2+} and Sr^{2+}, 2×10^{-3} mmol; Cs^+, 1×10^{-2} mmol. Top: Eluted immediately after adsorption of the metal ions; flow rate, 1.1 ml/min. Bottom: Eluted after keeping the metal ions on the top of the C-SbA column for 15 hr; flow rate, 0.4 ml/min.

Separation of Magnesium and Cesium from Calcium and Strontium

In order to perform more rapid separations of Mg^{2+}, Cs^+, Ca^{2+}, and Sr^{2+}, a heated column was used. The column was prepared by using a quartz tube and filling the column with C-SbA up to the 0.8-cm level. The heated column consisted of a quartz tube inside a jacket through which thermostatic water was pumped. The quantitative separation of magnesium and cesium ions from calcium and strontium ions was performed. The adsorbed calcium and strontium ions were retained with

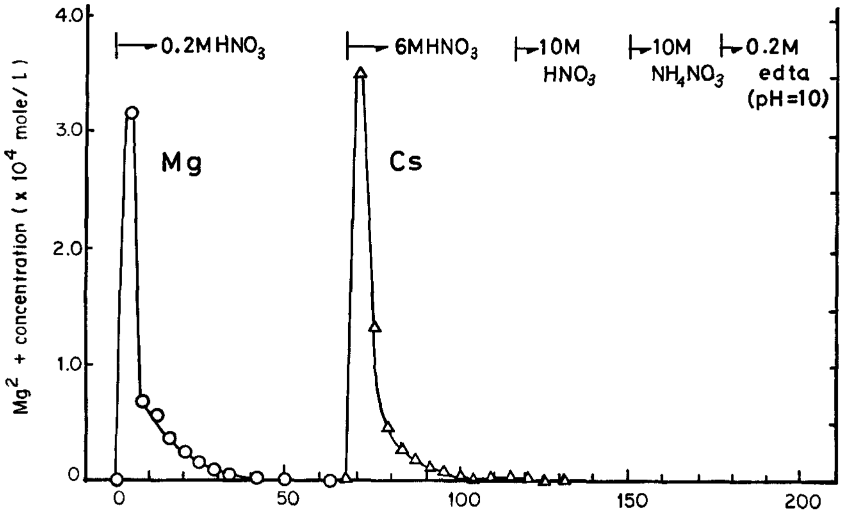

FIG. 6. Separation of Mg^{2+}–Cs^{+}–Ca^{2+}, Sr^{2+} with the C-SbA column heated at 40°C. Column: 0.8 × 0.5 cm i.d.; flow rate, 0.1 ml/min. Metal ions adsorbed: Mg^{2+}, 2×10^{-3} mmol; Ca^{2+} and Sr^{2+}, 1×10^{-3} mmol; Cs^{+}, 1×10^{-2} mmol.

generation by a concentrated nitric acid, 10 *M* ammonium nitrate, and 0.2 *M* ethylendiaminetetraacetic acid (edta) adjusted to pH 10 (Fig. 6). These procedures may be useful for the separation of the radioactive nuclides of cesium, barium, and strontium from fission product.

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