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Synthetic Inorganic Ion-Exchange Materials. XVI. Chromatographic Separation of Microamounts of Sodium and Potassium from a Large Quantity of Lithium Chloride by Using Crystalline Antimonic(V) Acid as a Cation Exchanger

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Abstract

Crystalline antimonic acid (C-SbA) as a cation exchanger shows a low distribution coefficient value (0.33) for lithium ions and a relatively high value ($>4.8\times10^2$) for sodium and potassium ions in 0.1*M* nitric acid solution, and has a reasonable rate of adsorption and desorption for these metal ions. A new method is presented for removing microamounts of sodium and potassium from a large quantity of lithium chloride by using a frontal chromatographic technique. A favorable separation is obtained by passage of the lithium chloride solution containing microamounts of sodium and potassium, dissolved in 0.1 *M* hydrochloric acid solution, on a C-SbA column of 6.0×0.8 cm i.d. The retention is quantitative with a maximum capacity of 1.81 meq/g for sodium ions and 1.15 meq/g for potassium ions in a 0.1 *M* nitric acid solution. The adsorbed sodium and potassium ions are readily eluted with a 5 *M* ammonium nitrate solution containing 1 *M* nitric acid as the eluant, and then the C-SbA column is easily regenerated by using a 1 *M* nitric acid solution. The method is applied for the removal of microamounts of sodium and potassium from commercial reagents of lithium chloride.

INTRODUCTION

The separation of alkali metals by cation exchange resins has been studied extensively for analytical purposes by several authors (*1–6*). The chromatographic separation of lithium from sodium on sulfonated cation exchange resins is not favorable because the separation factor is only about 1.5 to 2.0 in aqueous inorganic acid solutions, such as HCl, HNO_3, H_2SO_4, and $HClO_4$, used as the eluting agents. A fairly large column is required to separate millimole amounts of these metals quantitatively.

Okuno et al. (*7*) have improved the separation factor to about 3 for the lithium–sodium pair by using a 0.2 *M* HCl solution containing 30 to 50% methanol. The method has been applied for the determination of lithium in water (*8*, *9*) and rock sample (*10*). Increased separation factors are also obtained by using the eluting agents of aqueous inorganic acid solutions containing different organic solvents such as ethanol (*11*) and acetone (*12*). Šulcek et al. obtained a separation factor of 5 for the lithium–sodium pair in a 0.5 *M* HCl solution containing 80% methanol (*13*, *14*).

A much higher separation factor for alkali metals can be obtained by using inorganic ion-exchange materials, for example, the zirconium acid salt of phosphate (*15*), tungstate (*16*), molybdate (*17*), or antimonate (*18*, *19*).

Commercial lithium chloride usually contains small amounts of other alkali metals and alkaline earth metals. Highly purified lithium chloride, especially free from sodium, is required for analytical purposes in mass spectroscopy (*20*) and isotope separation (*21*). The selective separation of small amounts of sodium or potassium from lithium chroride solution at higher concentrations is more difficult than the separation of a small amount of lithium from a large quantity of sodium.

Crystalline thorium arsenate has selective adsorption properties for lithium ions; Na^+, K^+, Rb^+, and Cs^+ are not absorbed at all (*22*). However, this material has less advantage for the separation of sodium ions from a large quantity of lithium ions because of its limited retention capacity for lithium ions. The adsorption properties on the hydrous oxides of polyvalent metals have been studied extensively for their use as ion exchangers (*16*, *23*, *24*). Among them the hydrous antimony pentaoxide (so-called antimonic acid) exhibits relatively a high adsorption capacity with a reasonable rate of adsorption and desorption for alkali metal ions when used in the usual column operation (*25–27*). Among three different antimonic acids, C-SbA showed unusual selectivity for alkali metals as compared with the strong acid-type cation exchange resins and other inorganic ion-exchange materials (*26*, *28*). From the results of batch equilibrium at micro-uptake of alkali metals, the following series were found for C-SbA selectivity: Li ≪ K < Rb ≪ Na in nitric acid solution and Li < K < Rb < Cs < Na in ammonium nitrate solution (*28–31*). Sodium ions are more strongly adsorbed on C-SbA than any other alkali metal ions. The adsorbed sodium ions cannot be eluted even by a 10 *M* nitric acid solution, but they are easily eluted by a 2 *M* ammonium nitrate solution. Extremely higher selectivity for lithium–sodium and –potassium pairs was observed on the C-SbA (*32*).

This paper describes a procedure for separating microamounts of sodium and potassium from a large quantity of lithium ions using the frontal chromatographic technique. The method were also carried out on Amberlite IR–120 for comparison.

EXPERIMENTAL

Reagents

Antimony pentachloride (Yotsuhata Chemical Co. Ltd., Japan) was used without further purification. ^{24}Na and ^{42}K (both from Japan Atomic Laboratory) were used as test compounds. The other reagents used were all of analytical grade.

Preparation of Ion-Exchange Materials

The C-SbA was prepared as described previously (*30*); the aqueous solution of antimony pentachloride (75 ml $SbCl_5$ + 75 ml H_2O) was hydrolized in 5 liters of demineralized water at 25 °C. The precipitate was kept in the mother liquor at 30 °C for over 20 days, and then washed with cold demineralized water with the aid of a centrifuge (about 10,000 rpm) until free from 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.

Amberlite IR–120 (Rohm & Hass Co., C.G. 100–200 mesh size) was conditioned by alternate treatment in the usual manner with 1 *M* HCl and 1 *M* NaOH solution before use (*33*).

Distribution Coefficients of Alkali Metal Ions

The distribution coefficients (K_d) were determined by shaking 0.250 g of exchanger with 25.0 ml of 0.1 M HNO_3 solution containing 1×10^{-3} mole/l of an alkali metal ion. Equilibria were attained within 24 hr. The K_d values were calculated from

$$K_d = \frac{\text{amount of the metal ions in exchanger}}{\text{amount of the metal ions in solution}} \times \frac{\text{ml of solution}}{\text{g of exchanger}} \tag{1}$$

The C-SbA had too low to a value determine K_d for lithium ions by using the above experimental conditions in batch equilibration, thus the column technique was used.

From plate theory the following correlation may be obtained between the K_d value and the peak elution volume $\bar{v}$, i.e., the volume of eluant required to elute the maximum of the elution band (*34*).

$$\bar{v}/X' = i + mK_d \tag{2}$$

where i and m are the interstitial volume and the weight of exchanger in unit volume of the column, respectively, and X', X, and X_0 represent the corrected bed volume, the total bed volume, and the volume of original load band, respectively. Thus

$$X' = X - X_0/2 \tag{3}$$

The term $X_0/2$ in Eq. (3) is fairly small and can be neglected in the case of the micro or trace amounts of solute. Thus Eq. (2) becomes

$$\bar{V} = I + MK_d \tag{4}$$

where $\bar{V}$, I, and M are the peak elution volume, the total interstitial volume, and the weight of exchanger in the column, respectively. The K_d value for lithium ions on C-SbA can be determined from Eq. (4) by finding the maximum peak of the elution band.

Column Experiments

The ion-exchange columns used were 6.0 × 0.8 cm i.d. and had a flow rate of 0.6 ± 0.1 ml/min for both the C-SbA and Amberlite IR–120, except for the determination of the breakthrough capacities of C-SbA (5.5 × 0.41 cm i.d.).

Preparation of the Lithium Chloride Solution for the Removal of Sodium and Potassium

Solution A was prepared by dissolving a commercial grade of lithium chloride from Company W. Solution B was prepared by dissolving lithium chloride together with labeled ^{24}Na (2 mCi) and a small amount of sodium chloride as a carrier. Solution C was prepared by substituting ^{42}K for the ^{24}Na in Solution B. The acidity of the solutions were adjusted with 0.1 *M* HCl. The concentrations of sodium and potassium in the solutions were determined by using the standard addition method with atomic absorption spectrometry after decay of ^{24}Na and ^{42}K. Table 1 summarizes the concentrations of alkali metals in Solutions A, B, and C.

TABLE 1

Concentrations of Alkali Metals in the Solutions for Separating Sodium and Potassium

Solution	Concentration of the elements (mole/l) Li$^+$	Na$^+$	K$^+$	HCl (*M*)
A	0.52	0.7×10^{-3}	2.0×10^{-4}	0.1
B (with ^{24}Na)	0.50	1.5×10^{-3}	1.25×10^{-2}	0.1
C (with ^{42}K)	0.50	0.8×10^{-3}	2.9×10^{-2}	0.1

RESULTS AND DISCUSSION

Chemical and Physical Properties of C-SbA

The results of TGA, DTA, and x-ray studies showed good agreement with our earlier reports (*28, 29*). The empirical formula of the C-SbA may be written as $Sb_2O_5 \cdot 4H_2O$, with the composition approaching $Sb_2O_5 \cdot 4.07 \pm 0.02H_2O$ after drying in air for a few months at 25 to 30°C. The water content was determined on the basis of the formation of Sb_6O_{13} from C-SbA heated at 700°C for 5 hr (*29*). Baetsle et al. reported that the chemical composition of crystalline polyantimonic acid (PAA) corresponds to the empirical formula $Sb_2O_5 \cdot 4H_2O$ for a sample dried at up to 50°C under vacuum for long time (*35*).

Air-dried C-SbA is very stable against most reagents, e.g., concentrated HNO_3 and HCl or 2 *M* NaOH solution. Caletka et al. showed that PAA heated at 270°C was completely dissolved in concentrated HCl at elevated temperatures (*36*). C-SbA heated to 300°C has less stability against concentrated HCl.

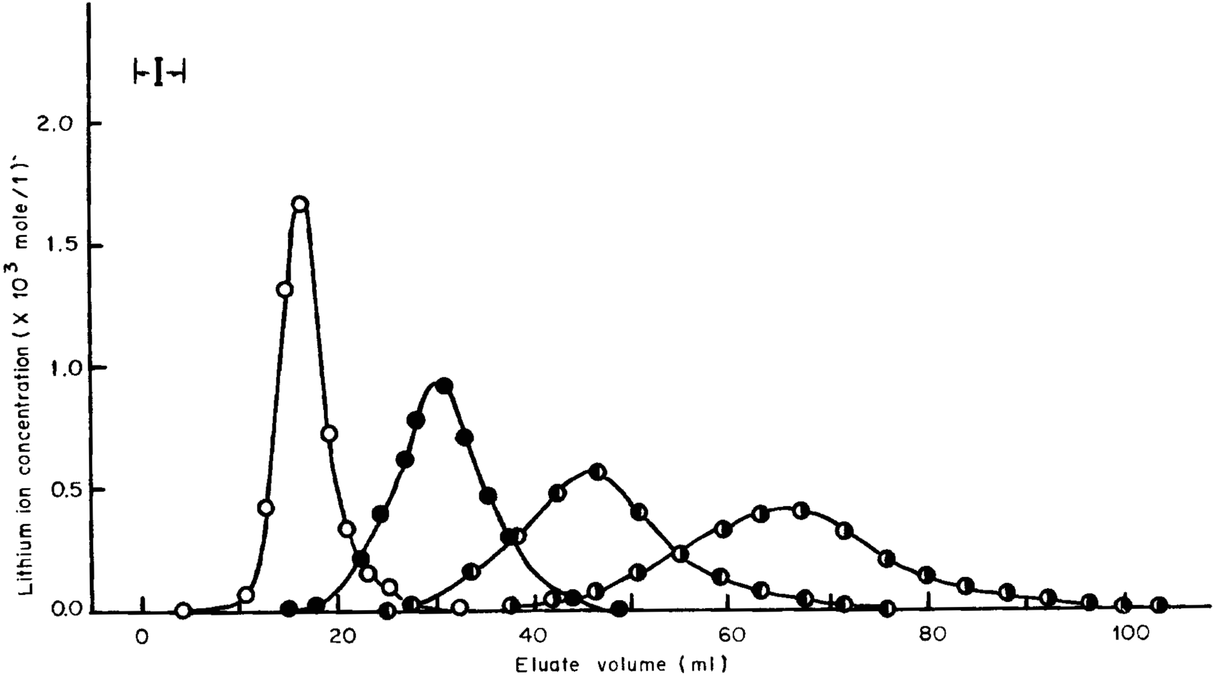

FIG. 1. Elution curves of lithium ions on C-SbA at various concentrations of nitric acid solution. Column, 6.0 × 0.8 cm i.d.; flow rate, 0.6 ml/min; lithium ion loading, 0.01 mmole each; I, interstitial volume of the column. Concentration of nitric acid solutions: (○), 0.01 *M*, (●) 0.005 *M*, (◐) 0.003 *M*, and (◑) 0.002 *M*.

Elution Curves of Lithium Ions with Solutions of HCl and HNO_3

The individual curves of Li^+ eluted with different concentrations of HCl and HNO_3 showed bell-sharp peaks without a tailing effect (Figs. 1 and 2). The calculated log K_d values from Eq. (4) vs log $[H^+]$ are shown in Fig. 3. The slopes of $d \log K_d / d \log [H^+]$ were found to be -1.01 for HNO_3 and 1.03 for HCl, respectively, as expected for an "ideal 1:1" ion-exchange reaction. The K_d value of Li^+ in 0.1 M HNO_3 solution was determined by extrapolating the log-log plot of K_d vs $[H^+]$ to 0.1 M HNO_3.

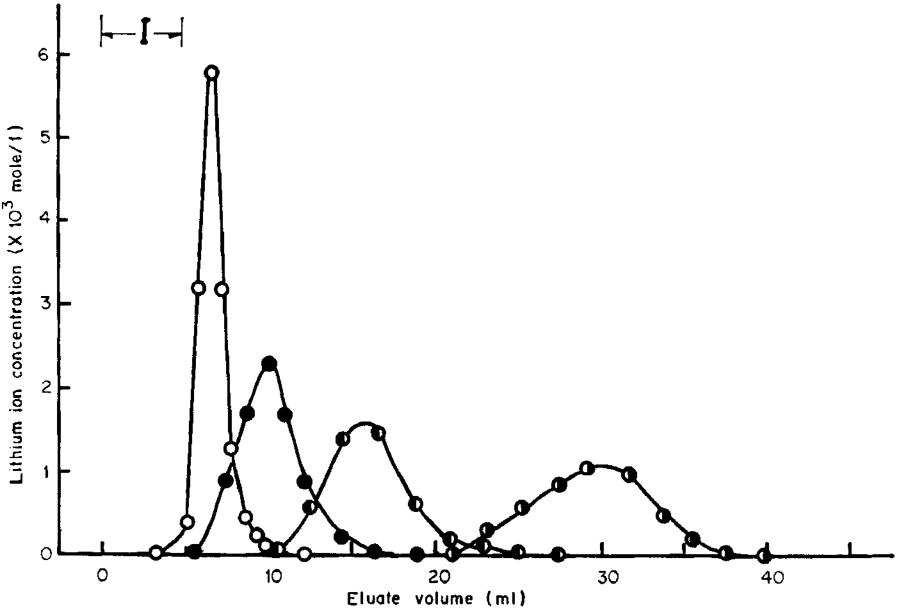

FIG. 2. Elution curves of lithium ions on C-SbA at various concentrations of hydrochloric acid solution. Column, 0.6 × 0.8 cm i.d.; flow rate, 0.6 ml/min; lithium ion loading, 0.01 mmole each; I, interstitial volume of the column. Concentration of hydrochloric acid solutions: (○) 0.05 M, (●) 0.02 M, (◐) 0.01 M, and (◑) 0.005 M.

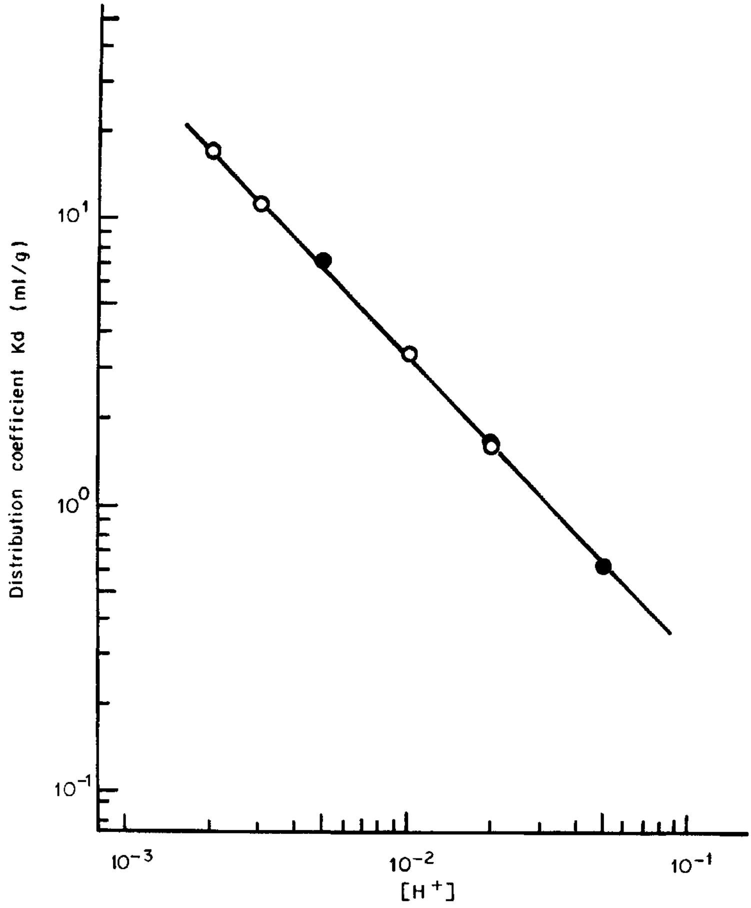

FIG. 3. Calculated distribution coefficients of lithium ions from Eq. (4) on C-SbA at different concentrations of [H^+]: (●) HCl, and (○) HNO_3.

Distribution Coefficients (K_d) of Li^+, Na^+, and K^+ on C-SbA and Amberlite IR-120

The values of K_d and the separation factor, $\alpha(A/B) = K_{d_A}/K_{d_B}$, where A and B are alkali metal, are summarized in Table 2.

The increased separation factors on Amberlite IR-120 obtained by the addition of ethanol are in good agreement with the results of several authors (*7*, *10*). The affinity series on C-SbA, $Li^+ \ll K^+ \ll Na^+$, agrees

TABLE 2

K_d Values and Separation Factors for Alkali Metals on C-SbA and Amberlite IR-120

Ion exchanger	Solution	Parameter[a]	Li	K	Na
C-SbA	0.1 M HNO_3	K_d	0.33	4.8×10^2	8.5×10^4
		α		1.45×10^3	1.77×10^2
			Li	Na	K
Amberlite IR-120	0.1 M HNO_3	K_d	29.2	51.3	123
		α		1.75	2.4
Amberlite IR-120	0.1 M HNO_3 (25% ethanol)	K_d	34	79	213
		α		2.3	2.7

[a] α is the separation factor for neighboring ions.

well with our previous report (*28*). The K_d value of lithium ions in this result was slightly lower than that obtained in the earlier work (*32*), and the difference may be due to the smaller accuracy of batch equilibration. The separation factors for neighboring pairs are seen to be more than a hundred times higher for C-SbA than for Amberlite IR-120. This allows for much more efficient separation of the alkali metals on the C-SbA column than for synthetic organic ion-exchange resins, as has already been described (*32*). Such extremely high selectivities on C-SbA can be applied toward the separation of trace or microamounts of sodium and potassium from a large quantity of lithium because of the low uptake of lithium ions in the acid solution at relatively lower concentrations.

Removal of Sodium and Potassium from a Large Quantity of Lithium on C-SbA by Frontal Chromatography

Among chromatographic separations, the simplest procedure is frontal chromatography which consists of a continuous injection of the solution containing the components that are to be separated at the top of the column. Processes of this type can be applied for the removal of relatively small amounts of undesirable components when these are more strongly adsorbed than the bulk of the material. The acid concentration of the influent was adjusted to 0.1 M for the smaller uptake of lithium ions on C-SbA.

Solution A was charged continuously at the top of the column in hydrogen ion form. On the Amberlite IR-120, a quantitative uptake of lithium ions as well as of sodium and then potassium ions was observed

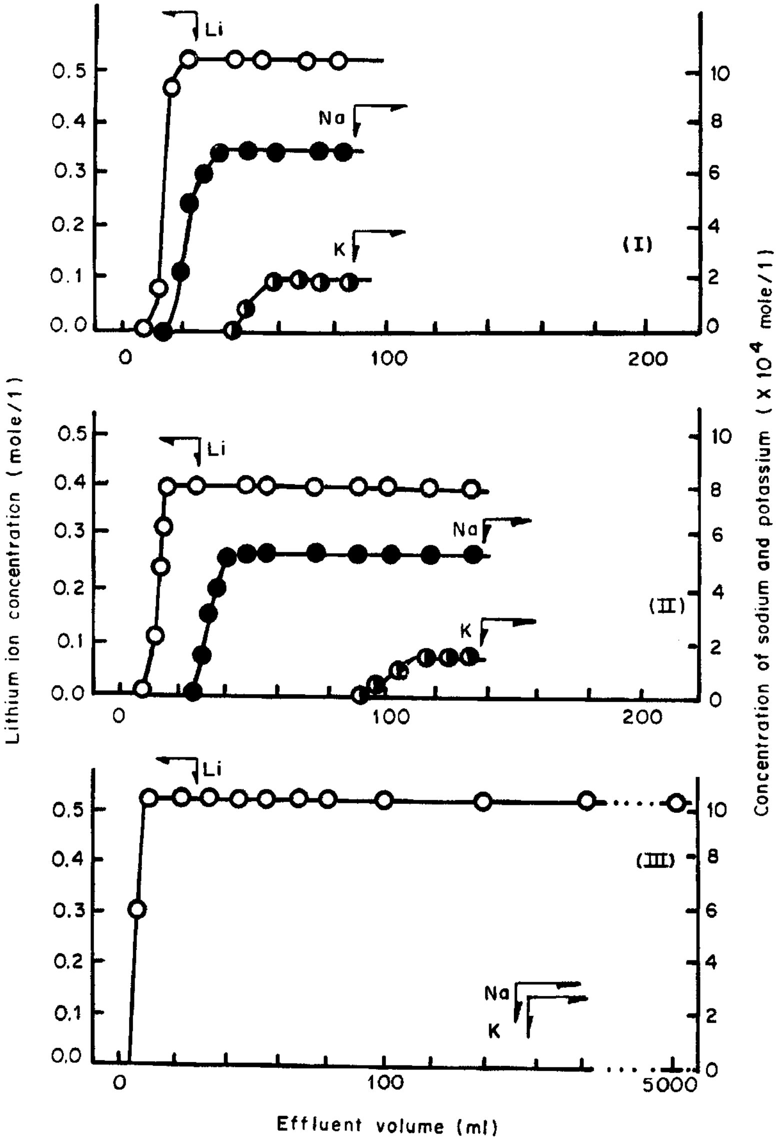

FIG. 4. Chromatographic removal of sodium and potassium from the lithium chloride Solution A with Amberlite IR-120 [(I) and (II)] or C-SbA (III). Column, 6.0 × 0.8 cm i.d.; flow rate, 0.6 ml/min. Influent: (I) and (III), 0.525 *M* LiCl + 0.1 *M* HCl; (II) mixed solution of (0.525 *M* LiCl + 0.1 *M* HCl: 0.75) and (ethanol: 0.25).

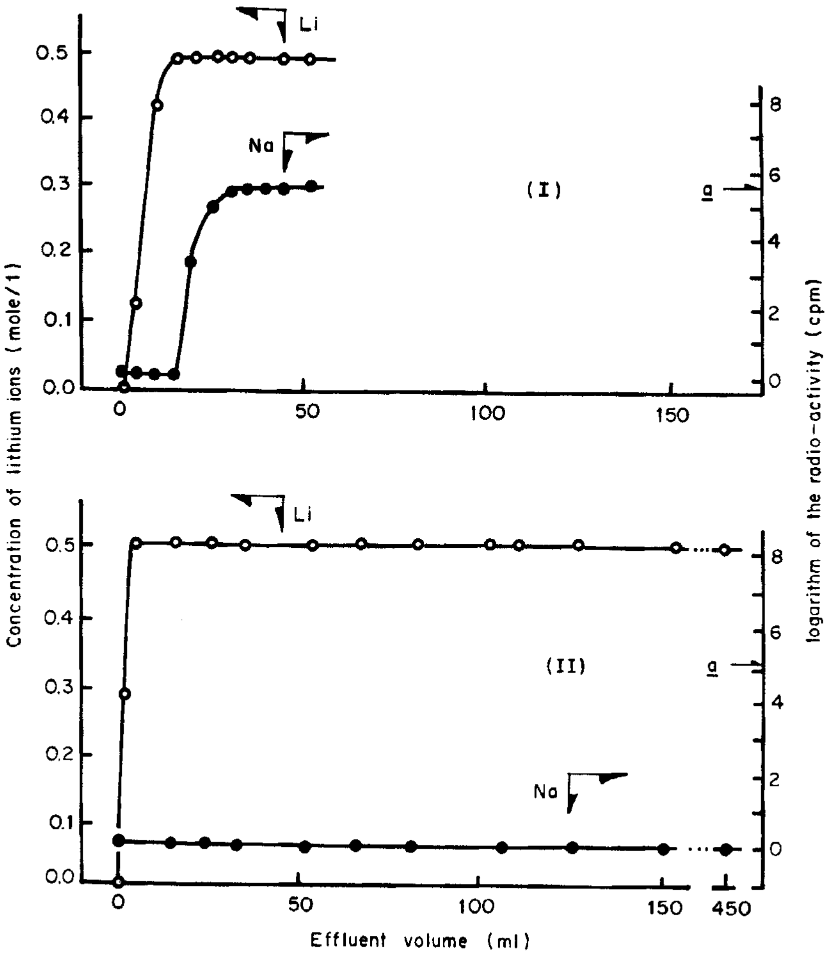

FIG. 5. Chromatographic removal of sodium ions from the lithium chloride Solution B containing ^{24}Na tracer with Amberlite IR-120 (I) or C-SbA (II) column. Column, 6.0 × 0.8 cm i.d.; flow rate, 0.6 ml/min. *a*: initial radioactivity at beginning on injection of the influent.

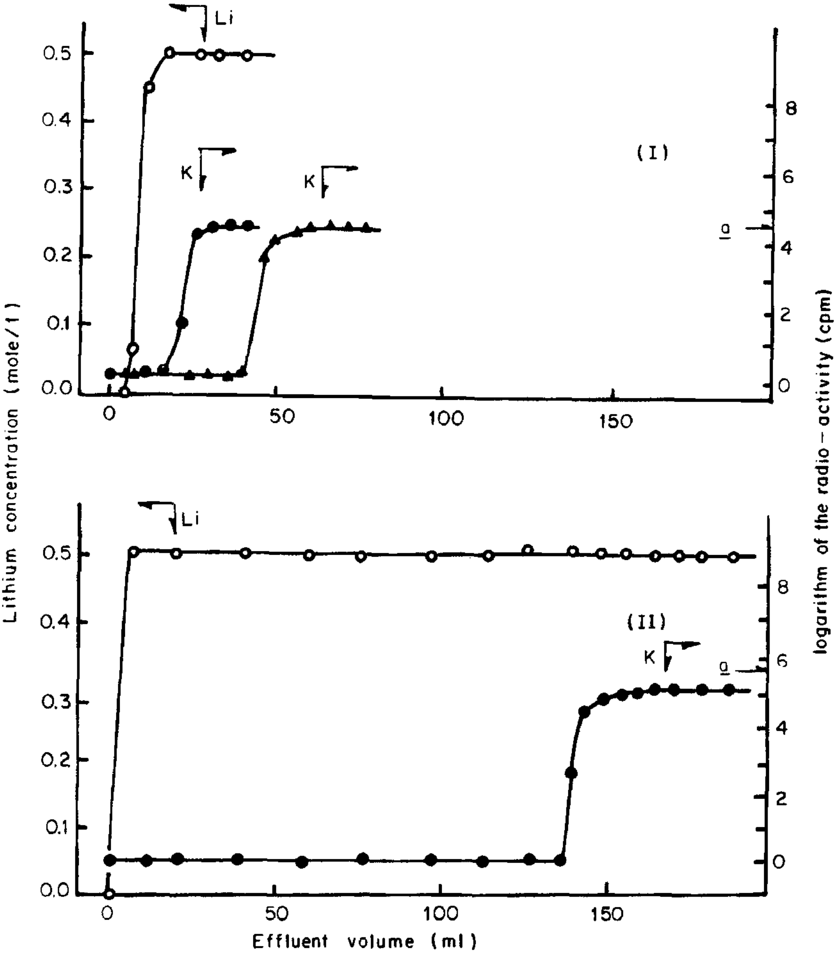

FIG. 6. Chromatographic removal of potassium ions from the lithium chloride Solution C containing ^{42}K tracer with Amberlite IR-120 (I) or C-SbA (II) column. Column, 6.0 × 0.8 cm i.d.; flow rate, 0.6 ml/min. Influent, (●) Solution C, (▲); solution containing 25% ethanol. *a*: initial radioactivity at beginning on injection of influent.

at the beginning. After a certain time the breakthrough points were attained for lithium, sodium, and potassium ions; Fig. 4(I). A few milliliters of a fraction free from sodium and potassium ions were achieved by the column of Amberlite IR–120. Improved separation was observed by the addition of 25% ethanol; Fig. 4(II). On C-SbA, no detectable uptake of lithium was observed, and the elution curve of lithium ions in the sharp front was quite similar to that obtained for the determination of interstitial volume of this column by using 0.1 *M* HCl solution; Fig. 4(III).

Much favorable separation was performed on C-SbA, and no detectable amount of sodium and potassium ions was observed with up to 5 liters of effluents. From a purely practical point of view, the tracer test was applied with the aim of determining the completeness of removal of sodium and potassium from a large quantity of lithium with almost the same conditions.

After passing through Solutions B and C, the radioactivities of the effluents were determined (Figs. 5 and 6). Maximum decontamination factors higher than 10^5 were achieved for both ^{24}Na and ^{42}K on C-SbA and Amberlite IR-120. Girardi et al. showed a decontamination factor of 10^{10} for the removal of sodium on a column (3 × 0.7 cm i.d.) of hydrated antimony pentoxide (HAP) (*37*), and Caletka et al. reported that a maximum decontamination factor of more than 10^3 was attained on a column (0.5 cm i.d.) filled with 1 g of PAA supported on silica gel (*36*). The more accurate decontamination factor in this column operation is limited for the high natural background and the relatively low radiochemical purity of nuclide. The apparent amounts of sodium could not be observed in the effluent up to 450 ml by passing Solution B with ^{24}Na tracer; Fig. 5(II). The breakthrough curve on C-SbA was observed as a result of saturation of the potassium ions by passing Solution C; Fig. 6(II). The breakthrough capacity showed 1.15 meq/g, which is equal within experimental error to that obtained from the passage of a 3×10^{-2} mole/l KCl solution containing 0.1 *M* HNO_3 (without lithium chloride). This result shows that the low uptake of lithium does not affect the value of the breakthrough capacity of C-SbA for the above experimental condition.

Breakthrough Capacities for Sodium Ions

In general, the breakthrough capacities on inorganic ion-exchangers are lower than those on organic ion-exchange resins, and moreover they vary extensively with the experimental conditions; e.g., pH, the ion investigated, the co-ion present, and the flow rate. In order to estimate the maximum uptake of sodium ions, the breakthrough curve was determined by a 0.03 *M* NaCl solution containing 0.1 *M* HCl. The curve for a neutral solution of NaCl was determined for comparison. The elution curve for the 0.03 *M* NaCl solution shows that hydrogen ions are liberated quantitatively for the uptake of sodium ions by the ion-exchange reaction (Fig. 7). The breakthrough curve for the 0.03 *M* NaCl solution containing 0.1 *M* HCl is steeper than that for the neutral solution (Fig. 8). pH titration studies of antimonic acid indicate that this material is a weak acid exchanger which contains a number of functional groups with different overlapping pK_a values (*38*). The uptake of sodium ions on C-SbA increases with increasing pH values of the external solution of the column by continuously passing the neutral solution of sodium chloride. The breakthrough capacity of C-SbA for 0.03 *M* NaCl is 2.64 meq/g $Sb_2O_5 \cdot 4H_2O$ and 3.2 meq/g Sb_2O_5, which is much higher than that reported by Caletka et al. for PAA fixed on silica gel from 0.1 *M* NaCl (2.24 meq/g Sb_2O_5) (*36*). The breakthrough capacity of C-SbA for sodium in 0.1 *M* HCl is 1.81 meq/g $Sb_2O_5 \cdot 4H_2O$ and 2.20 meq/g Sb_2O_5. Girardi et al. reported that the retention capacity for Na^+ in 0.1 *M* HNO_3 was a somewhat higher value of 2.88 meq/g Sb_2O_5 (recalculation based on HAP containing 90.7% Sb_2O_5) (*39*).

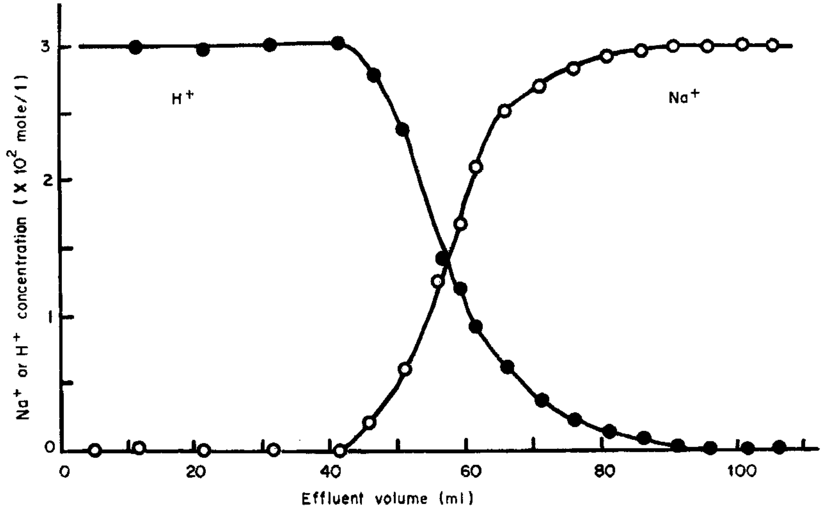

FIG. 7. Breakthrough curve for 0.03 *M* NaCl on C-SbA column. Column, 5.5 × 0.41 cm i.d. (0.662 g C-SbA); flow rate, 0.6 ml/min. (●) H^+, and (○) Na^+.

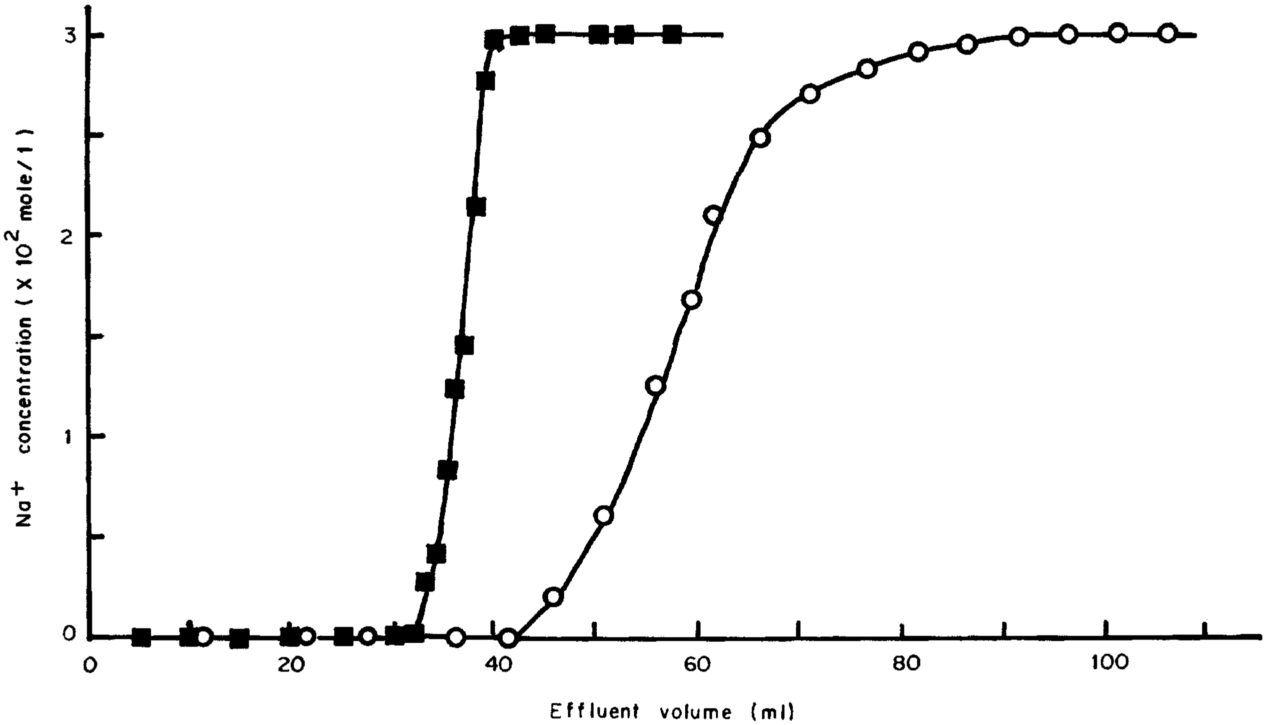

FIG. 8. Breakthrough curves for 0.03 *M* NaCl and 0.03 *M* NaCl + 0.1 *M* HCl on C-SbA column. Column, 5.5 × 0.41 cm i.d.; flow rate, 0.6 ml/min. (○) 0.03 *M* NaCl, and (■) 0.03 *M* NaCl + 0.1 *M* HCl.

The volume of the fraction and the weight of lithium chloride free from Na^+ and K^+ by frontal chromatographic separation by passing Solutions A, B, and C are summarized in Table 3.

As may be seen in Table 3 (Runs 1, 4, and 6), the effective separation of sodium and potassium ions performed on C-SbA is several hundred times larger than those on Amberlite IR-120 based on the volume of Solution A to be separated. The removal on C-SbA is much more favorable in the case of the lithium chloride solution containing much smaller amounts than the microamounts of sodium and potassium ions (see Runs 1 and 2).

A semiquantitative determination by emission spectrometry before and after passing through the desired columns, indicates that Solution A contains microquantities (10^{-4} mole/l) of the alkaline earth metals, such as magnesium and calcium, and that C-SbA shows satisfactory removal of calcium ions, but not of magnesium ions, while Amberlite IR-120 shows good separation behavior for these metal ions under similar experimental conditions.

The C-SbA column saturated by sodium ions was washed with a few milliliters of demineralized water, and the adsorbed sodium ions were eluted by using different eluants (Fig. 9). A complete elution of sodium ions was attained with 99 to 100% recovery in a relatively short time with a 5 *M* NH_4NO_3 solution containing 1 *M* HNO_3 as the eluant. The use of 1 *M* HNO_3 or 5 *M* NH_4NO_3 as an eluant led to an elution curve with

TABLE 3

Volume of the Fraction and the Weight of Lithium Chloride Free from Na^+ and K^+ by Different Ion Exchangers

Ion exchanger[c]	Run no.[a]	Free from	LiCl Fraction volume (l)	LiCl Weight (g)
C-SbA	1	Na, K	9.0[b]	200[b]
	2	^{24}Na	4.2[b]	89[b]
	3	^{42}K	0.138	2.9
Amberlite IR-120	4	Na, K	0.0056	0.12
	5	^{24}Na	0.010	0.22
Amberlite IR-120 (25% ethanol)	6	Na, K	0.0135	0.22
	7	^{24}Na	0.005	0.11
	8	^{42}K	0.030	0.64

[a] 1 and 4, Solution A; 2, Solution B; 3 and 5, Solution C; 6, Solution A (75%) + ethanol (25%); 7, Solution B in 25% ethanol; and 8, Solution C in 25% ethanol.

[b] Estimated value on the basis of the breakthrough capacity in 0.1 *M* HCl.

[c] Ion exchange column: 6.0 × 0.8 cm i.d.

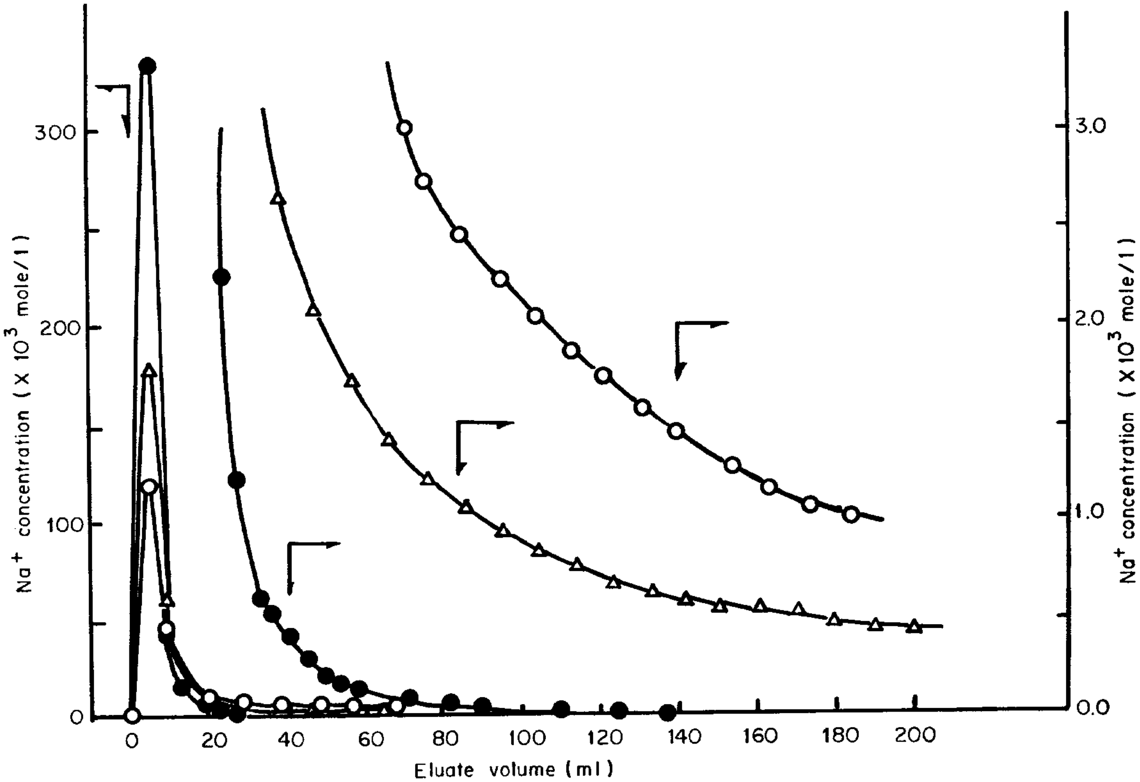

FIG. 9. Elution curves of sodium from C-SbA with various eluants. Column, 5.5 × 0.41 cm i.d.; flow rate, 0.6 ml/min. Eluents: (○) 5 *M* NH_4NO_3, (△) 1 *M* HNO_3, and (●) 5 *M* NH_4NO_3 + 1 *M* HNO_3.

sharp front and a tailing rear, so that desorption of sodium could be performed only with about 89 and 68% recovery by passing through 180 ml of 1 *M* HNO_3 and 5 *M* NH_4NO_3, respectively. Elution curves of the latter type are caused by the presence of only a limited number of sites available for adsorption, and are functions of the concentration of sodium ions and the eluants.

After the complete elution of sodium ions with a 5 *M* NH_4NO_3 solution containing 1 *M* HNO_3, the C-SbA column contains ammonium ions equal to about one-fifth of the breakthrough capacity for a 0.03 *M* sodium chloride solution. The adsorbed ammonium ions are readily eluted with 1 *M* HNO_3 as an eluant, and the C-SbA column can therefore be used repeatedly under the usual conditions of column operation.

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