Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

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To cite this Article Abe, Mitsuo and Kasai, Kazuo(1979) 'Synthetic Inorganic Ion-Exchange Materials. XXII. Distribution Coefficients and Possible Separation of Transition Metals on Crystalline Antimonic(V) Acid as a Cation-Exchanger', Separation Science and Technology, 14: 10, 895 — 907
To link to this Article: DOI: 10.1080/01496397908058100
URL: http://dx.doi.org/10.1080/01496397908058100

SEPARATION SCIENCE AND TECHNOLOGY, 14(10), pp. 895–907, 1979

Synthetic Inorganic Ion-Exchange Materials. XXII. Distribution Coefficients and Possible Separation of Transition Metals on Crystalline Antimonic(V) Acid as a Cation-Exchanger

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Abstract

Cation-exchange distribution coefficients with crystalline antimonic(V) acid (C-SbA) are presented for the transition metals in nitric acid solution at different concentrations. The affinity series ($Ni^{2+} < Mn^{2+} < Zn^{2+} < Co^{2+} < Cu^{2+} \ll Cd^{2+}$) was found for microquantities of the transition metals. On the basis of the distribution coefficients, the effective separation of Ni^{2+} or Cd^{2+} from Zn^{2+} and Cu^{2+} has been achieved with a small column (2.0 × 0.4 cm i.d.) of the C-SbA.

The analytical application of inorganic ion-exchangers has received considerable attention owing to their high selectivities with respect to certain elements (*1*, *2*). Among them, crystalline antimonic(V) acid (C-SbA) exhibits a relatively high ion-exchange capacity with a reasonable rate of adsorption and desorption for alkali metals when used in the usual column operations (*3–5*). C-SbA shows unusual selectivity for alkali metals and alkaline earth metals compared with the strong acid-type cation-exchange resins and other inorganic ion-exchange materials. The order of selectivity is $Li < K < Cs < Rb < Na$ for microquantities of alkali metals and $Mg < Ba < Ca < Sr$ for those of alkaline earth metals in nitric acid media (*3*, *6*). The selectivity sequence for C-SbA depends on the loading of the exchanging metal ions as well as on the sorption media (*7*, *8*). A mutual separation of alkali metals can be achieved by using a relatively small column (6.0 × 0.8 cm i.d.) of C-SbA (*5*). The effective separations of Mg-Cs-Ba and Mg-Cs-Ca, Sr can also be performed by using a small column of the C-SbA (*6*).

A great deal has been published on the separation of transition metals during the last two decades. The separation factors between a transition metal and adjacent metal are very small in nitric acid media (*9*). Most prominent are those using cation-exchange resins (10–13) and anion-exchange resins (*14*–*16*) in halide solution as the complexing agents. The addition of water-miscible organic solvents (methanol, ethanol, acetone, etc.) promotes metal-halide complex formation for selective elution of transition metals from cation-exchange resins (*17*). The use of bromide or iodide systems for ion-exchange separation of cadmium offers the promise of a large separation factor for some critical elements (*16*). Hydrobromic acid is considerably more stable than hydroiodic acid, while the separation factor between cadmium and zinc is larger than in hydrochloric acid solution. Unfortunately, zinc cannot be separated completely from cadmium because of some tailing effect in a column of AG1-X8 resin when using 0.1 *M* hydrobromic acid as the eluant (*16*). This behavior is not advantageous for the separation of small amounts of cadmium from large amounts of zinc. Improved separation of cadmium from zinc and copper(II) can be performed by an anion-exchange resin by using 0.5 *M* nitric acid containing 0.1 *M* hydrobromic acid as the eluant, but a very small amount of zinc and copper is still observed in the cadmium fractions (*18*).

This paper describes the measurement of the distribution coefficients of transition metals in nitric acid solution and their possible separation on a C-SbA column.

EXPERIMENTAL

Reagents, Solutions, and Apparatus

Antimony pentachloride (Yotsuhata Chemical Co., Japan) was used without further purification. Transition metal solutions were prepared by dissolving the high purity (>99.9%) metals in a limited amount of nitric acid and then evaporating the excess nitric acid.

Hydrochloric acid–water–acetone solutions were prepared so that the amount of acetone was expressed as percent by volume and the hydrochloric acid concentration as molarity. For example, the solution of 1 *M* HCl–0.5 *M* KCl–50% acetone of 1 liter was prepared by dissolving 38.28 g of potassium chloride in the mixed solution of 500 ml of acetone and 400 ml of 2.5 *M* hydrochloric acid solution and then adjusting the corrected volume with demineralized water. The water used was distilled and then passed through a deionizer. The other reagents used were all of analytical grade.

Atomic absorption measurements were carried out for the determination of the concentration of the metals with a Varian-Techtron 1100 instrument.

Preparation of C-SbA

The C-SbA was prepared as described previously (*4*): 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 40°C for over 20 days and then washed with cold demineralized water with the aid of a centrifuge (about 10,000 rpm) until it was 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 and then dried in air.

Distribution Coefficients (K_d)

The coefficients were determined by equilibrating 0.25 g of dry C-SbA in hydrogen ion form with 25.0 ml of a 1×10^{-4} *M* transition metal solution containing nitric acid at different concentrations at 30 ± 0.1°C with intermittent shaking. The concentration of the metal ions in the solid and in the solution phase was deducted from the concentration relative to the initial concentration in the solution. The K_d values of the metal ions were calculated after attainment of equilibrium by using the following expression:

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

Column Preparation

A column containing 0.3 g of the C-SbA was pretreated by passing through about 50 ml of 6 *M* nitric acid solution in order to eliminate trace amounts of zinc and copper in the C-SbA. The column was prepared by using a borosilicate glass tube of 4 mm diameter and filling the column with C-SbA up to the 20-mm level. The heated column consisted of the borosilicate glass tube inside a jacket through which thermostatic water at 50°C was pumped.

Elution Curves

A solution containing 2×10^{-4} mmole of each metal in 2.0 ml was added on the top of the C-SbA column. The column was washed with a small portion of the demineralized water and then eluted with the nitric acid solution at different concentrations. In the case of the separation of cadmium from zinc and copper(II), the column was pretreated with a 3 *M* nitric acid solution, and a solution containing the metals in 3 *M* nitric acid was then added to the column in order to prevent a tailing effect. The metals were eluted with 3 *M* nitric acid solution and then with different eluants.

RESULTS AND DISCUSSION

Adsorption of Transition Metals

The time dependence of adsorption of different metals was measured qualitatively in order to determine the equilibrium distribution coefficients (Fig. 1). The ion-exchange reactions of the transition metals are slower than those of alkali metals and barium ions, about 4 days being required for the attainment of equilibrium in the cases of copper(II), zinc, and manganese(II). The reactions of nickel and cobalt(II) are very slow, about 1 month being required.

Distribution Coefficients

The equilibrium distribution coefficients of transition metals 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 the transition metals studied, as expected for an "ideal" 2:1 ion-exchange reaction. The following affinity series was observed for C-SbA selectivity: $Ni^{2+} < Mn^{2+} < Zn^{2+} < Co^{2+} < Cu^{2+} \ll Cd^{2+}$ in nitric acid media. The K_d values obtained and the separation factors, $\alpha(A/B)$, where A and B are transition metals, are summarized in Table 1, the values obtained on Dowex 50W-X8 being included for comparison.

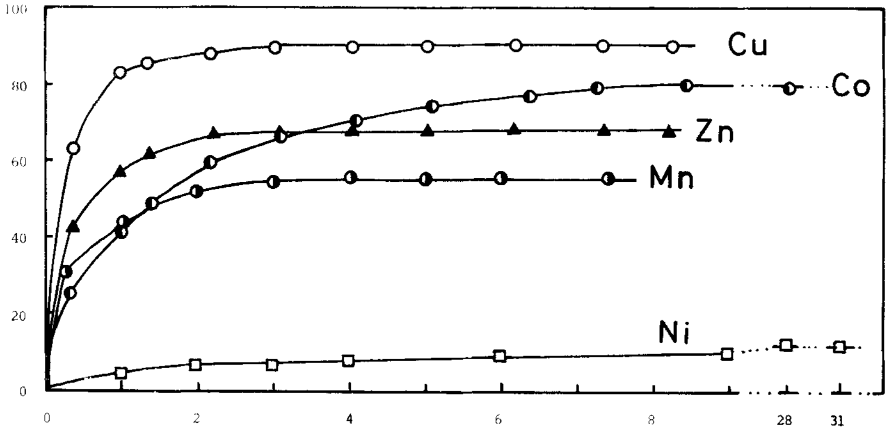

FIG. 1. Time dependence on the adsorption of transition metal ions on C-SbA in 0.2 *M* nitric acid solution. Initial concentration of metal ions, 1 × 10^{-4} *M*; C-SbA, 0.25 g; total volume, 25.0 ml; temperature, 30 ± 0.1 °C. Ordinate: Adsorption (%). Abscissa: Time (days).

The selectivity sequence on the Dowex 50W-X8 is in good agreement with the results reported by Strelow et al. (*19*). The separation factors for neighboring pairs on C-SbA are higher than those obtained on Dowex 50W-X8. The separation factor for the copper(II)–cadmium pair, with a value of 240, seems to be the largest one known so far in nitric acid media.

Ion-Exchange Separation

It is evident from studies of the distribution coefficients on C-SbA that some selective separations are feasible for transition metals. The column technique was employed in order to establish the applicability of the selective separation of transition metals.

Elution Curves of Nickel, Cobalt, Zinc, and Copper(II)

The elution sequence for nickel, zinc, and copper(II) is in good agreement with the equilibrium distribution coefficient, while cobalt can apparently be detected in the first few milliliters of the eluate with 0.05 *M* nitric acid solution (Fig. 3). An individual elution peak with a sharp front and a tailing rear was observed. The quantitative separation of nickel

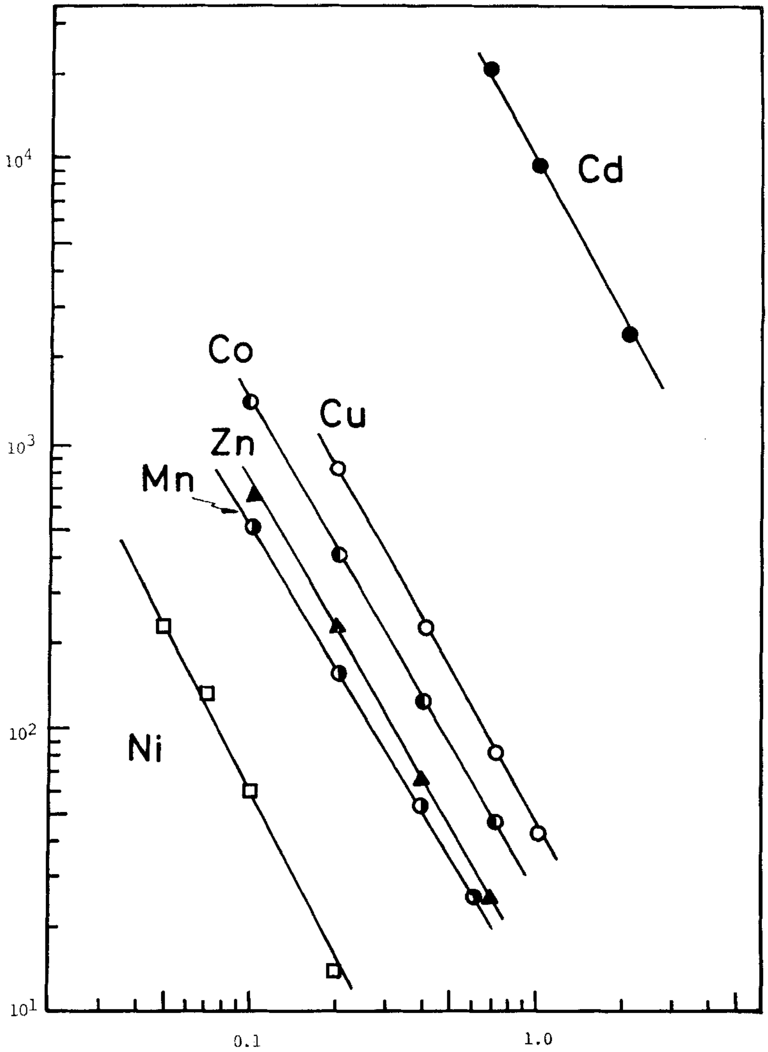

FIG. 2. Distribution coefficients of transition metal ions on C-SbA at different concentrations of nitric acid solution. Initial concentration of metal ion, 1×10^{-4} *M*. Ordinate: K_d (ml/g). Abscissa: Effluent volume (ml).

TABLE 1

Distribution Coefficients (K_d) and Separation Factors (α)[a] for Transition Metals on C-SbA and Dowex 50W-X8 in 0.2 *M* Nitric Acid at 30°C

Ex-changer	Param-eter	Ni^{2+}		Mn^{2+}		Zn^{2+}		Co^{2+}		Cu^{2+}		Cd^{2+}
C-SbA	K_d	17		170		220		400		800		1.9×10^5[b]
	α		10		1.3		1.8		2.0		240	
		Zn^{2+}		Cu^{2+}		Ni^{2+}		Mn^{2+}		Cd^{2+}		Co^{2+}
Dowex 50W-X8	K_d	445		505		547		570		576		605
	α		1.1_3		1.0_9		1.0_4		1.0_1		1.0_5	

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

[b] Extrapolated value up to 0.2 *M* nitric acid on Fig. 2.

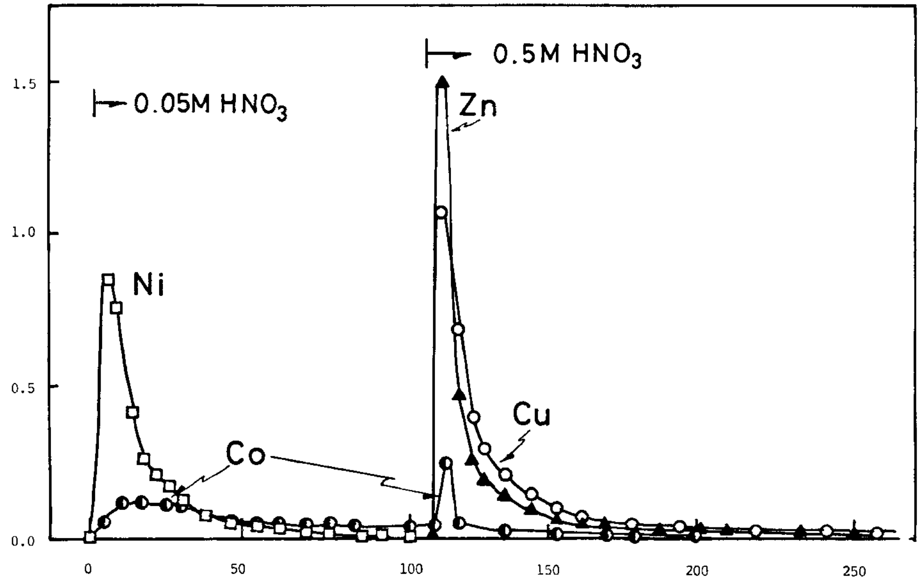

FIG. 3. Elution curves of Ni^{2+}, Co^{2+}, Zn^{2+}, and Cu^{2+} with C-SbA by various nitric acid solutions as the eluants. C-SbA column, 2.0 × 0.4 cm i.d.; flow rate, 0.5 ml/min. Adsorption on the column, 2×10^{-3} mmole of each of the metal ions. Ordinate: Concentration of metal ions ($\times 10^4$ mole/l). Abscissa: Effluent volume (ml).

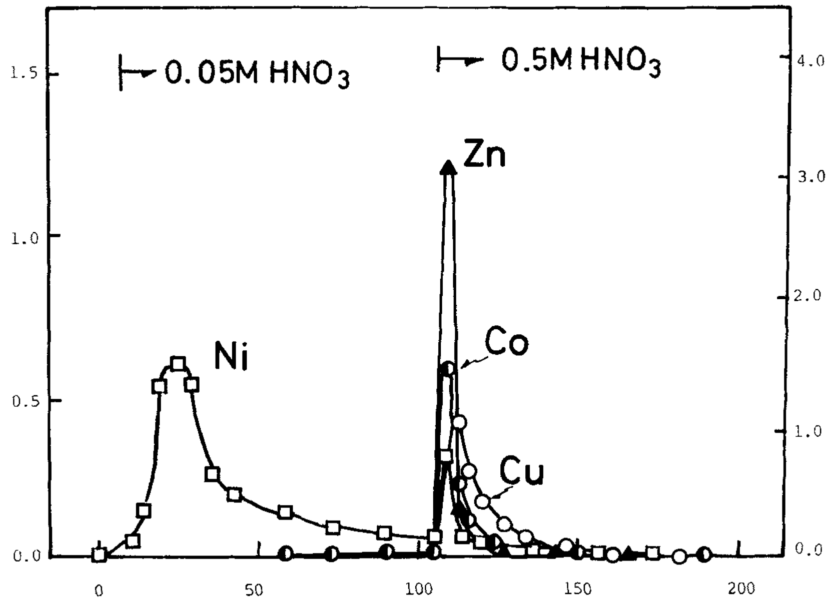

FIG. 4. Elution curves of Ni^{2+}, Co^{2+}, Zn^{2+}, and Cu^{2+} with the C-SbA column heated at 50°C by various nitric acid solutions. Heated C-SbA column, 2.0 × 0.4 cm i.d.; flow rate, 0.5 ml/min. Adsorption on the column, 2×10^{-3} mmole of each of the metal ions. Left-hand ordinate: Concentration of Ni^{2+} ($\times 10^4$ mole/l). Right-hand ordinate: Concentration of Zn^{2+}, Co^{2+}, and Cu^{2+} ($\times 10^4$ mole/l). Abscissa: Effluent volume (ml).

from zinc and copper(II) was performed with 99 % recovery. The adsorbed zinc and copper were eluted by 0.5 *M* nitric acid with about 97 % recovery up to 300 ml of eluate.

The heated column was then employed in order to obtain more rapid elution of zinc and copper (Fig. 4). The elution sequence seems to be in fairly good agreement with that of batch equilibration. Very sharp curves were obtained for the elution of zinc and copper(II), while incomplete separation of nickel was performed with a heavy tailing effect. Cobalt was detected in the first 50 ml of the eluate, and it was eluted with 62 % recovery up to 300 ml of a 0.5 *M* nitric acid solution. This may be due to the slow rate of sorption and desorption for nickel and cobalt on the C-SbA column, as expected from the results of time dependence on the adsorption (Fig. 1).

A satisfactory separation was achieved with 99 % recovery of pure nickel

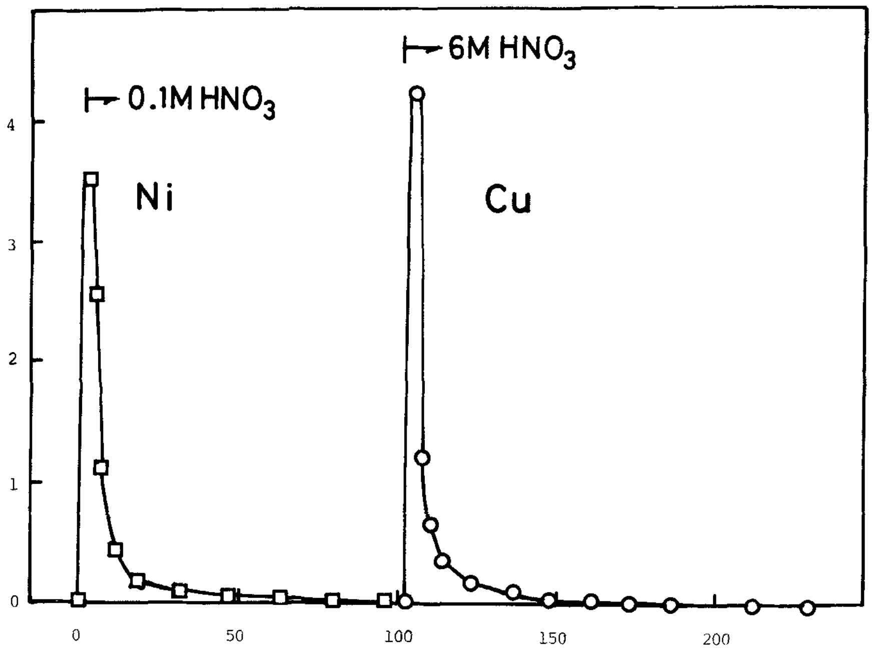

FIG. 5. Separation of Ni^{2+} from Cu^{2+} with C-SbA solutions at room temperature. C-SbA column, 2.0 × 0.4 cm i.d.; flow rate, 0.5 ml/min. Adsorption on the column, 2×10^{-3} mmole of each of the metal ions. Ordinate: Concentration of metal ions ($\times 10^4$ mole/l). Abscissa: Effluent volume (ml).

and copper(II) by using an eluant of 0.1 and 6 *M* nitric acid solution at the usual column operation conditions (Fig. 5). A similar profile of elution curves was observed for the separation of nickel and zinc with the same column operation conditions. The adsorbed cadmium on the C-SbA column was not eluted, even by using a concentrated nitric acid.

The extensive distribution coefficients of transition metals at various concentrations of hydrochloric acid measured by Strelow et al. (*19*), and Fritz and Rettig (*17*) are a useful guide to possible cation-exchange separation in aqueous solution. The K_d values of cadmium decrease with an increasing concentration of hydrochloric acid on organic cation-exchange resins of the strong acid type. It is known that the K_d values of cadmium on organic exchange resins are decreased by the addition of an appreciable amount of a water-miscible organic solvent to hydrochloric acid solution, and that acetone is the most effective of the solvents tested by Pietrzyk (*20*).

The K_d values of cadmium were measured in organic solvent–hydrochloric acid systems in order to choose the elution conditions for cadmium (Table 2). The K_d values decrease markedly with an increase of the concentration of hydrochloric acid and solvent. Acetone is more effective than ethanol for decreasing the distribution coefficient of cad-

TABLE 2

Distribution Coefficients of Cadmium on C-SbA in Organic Solvent–Hydrochloric Mixture at 30°C

HCl (*M*)	Aqueous solution	80% ethanol	50% acetone	0.5 *M* KCl + 50% acetone
1.0	7.7×10^2	318	179	< 1
1.5		20	18	< 1
2.0	310	2.1	< 1	

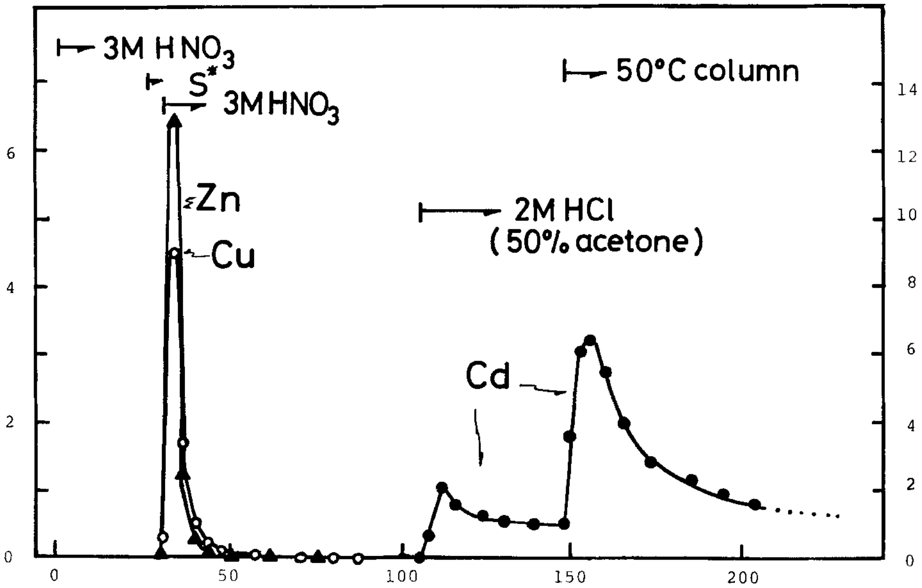

FIG. 6. Separation of Cd^{2+} from Zn^{2+} and Cu^{2+} by various eluants with C-SbA at room temperature and at 50°C. C-SbA column, 2.0 × 0.4 cm i.d.; flow rate, 0.5 ml/min; S*, sample solution (2 ml) containing 2×10^{-3} mmole of each of the metals in 3 *M* nitric acid. Left-hand ordinate: Concentration of Zn^{2+} and Cu^{2+} ($\times 10^4$ mole/l). Right-hand ordinate: Concentration of Cd^{2+} ($\times 10^5$ mole/l). Abscissa: Effluent volume (ml).

mium, as expected from the results of organic exchange resins. An eluant containing 2 *M* hydrochloric acid in 50% acetone solution was chosen for the elution of the cadmium adsorbed on the C-SbA column after the end of the elution for zinc and copper(II) with 3 *M* nitric acid as the eluant. The elution curve obtained for cadmium revealed a heavy tailing effect at room temperature. An improved elution curve was obtained by using a C-SbA column heated at 50°C with the same eluant, but the tailing effect was still observed (Fig. 6). When a solution containing cadmium in 2 *M* hydrochloric acid–50% acetone solution was passed through the C-SbA column after treatment by the above eluant, a negligible amount of adsorption for cadmium was observed. It is evident that the tailing observed on the elution of cadmium is due to the slow rate of adsorption and desorption on the C-SbA column.

It has been reported that the lattice constant of the C-SbA in hydrogen form is decreased from 1.038 to 1.026 nm by the ion-exchange of cadmium,

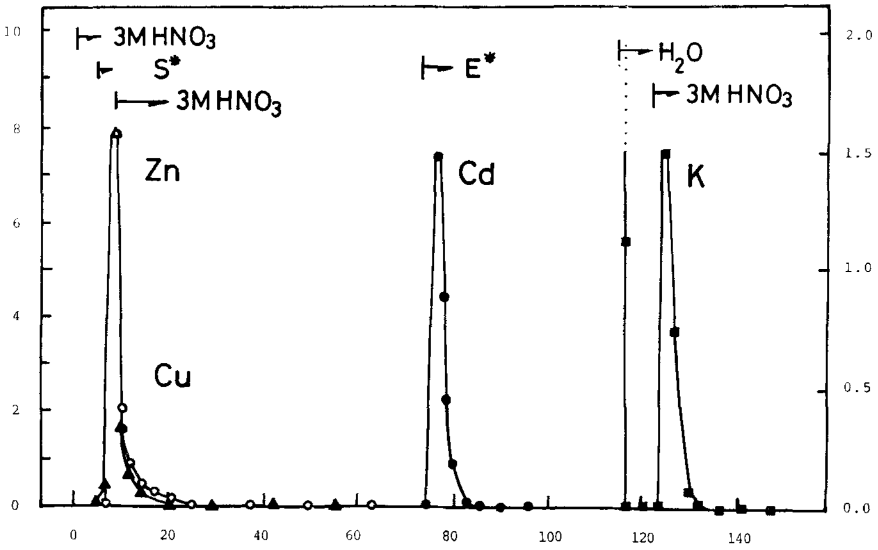

FIG. 7. Separation of Cd^{2+} from Zn^{2+} and Cu^{2+} with the C-SbA column heated at 50°C. S*, sample solution (2.0 ml) containing 2×10^{-3} mmole of each of the metals in 3 *M* nitric acid. E*, eluant containing 0.5 *M* potassium chloride in 1 *M* hydrochloric acid–50% acetone solution. Heated column, 2.0 × 0.4 cm i.d.; flow rate, 0.6 ml/min. Left-hand ordinate: Concentration of Zn^{2+}, Cu^{2+}, and Cd^{2+} (mole/l). Right-hand ordinate: Concentration of K^+ (× 10 mole/l). Abscissa: Effluent volume (ml).

while there is an increase to 1.047 nm by the ion-exchange of potassium without any change in the space group (*Fd*3*m*) of the crystal system (*21*). To this extent the lattice of C-SbA seems to be useful for the rapid elution of the elements, so that an eluant containing 0.5 *M* potassium chloride in 1 *M* hydrochloric acid–50% acetone solution has been tested in order to improve the elution of cadmium. The proposed eluant for cadmium completely eliminated the tailing of cadmium observed with 2 *M* hydrochloric

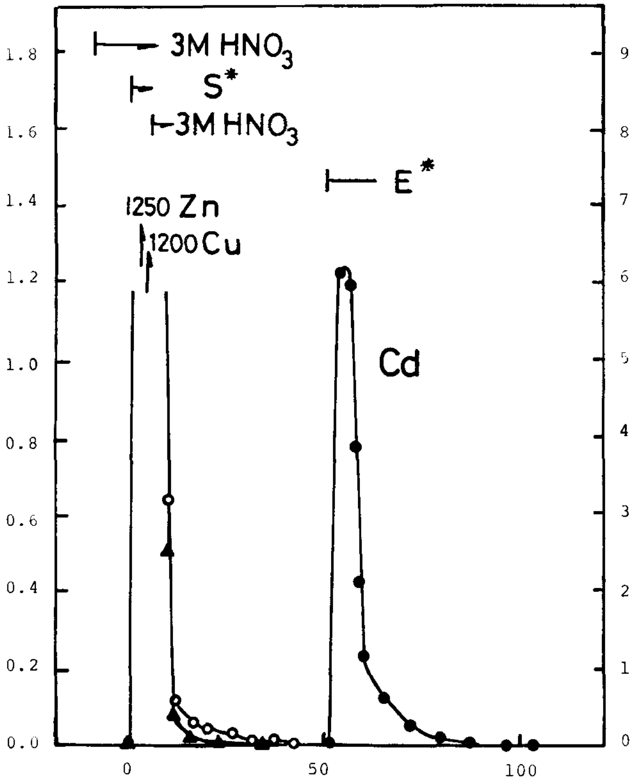

FIG. 8. Separation of Cd^{2+} from a large amount of Zn^{2+} and Cu^{2+} with the C-SbA column heated at 50°C. S*, sample solution (2.0 ml) containing 4×10^{-4} mmole of Cd^{2+}, 0.04 mmole of each of Zn^{2+} and Cu^{2+} in 3 *M* nitric acid. E*, eluant containing 0.5 *M* potassium chloride in 1 *M* hydrochloric acid–50% acetone solution. Heated column, 2.0 × 0.4 cm i.d.; flow rate, 0.6 ml/min. Left-hand ordinate: Concentration of Zn^{2+} and Cu^{2+} ($\times 10^5$ mole/l). Right-hand ordinate: Concentration of Cd^{2+} ($\times 10^5$ mole/l). Abscissa: Effluent volume (ml).

acid–50% acetone solution, and the cadmium in the last 100 ml of eluate remained below the detection limit of the atomic absorption method (0.01 ppm) (Fig. 7). Zinc and copper(II) showed practically no tailing effect. Thus quantitative separation was performed with 99 to 100% recovery for cadmium from zinc and copper(II). From x-ray diffraction analysis, a lattice constant of 1.039_4 nm was measured for the heated C-SbA exchanged with 1.03 meq of potassium ions per gram of the C-SbA in hydrogen ion formed by injection of the proposed eluant. The adsorbed potassium ions on the heated column were eluted easily with a 3 *M* nitric acid solution as eluant. Therefore, the C-SbA column can be used repeatedly.

The separation was repeated with 4×10^{-4} mmole of cadmium and with 0.04 mmole each of zinc and copper(II) with almost the same experimental conditions. The result indicates that the tailing of metals becomes almost negligible; the concentration axis on Fig. 8 has been enlarged intentionally in order to demonstrate to what extent tailing has been eliminated. Bubble formation can be seen occasionally in the heated column, but the bubbles do not seriously affect the subsequent elution of metals through the small column.

REFERENCES

1. M. Abe, *Bunseki Kagaku*, *23*, 1254 (1974).
2. M. Abe, *Ibid.*, *23*, 1561 (1974).
3. M. Abe and T. Ito, *Bull. Chem. Soc. Jpn.*, *40*, 1013 (1967).
4. M. Abe and T. Ito, *Ibid.*, *41*, 333 (1968).
5. M. Abe, *Ibid.*, *42*, 2683 (1969).
6. M. Abe and K. Uno, *Sep. Sci. Technol.*, *14*, 355 (1979).
7. M. Abe, *J. Inorg. Nucl. Chem.*, *41*, 85 (1979).
8. M. Abe, *Bull. Chem. Soc. Jpn.*, *52*, 1386 (1979).
9. F. W. E. Strelow, R. Rethemeyer, and C. J. C. Bothma, *Anal. Chem.*, *37*, 106 (1965).
10. Y. Yoshino and M. Kojima, *Bunseki Kagaku*, *5*, 311 (1955).
11. F. W. E. Strelow, *Anal. Chem.*, *32*, 363 (1960).
12. S. Kallmann, H. Oberthin, and R. Liu, *Ibid.*, *32*, 58 (1960).
13. J. S. Fritz and B. B. Garralda, *Ibid.*, *34*, 102 (1962).
14. S. Kallmann, H. Oberthin, and R. Liu, *Ibid.*, *30*, 1846 (1958).
15. T. Anderson and A. B. Knutsen, *Acta Chem. Scand.*, *16*, 8491 (1960).
16. F. W. E. Strelow, W. J. Louw, and C. H.-S. W. Weinhert, *Anal. Chem.*, *40*, 2021 (1968).
17. J. S. Fritz and T. A. Rettig, *Ibid.*, *34*, 1562 (1962).
18. F. W. E. Strelow, *Anal. Chim. Acta*, *97*, 87 (1978).
19. F. W. E. Strelow, C. R. Van Zyl, and J. C. Bothma, *Ibid.*, *45*, 81 (1969).
20. D. J. Pietrzyk, Ph.D. Thesis, Iowa State University, Ames, Iowa, 1961, cf. Ref. *16*.
21. M. Abe and K. Sudoh, *J. Inorg. Nucl. Chem.*, In Press.

Received by editor May 29, 1979