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Cation-Exchange Study on a Crystalline and Thermally Stable Phase of Antimony Silicate. Effect of Irradiation on Ion-Exchange Behavior and Separation of Cd(II) from Zn(II) and Mn(II) and of Mg(II) from Ba(II), Ca(II), and Sr(II)

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Cation-Exchange Study on a Crystalline and Thermally Stable Phase of Antimony Silicate. Effect of Irradiation on Ion-Exchange Behavior and Separation of Cd(II) from Zn(II) and Mn(II) and of Mg(II) from Ba(II), Ca(II), and Sr(II)

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Abstract

A systematic ion-exchange study has been performed on antimony silicate, which includes its ion-exchange capacity, elution behavior, pH titrations, and distribution coefficients of common metal ions. The K_d values for alkali metals vary with the pH of the solution and the material is found to be highly selective for Rb(I) at pH values greater than 1. On the basis of distribution studies, the separation of Cd(II) from Zn(II) and Mn(II) has been achieved. Similarly, Mg(II) has been separated from Ba(II), Ca(II), and Sr(II) to illustrate its utility. Antimony silicate is very stable both thermally and chemically and possesses reproducible ion-exchange properties; also, the effect of irradiation on the ion-exchange behavior is negligible. A tentative formula of the material has also been proposed based on chemical, infrared, and thermogravimetric analysis studies. The x-ray studies reveal that the exchanger is crystalline with a *d*-value of 6.09 Å.

INTRODUCTION

Silicates form one of the most important classes of the ion-exchange materials as they are temperature resistant and stable under chemical attack (*1–4*). Antimony salts such as Zr(IV), Ti(IV), and Sn(IV) antimonates (*5–8*) have received attention because of their reproducible ion-exchange behavior while the antimony-silicon cation exchangers have been prepared and studied by Novikov and co-workers (*9–13*). However, a systematic ion-exchange study of antimony silicate has been lacking. Our study is summarized in the following pages. The effect of irradiation on the ion-exchange properties of this material is also included.

EXPERIMENTAL

Reagents

The antimony pentachloride used in this study was of ~95% purity obtained from Koch-Light Laboratories Ltd. (Colnbrook, Bucks, England) and the sodium silicate was a Riedal (DEHAENAG, Seelze-Hannover) product. All other reagents and chemicals were of AnalaR grade.

Apparatus

pH measurements were made on an Elico (India) model LI-10 pH meter while infrared studies were performed on a Beckmann IR-20 spectrophotometer. X-ray studies were made on a Philips X-ray unit using a Mo-K_α target, and the radioactivity was measured in a well-type single channel counter of the Electronics Corporation of India Ltd. using a NaI(Tl) detector. A Bausch and Lomb spectronic-20 colorimeter was used for the spectrophotometric studies.

Preparation of the Reagent Solutions

A stock solution (1.0 *M*) of antimony pentachloride was prepared in concentrated HCl and was diluted to the desired concentration with demineralized water (DMW) so that the final concentration of HCl was not less than 4 *M* in the solution. Sodium silicate was dissolved directly in DMW by heating. For distribution studies, the metal salts were also generally dissolved in DMW except the tri- and tetravalent metals for which 2–3 drops of the corresponding acids were necessary to prevent hydrolysis.

Synthesis of the Material

Different samples of antimony silicate were prepared by varying the concentration of the mixing solutions as given in Table 1 and the pH was fixed in the range 0–1 by adding HNO_3 with constant stirring. The gel thus obtained was kept at room temperature (30°C) overnight, filtered, washed

TABLE 1
Preparation of Antimony Silicate (SbSi)

Sample	Concentration of each mixing solution (M) ($SbCl_5$ + Na-silicate)	Mixing ratio (Sb:Si) by volume	Ion exchange capacity (meq/g)
S-1	0.5	1:1	Unstable in solution
S-2	0.4	1:1	1.6
S-3	0.3	1:1	1.7
S-4	0.2	1:1	1.5
S-5	0.1	1:1	1.7
S-6	0.1	1:2	1.6

with DMW, and dried at 45°C in an air oven. It was then immersed in DMW and the granules were converted into the H^+ form as usual (*14*). On the basis of its apparent chemical stability and general appearance, Sample S-6 was selected for further study. The reproducibility was checked by preparing the samples several times by the same procedure.

Composition

250 mg of the powdered exchanger was fused with ~4 g of Na_2CO_3 in a platinum crucible and transferred in a 100-mL solution of 4 M HCl. The amounts of antimony and silica in this solution were determined by standard methods (*15*, *16*) and were found to be in the mole ratio 1:3.

Chemical Stability

250 mg of the material was placed in a 25 mL solution of an acid or a base with intermittant shaking for 24 h. The solution was then analyzed for the dissolved antimony and silica content using standard spectrophotometric methods (*17*, *18*). The results are shown in Table 2.

Irradiation Studies

Antimony silicate (S-6) was irradiated by γ-rays obtained from a ^{60}CO source for 96 h under a dose rate of 0.4 Mrd/h using $FeSO_4$ as the dosimatter.

TABLE 2
Chemical Stability of SbSi

Solvent	Amount dissolved in (mg) per 25 mL	
	Sb	Si
1 *M* HNO_3	0.65	0.00
2 *M* HNO_3	2.34	0.00
4 *M* HNO_3	2.95	0.07
1 *M* HCl	1.31	0.00
2 *M* HCl	1.40	0.00
4 *M* HCl	5.51	0.00
1 *M* H_2SO_4	1.68	0.00
4 *M* H_2SO_4	3.50	0.00
2 *M* $NaNO_3$	0.00	2.02
4 *M* $NaNO_3$	0.23	2.02
2 *M* KNO_3	0.09	1.55
0.05 *M* NaOH	4.58	3.50
0.1 *M* NaOH	Dissolved appreciably	Dissolved appreciably
0.1 *M* KOH	Dissolved appreciably	Dissolved appreciably
0.1 *M* NH_4OH	1.68	3.15
0.5 *M* NH_4OH	4.44	3.15

Ion-Exchange Capacity (i.e.c.)

The i.e.c. was determined as usual by the column process taking 1 g exchanger (H^+-form) in a glass tube of i.d. ~1 cm and maintaining the flow rate at ~0.5 mL/min. The total volume of the eluant necessary for the complete elution of H^+-ions was 250 mL and the values in meq/dry g for different metals were Li(I) 1.05, Na(I) 1.60, K(I) 1.49, Mg(II) 1.53, Sr(II) 1.59, Ca(II) 1.10, Ba(II) 1.61, NH_4(I) 0.8.

Thermal stability

Several 1.0-g portions of Sample S-6 were heated at various temperatures in a muffle furnace for 1 h each, and the i.e.c. was determined as above by the column process after cooling them to the room temperature. The i.e.c. was also determined after heating the sample for 4h at 400 and 800°C.

Elution Behavior

Since the extent of elution depends upon the concentration of the eluant, a fixed volume (125 mL) of $NaNO_3$ solution of varying concentrations was passed through a column containing 0.5 g of the exchanger. It was observed that a 1.0 *M* concentration is sufficient for the complete elution of H^+-ions from this column. The elution was therefore done with a 1.0 *M* solution of $NaNo_3$ as an eluant. Figure 1 shows the histograms of the γ-irradiated and unirradiated samples of Sb(V) silicate.

pH Titrations

These were performed by the Topp and Pepper's method (*19*) by placing 500 mg of the exchanger in several 250 mL conical flasks, followed by equimolar solutions of alkali metal chlorides in different volume ratios, the final volume being 50 mL. The pH was recorded after keeping the solutions overnight for equilibrium and was plotted against the milliequivalents of the OH^- added. The experiment was repeated for the irradiated sample and the results are summarized in Fig. 2.

Distribution Studies

For Some Common Metal Ions

250 mg of the exchanger in the H^+ form were shaken at 30 ± 2°C for 4 h with a 25-mL solution containing the metal ion. The initial and final concentrations of the metal ion in the solution were determined by EDTA titrations (*20*) as usual (*21*). The K_d values obtained are summarized in Table 3.

For Alkali Metals

The K_d values for Na(I), K(I), Rb(I), and Cs(I) were determined using radiotracers. For this purpose 100 mg of the material in the H^+ form equilibrated with 20-mL of the solvent containing 1.0 mL of the tracer and 1.0 mL of the carrier solution of the required concentration. The initial and final metal concentrations in solution were determined by measuring the activity of the solution in the two cases. The K_d values were calculated with the following formula:

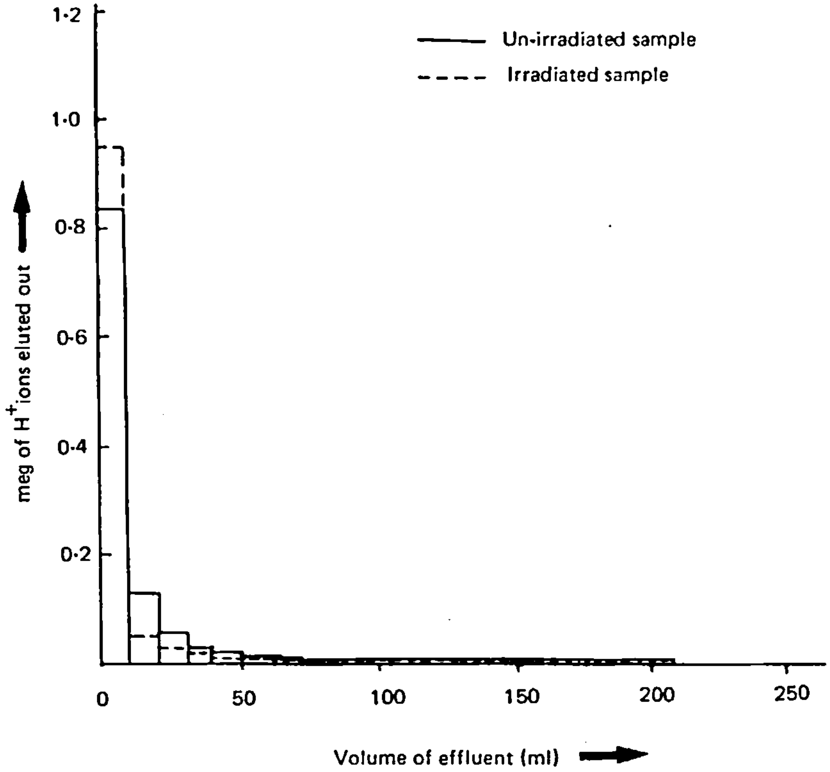

FIG. 1. Histograms showing the elution behavior of antimony(V) silicate exchanger.

$$K_d = \frac{I - F}{F} \times \frac{V}{M}\ \text{mL/g}$$

where I = initial volume of the EDTA used or initial activity of the solution

F = final volume of the EDTA used or the final activity of the solution

V = volume of the solution

M = mass of the exchanger

The following radiotracers were used in these studies with their half-life periods shown in parentheses: ^{24}Na (15 h), ^{42}K (12.5 h), ^{86}Rb (18.7 d), ^{137}Cs (30.2 years), ^{54}Mn (31.3 d), and ^{203}Hg (46.6 d). Figure 3 shows the variation of K_d values with the pH for different alkali metals.

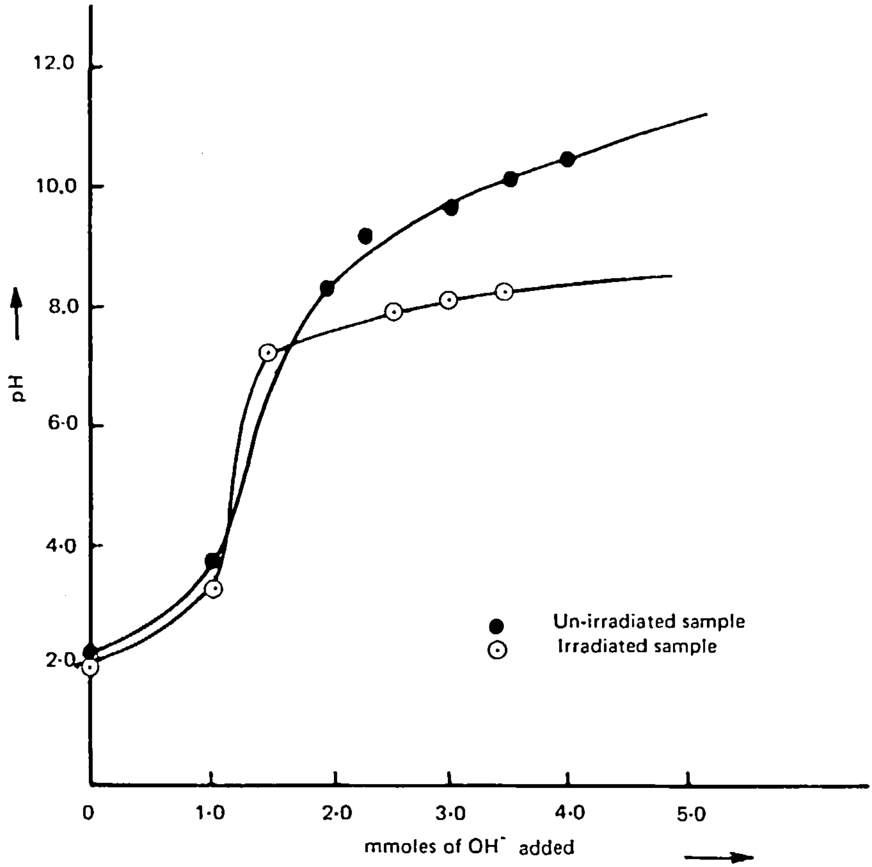

FIG. 2. pH titration curves for antimony(V) silicate.

Separations Achieved

Several binary separations were tried using a column containing 2 g of the sized (50-100 mesh) exchanger particles taken in a glass tube having an i.d. of ~0.6 cm. The flow rate was fixed as ~0.5 mL/min using eluants selected on the basis of the K_d values obtained.

RESULTS AND DISCUSSION

These studies reveal that antimony silicate is a highly stable and reproducible ion-exchange material. A comparison of its thermal stability

TABLE 3

K_d Values of Some Common Metal Ions on Antimony-Silicate in Different Media[a]

Metal ion	Solvent: pH:	K_d values DMW 7	0.01 *M* $HClO_4$ 2	0.01 *M* $HClO_4$ 1	10% HCl + 25% DMSO (1:20) 1.6	10% HCl + 25% DMSO (1:10) 1.2	10% HCl + 25% DMSO (1:5) 0.9	10% HCl + 25% DMSO (1:1) 0.4
Zn(II)		TA	1800	36	159	39	19	0
Cd(II)		TA	1900	1900	900	900	900	900
Hg(II)		TA	TA	1250	0	0	0	0
Mn(II)		TA	433	14	28	10	0	0
Mg(II)		TA	357	12	33	14	0	0
Ca(II)		TA	TA	TA	1500	1500	1500	357
Sr(II)		TA	TA	TA	TA	1350	1350	480
Ba(II)		TA	TA	1153	1153	616	526	150
Cu(II)		TA	TA	255	220	52	18	0
Ni(II)		TA	900	620	36	20	7	0
VO(II)		TA	866	16	45	32	16	0
Pb(II)		TA	TA	1400	TA	1400	1400	328
Co(II)		TA	655	54	78	54	36	13
Fe(III)		TA	TA	175	633	214	0	0
Al(III)		TA	TA	37	149	44	0	0
Zr(IV)		TA	TA	TA	800	1250	1250	1250
Th(IV)		TA	TA	600	1066	60	218	62
Y(III)		TA	TA	424	TA	424	1203	92
La(III)		TA	TA	572	TA	1000	450	312

[a] TA = total adsorption.

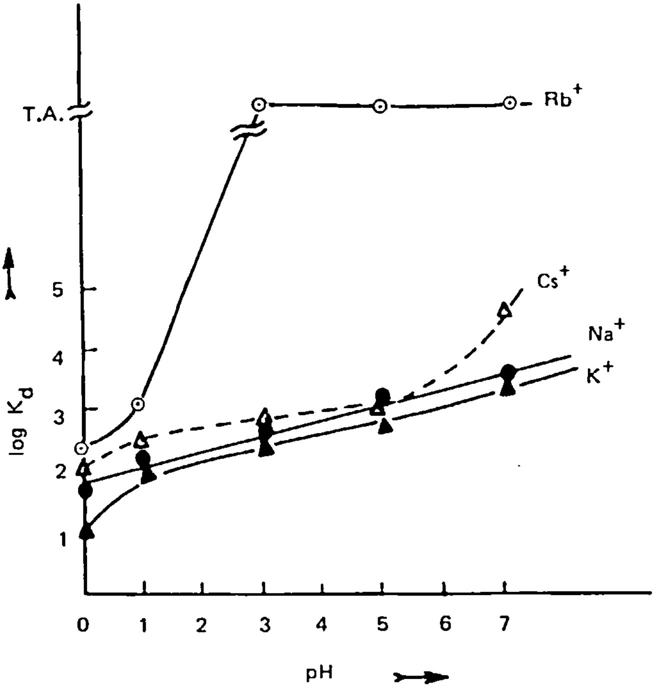

FIG. 3. Effect of pH on the K_d values of alkali metals on antimony(V) silicate.

with other exchangers of this class (Fig. 4) indicates a high percent retention in its i.e.c. on heating, almost comparable with the zirconium(IV) and titanium(IV) arsenophosphates prepared earlier (*21*). At 400°C, even heating for 4 h does not alter its i.e.c. appreciably, as seen in Table 4. This material also appears to be highly chemically stable (Table 2). The elution behavior indicates that the exchange is quite fast and almost all of the H^+-ions are eluted out in the first 50 mL of the effluent from a column of 1.0 g exchanger (Fig. 1). Moreover, the exchange takes place in one step as indicated by the pH titration curve shown in Fig. 2.

The distribution studies illustrate some of the interesting features of this material. A plot of pH versus log K_d for Na(I) and K(I) is a straight line; however, there is a positive deviation in this behavior for the Cs(I) ion above pH 5 (Fig. 3). For Rb(I), the material shows a total adsorption even above pH 1. In this respect, antimony silicate is different from Sn(IV) arsenophosphate (*22*) which shows a linear increase in K_d values for Rb(I) and Cs(I) with pH. Antimony silicate, therefore, appears to be specific for the Rb(I) ion and can be used for its extraction.

TABLE 4
Ion-Exchange Capacity and Appearance of SbSi After Heating to Various Temperatures

Drying temperature (°C)	Time of heating (h)	Na-ion exchange capacity (meq/dry g)	Appearance
45	1	1.60	White
100	1	1.52	White
300	1	1.42	Yellowish white
400	1	1.25	Yellowish white
600	1	1.20	Dark yellow
800	1	0.72	Yellowish white
400	4	1.18	Yellowish white
800	4	0.34	Yellowish white

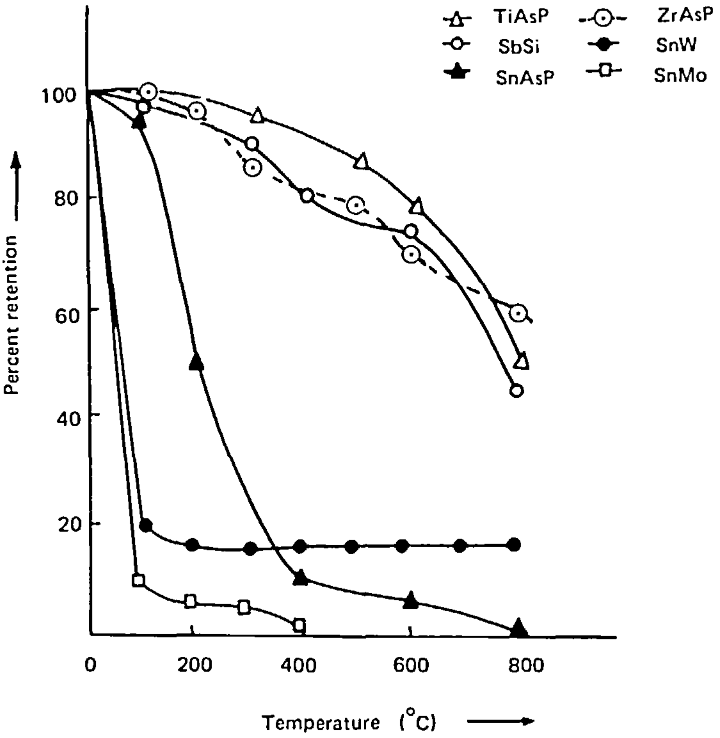

FIG. 4. Percent retention of the H^+ ions in the exchanger phase on heating.

On the basis of its chemical composition, pH titration, and TGA results, the antimony silicate, prepared in these studies, may be tentatively assigned the following formula: $[Sb_2O_5(H_2SiO_3)_6] \cdot nH_2O$

If it is assumed that all the exchangeable water molecules are removed on heating up to ~280°C, the first inflection point in the TGA curve (Fig. 5), the value of n can be calculated from

$$18n = \frac{X(M + 18n)}{100}$$

where X is the % weight loss (20%) in the exchanger on heating up to the inflection temperature and M is its molecular weight. The value of n thus obtained is 11. A further loss in weight above 280°C may be due to the

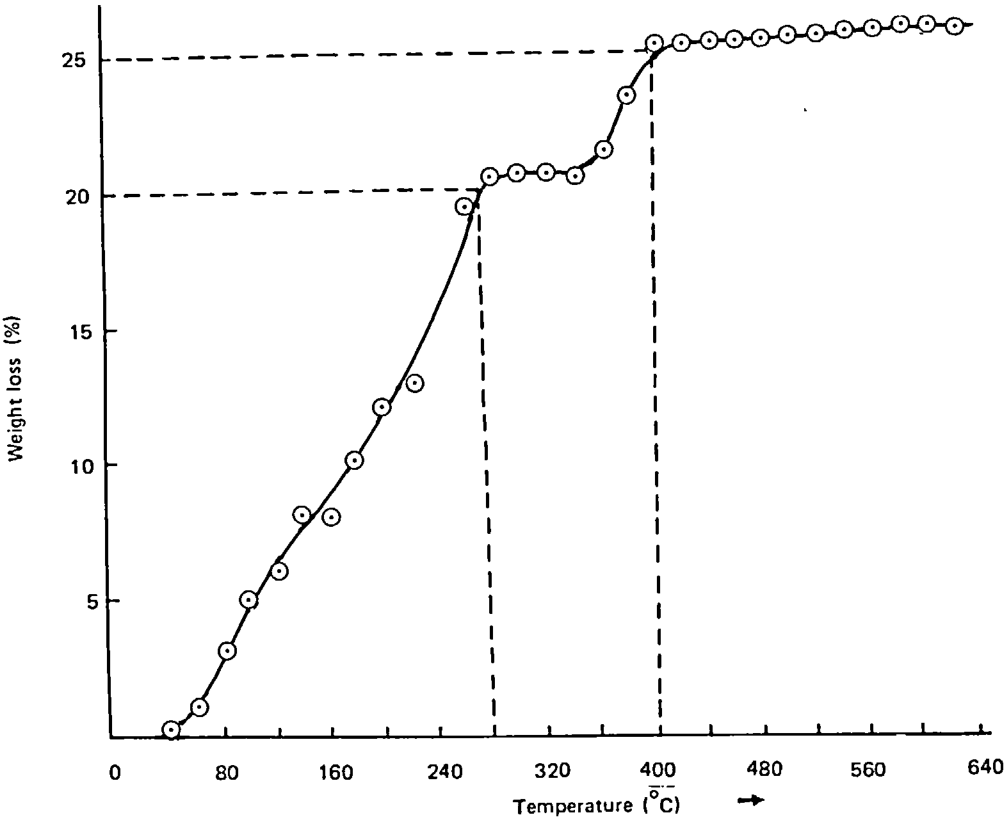

FIG. 5. Thermogram of antimony (V) silicate.

condensation process which probably continues up to 400°C, beyond which the oxides of Sb and Si are probably formed. An exhibition of the i.e.c. of SbSi even after heating to this temperature may be accounted for by the formation of antimonic acid when the oxide is dipped in aqueous solution. Antimonic acid has earlier been studied (*10, 23, 24*) as a cation exchanger.

The IR spectra show the peaks at ~450, 750, 1050, 1600, and 3300 cm^{-1} which represent (*25*) the presence of metal hydroxides (450 and 750) silicates (1050) and H_2O molecules (1600 and 3300) in the structure. The x-ray studies reveal the crystalline behavior of the material with a *d*-value 6.09 Å.

An irradiation of the sample by γ-rays for 96 h under a dose rate of 0.4 Mrd/h does not significantly change the ion-exchange behavior and the selectivity of metal ions as indicated in Table 5. Only a slight change in the elution rate (Fig. 1) and pH titration behavior (Fig. 2) is observed on irradiation.

The utility of this material was demonstrated by achieving separations of great analytical significance; for example, Mg(II) was separated from other alkaline earths (Figs. 6 and 7). Similarly, the rather difficult separation of Cd(II) from Zn(II) was performed on this ion-exchanger with a simple eluant 1 *M* $HClO_4$ (Fig. 8). Binary separations like Cd–Mn and Hg–Pb were achieved on the columns of SbSi. Although antimonic acid has earlier shown (*10*) a great affinity for Cd(II), it could not be utilized for its separation from Zn(II). For this purpose the SbSi exchanger prepared in these studies seems to have an added advantage. Table 6 shows the details of the six binary separations achieved on the column of this exchanger. It is clear from Table 6 that the % error observed in all cases is reasonably low and the separations can be said to be precise.

TABLE 5

Effect of Irradiation on the Adsorption of Mn^{2+}, Hg^{2+}, and Cs^+ on SbSi

	K_d values			
	Water		$HClO_4$	
Metal ion	Normal sample	Irradiated sample	Normal sample	Irradiated sample
Mn^{2+}	473	515	34.0	44.0
Hg^{2+}	420	373	102	194
Cs^+	38,394	36,298	97	110

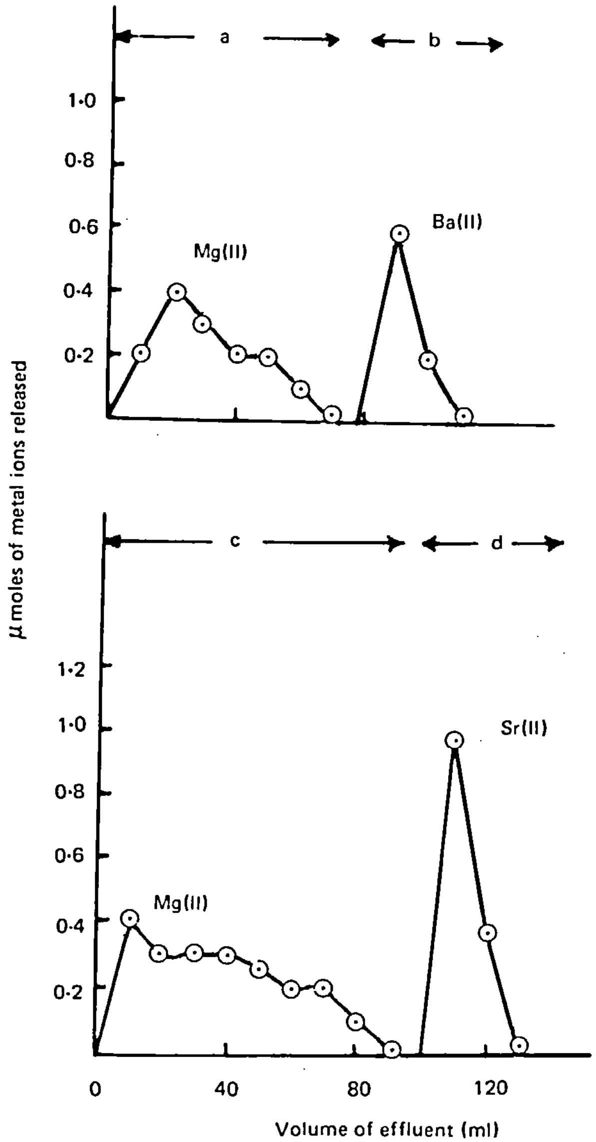

FIG. 6. Separationof Mg(II) from Ba(II) and Sr(II) on antimony(V) silicate columns: (a) and (c), 0.1 M $HClO_4$; (b) and (d) 1 M $HClO_4$.

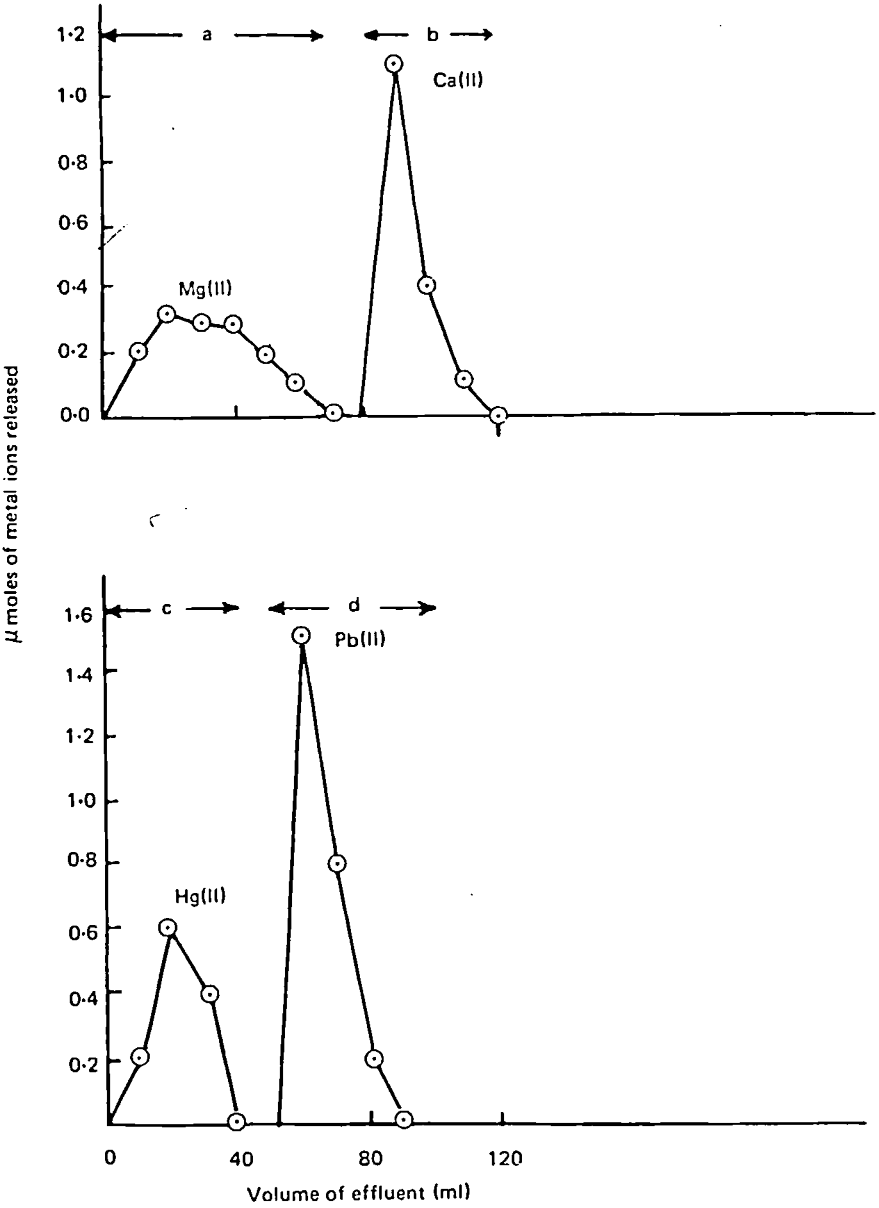

FIG. 7. Separation of Mg(II) from Ca(II) and of Hg(II) from Pb(II) on antimony(V) silicate columns: (a), 0.1 *M* $HClO_4$; (b) and (d), 1 *M* $HClO_4$; (c) 10% HCl + 5% DMSO.

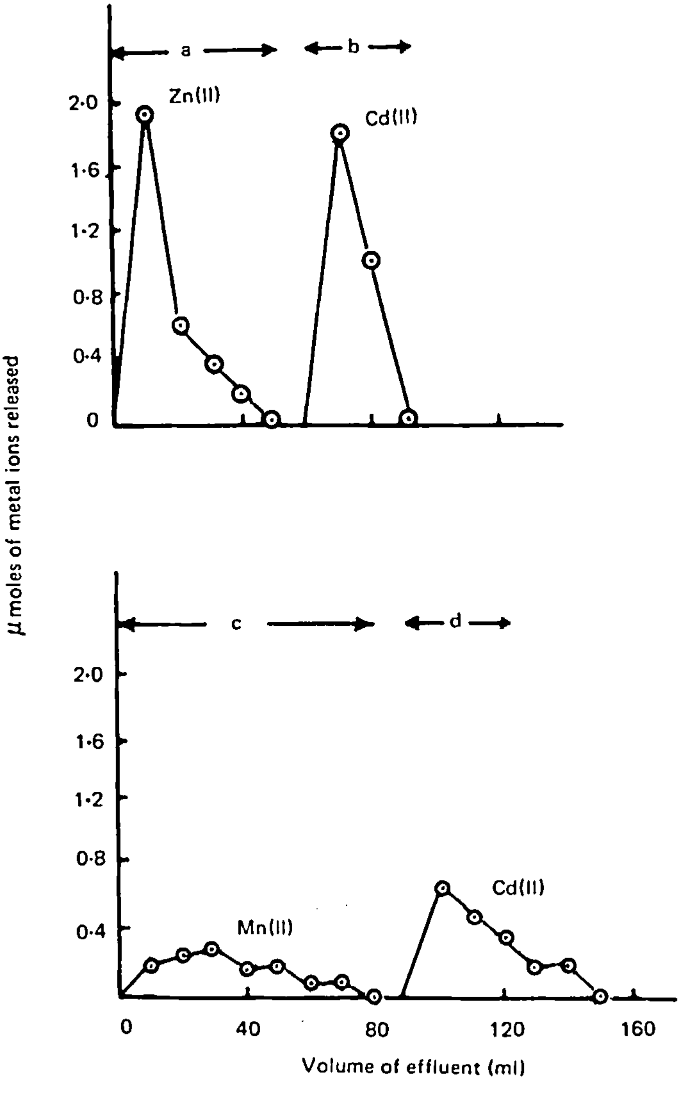

FIG. 8. Separation of Cd(II) from Zn(II) and of Mn(II) on antimony(V) silicate columns: (a) and (c), 0.1 *M* $HClO_4$; (b) and (d), 1 *M* $HClO_4$.

TABLE 6
Binary Separations Achieved on Antimony(V) Silicate Columns

Sample	Separations achieved (M_1–M_2)	Amount taken (μg)		Amount found (μg)		Error (%)		Eluent and its volume used for different metals
		M_1 (μg)	M_2 (μg)	M_1 (μg)	M_2 (μg)	M_1	M_2	
1	Zn–Cd	200.0	304.0	204.0	309.0	0.0	+1.6	Zn: 0.1 *M* $HClO_4$, 50 mL Cd: 1 *M* $HClO_4$, 30 mL
2	Mn–Cd	71.0	187.0	67.0	187.0	−5.6	0.0	Mn: 0.1 *M* $HClO_4$, 80 mL Cd: 1 *M* $HClO_4$, 60 mL
3	Hg–Pb	240.0	517.0	240.0	497.0	0.0	−3.8	Hg: 10% HCl + 5% DMSO, 40 mL Pb: 1 *M* $HClO_4$, 40 mL
4	Mg–Ca	34.0	64.0	35.0	64.0	+2.6	0.0	Mg: 0.1 *M* $HClO_4$, 70 mL Ca: 1 *M* $HClO_4$, 50 mL
5	Mg–Ba	34.0	112.0	34.0	112.0	0.0	0.0	Mg: 0.1 *M* $HClO_4$, 50 mL Ba: 1 *M* $HClO_4$, 60 mL
6	Mg–Sr	48.0	123.0	49.0	123.0	+2.0	0.0	Mg: 0.1 *M* $HClO_4$, 80 mL Sr: 1 *M* $HClO_4$, 20 mL

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