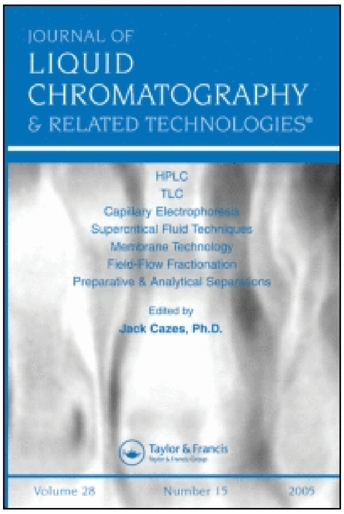

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METAL ION CHELATION CHROMATOGRAPHY ON COMPLEXON SORBED STANNIC SILICATE

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ABSTRACT

Stannic silicate has been sorbed with complexones like xylenol orange, eriochrome black T and 1,10-phenanthroline for use as a chelate ion exchanger. The sorption capacity for different metals has been worked out. Kd values have been determined. Xylenol orange was used for the separation of Th(IV) from Cd(II) and Zn(II) and Cu(II) from Cd(II) and Zn(II), 1,10 phenanthroline for the separation of Fe(II) from Fe(III). These separations are based on the stabilities of the various complexes formed by the interaction of metal inns with complexones. By elution of metal ions which forms less stable complexes with the complexones no evidence of complexing agent in the eluate was found.

INTRODUCTION

Use has been made of complexones for the preparation of new chelating resins for separating metal ions on the basis of complex formation (1-6). As a result they can be used as an analytical tool for separation purposes where theoretical principles can be applied and selective separations can be achieved. Inorganic ion exchangers can be used likewise. Zinc silicate sorbed with PAN, (1-(2-pyridyazo)-2-naphthol), has been used to separate Fe(III)-Pt(IV), Fe(III)-Au(III), Cu(II)-Ag(I) and Cu(II) and Au(III) (7). Sorption of 8-hydroxyquinoline on Porasil separates ions such as Co-Ni, Cd-Pb-Zn at trace levels (8). The present work summarizes the preparation of complexone sorbed stannic silicate and the separation of a number of metal ions on columns of this material. The complexing agents used are; xylenol orange, eriochrome black T and 1,10-phenanthroline.

MATERIALS AND METHODS

Reagents: Stannic chloride (Poland) and sodium silicate (Merck) were used. All other chemicals were of AnalaR grade.

Apparatus: A temperature controlled SICO shaker and an Elico pH meter model Li-10 were employed for shaking and pH measurements.

Synthesis: Stannic silicate was prepared by mixing 0.1M solution of stannic chloride and a saturated solution of sodium silicate (9). The filtrate was filtered and dried at 40°. The dried product was kept immersed in solutions of the desired complexone for 48 hrs. It was then washed first with demineralized water and then with ethanol. Washing was continued to remove excess complexone. The washed product was then dried at 40°.

RESULTS AND DISCUSSION

Stannic silicate which originally had the hydroger ion-exchange capacity of 0.5 m.eq.g^{-1} lost its hydrogen ion-exchange capacity after treatment with the complexones but gained the sorption capacity. This sorptive ability of the treated stannic silicate shows that adherence of the complexing agents to the exchanger offers sites for the chelation of metal ions. Sorption of complexing agents like xylenol orange, eriochrom black T and 1,10-phenanthroline were successfully achieved. Stannic silicate which is colourless originally acquired the colour of the sorbed complexone or complex formed by the action of metal ions with the complexone alone. The movement of the complex thus formed can be observed visually in the column.

Sorption capacity: The sorption capacity of the exchanger was determined by batch process. 0.5 g exchanger was shaken with a solution of 0.02M of the desired metal ion in a conical flask containing 25 ml of a solution of pH 6. After being shaken for 6 hrs. at room temperature the mixture was decanted and the amount of metal ion remaining in the filtrate was determined by chelometric titrations. The sorption capacity for some metal ions are reported in table 1. The sorption capacity ranges between 0.50 to 0.60 m.mol.g^{-1} for these ions. In these studies it has been observed that xylenol orange did not take up alkaline earth metal ions whereas stannic silicate sorbed with eriochrome black T exclusively retained alkaline earths. Application of 1,10-phenanthroline to stannic silicate made it selective to

TABLE 1

Sorption capacity of complexones sorbed stannic silicate for various metal ions

Name of complexing agent sorbed	Colour of the exchanger	Sorption capacity in m.mol per g					
		Fe(II)	Fe(III)	Cu(II)	Zn(II)	Th(IV)	Mg(I)
Xylenol orange	Yellow	0.38	0.38	0.60	0.00	0.62	0.00
Eriochrome black T	Violet	0.00	-	-	0.58	0.00	0.58
1,10-phenanthroline	White	0.60	0.00	-	-	-	-

Fe(II) ions and immune to Fe(III) ions. These results inferred that the metal ions forming stable complexes with complexones are preferred by the solid phase and this forms the basis of selectivity.

<u>Rate of sorption</u>: The rate of sorption of Th(IV) and Cu(II) was determined by a batch process. A fixed concentration (0.6 m.mole) of metal ions in a solution of pH 6 was shaken with xylenol orange sorbed stannic silicate at different intervals of time and amount of unsorbed ion was determined in the supernate. It can be seen from fig.1 that maximum sorption of both Th(IV) and Cu(II) is attained in 5 min. This fast equilibration rate is one of the desirable properties of chelating exchangers (10). Other desirable properties such as high capacity for metals of interest, high selectivity and high mechanical strength or toughness of the exchanger, are adequate with complexones sorbed on stannic silicate. The sorption capacity for metal ions is due to the presence of complexing agents whereas high selectivity depends upon the stability constant of the metal chelating group. The presence of all four qualities needed in a chelating ion-exchanger in

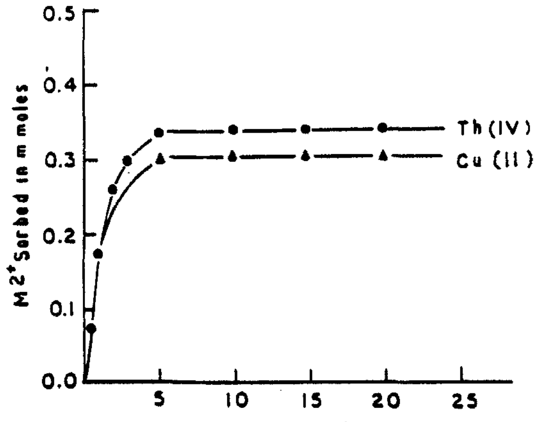

FIG.1 RATE OF SORPTION OF Cu^{2+} & Th(IV)

this case, constitutes its advantage over the organic chelating exchangers wherein high capacity and toughness are the two competitive factors.

Comparison with silica gel: Under similar condition, sorption of all the three complexing agents on silica gel was studied. It was observed that extremely poor adsorption of complexing agent occurs on silica gel. This observation is pointer to the reason why stannic silicate functions much better than silica gel.

pH range: The pH range within which the exchanger can be safely used was determined by shaking with solutions of different pH for 6 hrs. Results show that bleeding of complexones occurred in solutions where pH was less than 1 and more than 8.

Distribution coefficients of metal ions at different pH:

(i) Xylenol orange sorbed stannic silicate: To a stoppered conical flask containing 24 ml solutions of different pH (1 to 6) and 1 ml of 0.01M metal ion solution was added. The mixture was equilibrated with 200 mg exchanger for 4 hrs. The amount of unsorbed metal ion was then determined in the solution mixture.

$$Kd = \frac{\text{Amount of metal ion in exchange phase g}^{-1}}{\text{Amount of metal ion in solution phase ml}^{-1}}$$

The results of variation of Kd with pH for different metal ions are plotted in fig.2 from which it is observed that different ions behave in a different manner at different pH. Cu(II), Th(IV), Cd(II) and Y(III) are taken up by the exchanger while Zn(II) and Mg(II) are left unsorbed. Among those that are appreciably sorbed, the values at pH 3.0 gives the maximum difference in Kd values and made separations possible.

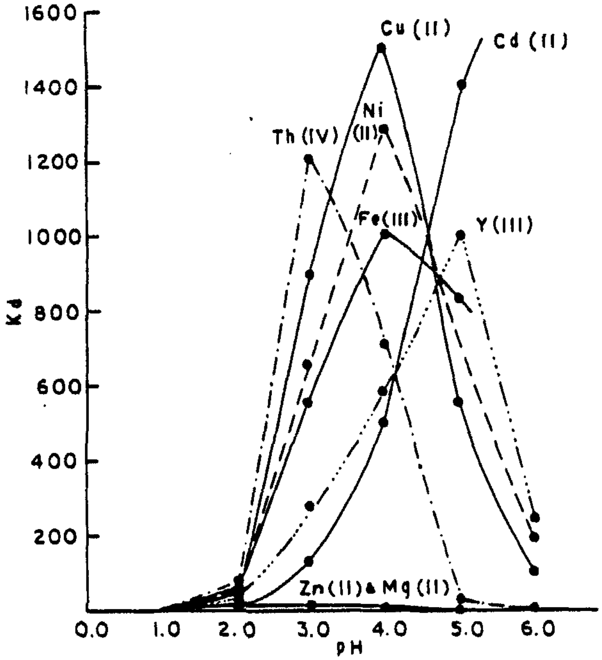

FIG. 2 Kd VALUES OF SOME METAL IONS AT DIFFERENT pH

(ii) Eriochrome black T adsorbed on stannic silicate: Kd values were determined in the same way as that for the xylenol orange. Results are given in table 2. These results show a similar behaviour for all alkaline earth group. Therefore, separations of alkaline earths is not possible. However, separations of alkaline earths from metal ions which do not form complexes with eriochrome black T might be tried.

Separations: On the basis of difference in Kd values separations were tried on a 30 x 0.39 cm^2 glass column. 2.0 g exchanger was taken on a glass wool support of the column solutions of metal ions to be separated were then passed through the column at a flow rate of 0.5 ml/min.

TABLE 2

Kd values of metal ions on stannic silicate

sorbed with eriochrome black T

Metal ions	Kd values									
	pH 1	pH 2	pH 3	pH 4	pH 5	pH 6	pH 7	pH 8	pH 9	pH 10
Ca^{2+}	0.00	52.50	300.00	43.50	1168.2	T.A.	T.A.	T.A.	T.A.	T.A.
Mg^{2+}	0.00	50.00	65.00	200.00	375.0	1075.0	T.A.	T.A.	T.A.	T.A.
Zn^{2+}	2.50	16.25	42.16	375.00	1150.0	T.A.	T.A.	T.A.	T.A.	T.A.
Ba^{2+}	8.03	275.00	375.00	510.00	125.0	T.A.	T.A.	T.A.	T.A.	T.A.
Sr^{2+}	0.00	24.75	31.25	37.50	210.0	300.0	T.A.	T.A.	T.A.	T.A.

T.A. = Total adsorption

(i) Separations on xylenol orange sorbed stannic silicate: Successful separations of four sets of metal ions, Cu-Zn, Cu-Cd, Th-Zn and Th-Cd have been achieved on a column containing stannic silicate sorbed with xylenol orange. Zn(II) was eluted with 0.5M NaCl and a mixture of (CH_3COONa + CH_3COOH) adjusted to pH 3 was used for the elution of Cd(II). Elution of Th(IV) and Cu(II) was made by a mixture of 0.1M NaCl and 0.1M HCl adjusted to pH 1. The results are presented in fig.3 (a-d) and in table 3a. The separation of Zn(II) from Cu(II) and Th(IV) is based on the formation of stable complexes of Cu(II) and Th(IV) with xylenol orange and not with Zn(II). The separation of Cd(II) from Cu(II) and Th(IV) is probably due to the difference in stabilities of the complexes formed.

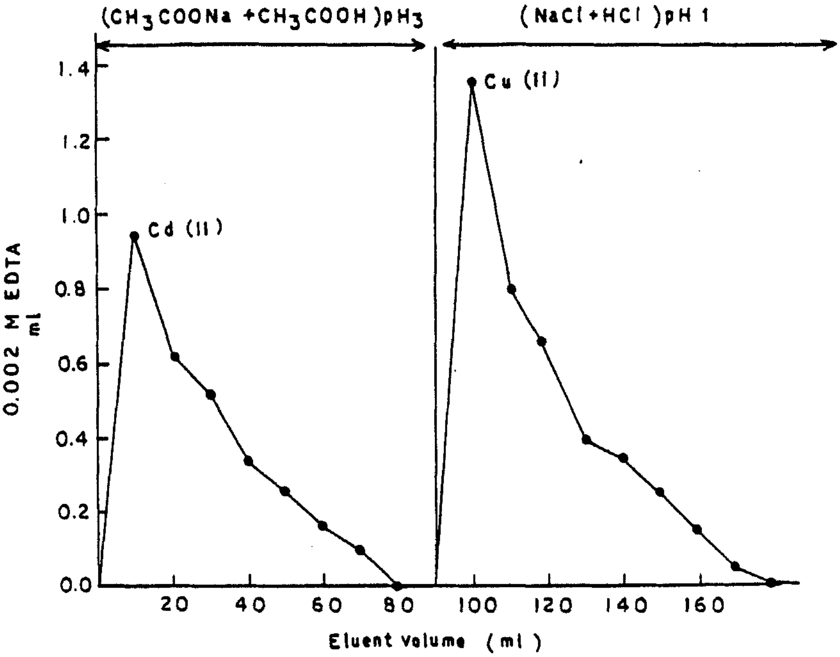

FIG. 3a SEPARATION OF Cd(II)-Cu (II)

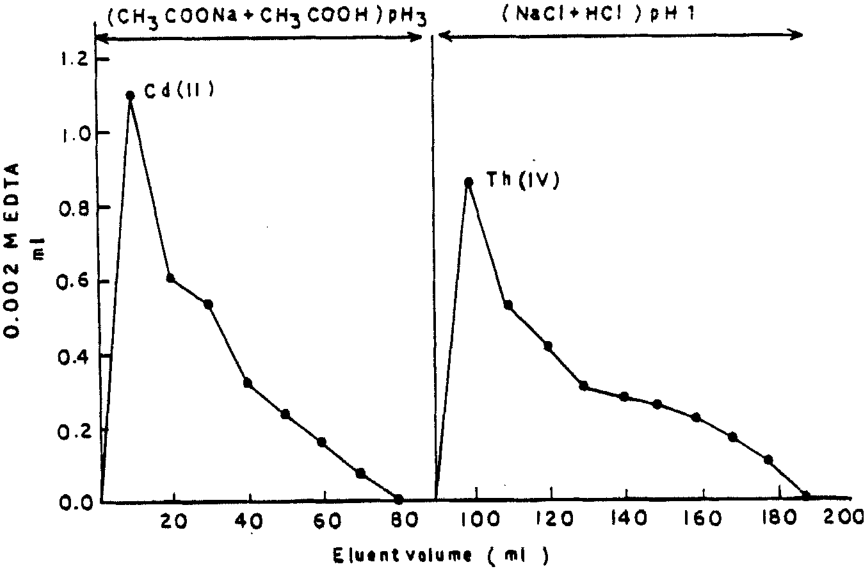

FIG. 3b SEPARATION OF Cd (II)-Th (IV)

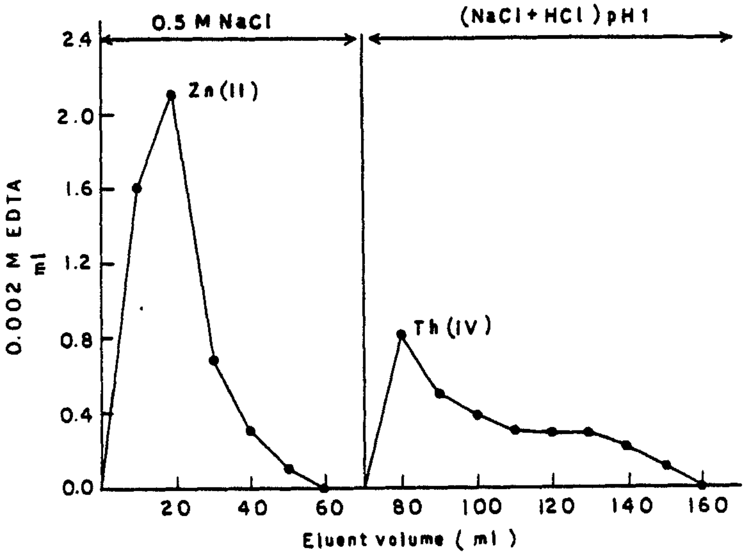

FIG. 3c SEPARATION OF Zn (II)-Th (IV)

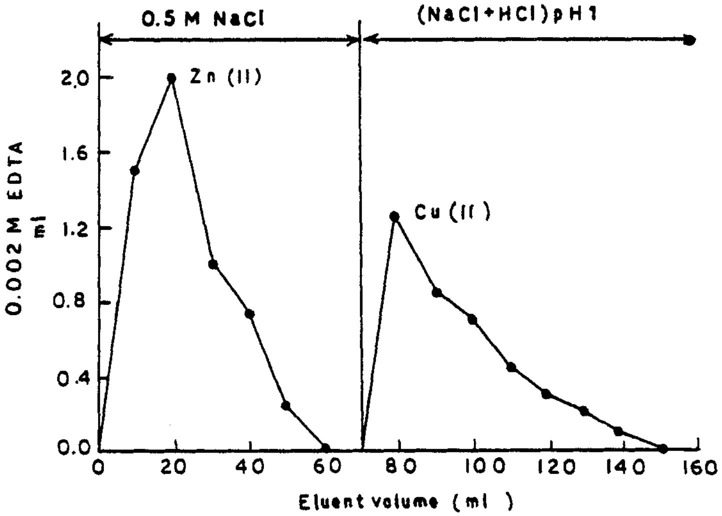

FIG. 3d SEPARATION OF Zn(II)-Cu(II)

TABLE 3a

Separations on stannic silicate xylenol orange column

Sl. No.	Mixture	Eluent	Eluate (cm^3)	Amount loaded µg	Amount found	% Error
1a	Cu(II)	(HCl + NaCl) pH 1	80	485	480.00	1.03
	Zn(II)	NaCl, 0.5M	50	510	503.00	1.37
b	Cu(II)	(HCl + NaCl) pH 1	80	485	485.00	0.62
	Cd(II)	(CH_3COOH + CH_3COONa) pH 3	70	500	490.33	1.92
c	Th(IV)	(HCl + NaCl) pH 1	90	568	569.00	0.20
	Cd(II)	(CH_3COOH + CH_3COONa) pH 3	70	500	492.50	1.50
d	Th((V)	(HCl + NaCl) pH 1	90	568	570.00	0.35
	Zn(II)	0.5M NaCl	70	510	508.20	0.35

(ii) Separations on 1,10-phenanthroline sorbed stannic silicate: Remarkable separations of iron(II) from iron(III) have been achieved on stannic silicate sorbed with 1,10-phenanthroline. Fe(III) was found to be unretained whereas Fe(II) was selectively retained by the exchanger. The results are summarized in table 3b. Fe(II) forms a stable complex with 1,10-phenanthroline and, therefore, is strictly adhered to stannic silicate and its elution as such was not possible. Its conversion to Fe(III) with HNO_3, however, causes the detachment

TABLE 3b

Separations on stannic silicate 1,10-phenanthroline columns

Sl. No.	Mixture	Eluent	Eluate (cm^3)	Amount loaded	Amount found	% Error
1a	Fe(III)	Demineralized water	20	500 µg	495.0 µg	1.00
	Fe(II)	HNO_3, 0.5M	90	525 µg	521.3 µg	0.70
b	Fe(III)	Demineralized water	20	1 mg	998.4 µg	0.16
	Fe(II)	HNO_3, 0.5M	90	525 µg	522.0 µg	0.60

of iron from the complexone. This separation gives an important application as the same metal in different valence states behaves in a different manner. Other separations based on this principle may also be tried.

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