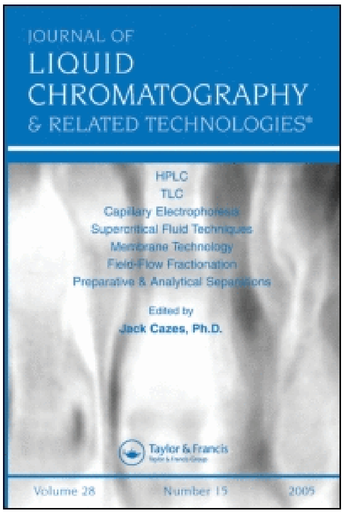

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SEPARATION AND RECOVERY OF SOME METAL IONS USING PAN SORBED ZINC SILICATE AS CHELATING ION EXCHANGER

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ABSTRACT

A new inorganic ion exchanger zinc silicate has been synthesized. Its properties such as ion exchange capacity, heat effect and stability etc. have been studied. Sorption of PAN over zinc silicate formed a chelate ion exchanger which showed greater selectivity for some metal ions especially for Cu^{2+}, Ni^{2+}, Co^{2+}, Fe^{3+}, Ag^{+}, Au^{3+} and Pt^{4+}. Selectivity has been determined on the basis of distribution coefficients of these metal ions. Separations of Pt(IV) from Fe(III), Au(III) from Fe(III), Ag(I) from Cu(II) and Au(III) from Cu(II) have been reported. The recovery of Pt(IV) and Au(III) from dilute solutions has also been studied.

INTRODUCTION

There is a revived interest towards the ion exchange properties of silicates (1-4) in recent years and their analytical importance has been demonstrated. The use of chelate ion exchangers is receiving attention during the last few years (5). The selectivity characteristics of chelating resins suggest their utility in a several types of separations over the conventional ion exchange resins (6). A number of such ion exchangers have been prepared by the incorporation of ligands on resins (7-9). Because of their high selectivity to certain metal ions the use can be made for chromatographic separations advantageously. Chromategraphy of metal ions on a chelating resin containing a thioglycoloyloxy-methyl functional group is reported (10). However, no such studies have been reported with inorganic exchangers. Zinc silicate was synthesized and it was found that the sorptión of PAN (1-(2-pyridyl-azo)-2 naphthol) over it forms a material which works as a chelate ion exchanger. The utility of this material has been studied for the selective separation and recovery of certain metals from very dilute solutions.

MATERIALS AND METHODS

Reagents. Zinc nitrate (BDH), sodium silicate and (1-(2-pyridylazo)-2-naphthol)(BDH) were used.

Apparatus. An electric temperature controlled SICO shaker and 'Metzer Spectra' 75 were used for shaking and spectrophotometric measurements respectively. Elico pH meter model Li-10 was used for pH measurements.

Synthesis. A number of samples of zinc silicate were prepared under a range of conditions given in table 1. 0.1M solution of zinc nitrate was mixed with 0.1M solution of sodium silicate in the varying ratios. The resulting white precipitate was kept standing for 24 hours at room temperature. pH adjustment, if any, was made by adding hydrochloric acid or sodium hydroxide. The precipitate was filtered, washed and dried, at 40°C

TABLE 1

Synthesis and properties of zinc silicate

Samples	Conditions of synthesis				Properties	
	Molarity of reagents		Mixing volume ratio	pH	Cation (M^{2+}) exchange capacity meq/g	Composition
	Zinc nitrate	Sodium silicate				Moles of Zn : SiO_2
1	0.1	0.1	1:1	0.0	2.35	1 : 1.25
2	0.1	0.1	2:1	0.0	2.25	-
3	0.1	0.1	1:1	1.0	0.95	-
4	0.1	0.1	1:1	2.0	0.63	-
5	0.1	0.1	1:1	3.0	0.58	-

in a temperature controlled oven. The dried product was kept immersed in a solution of 6M NH_4OH to convert the exchanger into NH_4^+ form. The treatment of exchanger with 6M NH_4OH is important since it increases the stability of the exchanger.

RESULTS AND DISCUSSION

The results of synthesis and properties of zinc silicate presented in table 1 together with the chemical stability results given in table 3 show that sample 1 is chemically more suitable than any of the other samples. Therefore, this product was chosen for the other studies.

Cation exchange capacity. The ion exchange capacity for H^+ ion was determined by taking the exchanger in H^+ form

TABLE 2

Exchange capacity of zinc silicate

Sl. No.	Eluted ion	Exchange capacity meq/g
1.	H^+	0.05
2.	Ca^{2+}	2.38
3.	Cu^{2+}	2.56
4.	Zn^{2+}	2.36
5.	Mg^{2+}	2.33
6.	Fe^{3+}	2.29

and then eluting with 1.0M solution of ammonium acetate. Metal ion capacity was determined by taking M^{2+} with the exchanger and eluting with a solution of ammonium acetate. From the results given in table 2 it can be inferred that zinc silicate works as an extremely weak cation exchanger and hence desisted any release of hydrogen ions. It is, therefore, desirable that the exchanger should not be allowed to make contact with any solution that contains hydrogen ions. The metal ions capacity, however, is sufficiently high and varies from 2.29 to 2.36 meq/g.

Chemical stability. 200 mg of the exchanger was shaken with 20 ml of the appropriate solvent for 6 hours at room temperature. Zinc and silicon in the supernatant liquid were determined by ethylenediaminetetraacetic acid and molybdenum blue methods (11) respectively. The results are presented

TABLE 3

Solubility of zinc silicate in different solvents

Amount of exchanger taken = 200 mg

Sl. No.	Solvents	Zinc in µg	Silica in µg
1.	Demineralized water	0.0	0.0
2.	Ammonium hydroxide 6.5M	1.8	0.0
3.	Methanol	0.0	0.0
4.	Nitric Acid, 2M	16.25	24.0
5.	Hydrochloric Acid 2M	48.75	13.9
6.	Sulphuric Acid 2M	40.00	48.9
7.	Ammonium Acetate 1M	0.0	0.0
8.	Oxalic Acid 1M	0.81	0.0
9.	Acetic Acid 1M	16.28	15.48
10.	Sodium nitrate 1M	0.0	0.0

in table 3. The results of the stability of sample 1 only are reported here. The values in the table refer to the amounts of Zn and Si dissolved in 20 ml solvent. The values show that zinc silicate can be used in nearly neutral media, water, salt solutions, alcohols, dilute acids and ammonia concentration upto 6M without an appreciable loss. High concentration of acid, however, affects the exchanger and causes dissociation of its constituents to some extent.

Chemical composition. A 200 mg portion of the exchanger was heated in a 50 ml of aqua regia for nearly half an hour. This resulted in the dissociation of zinc ions from the silicates. Zinc ions thus present in the supernatant liquid were filtered and quantitatively estimated by titration with ethylenediaminetetra acetic acid. The residue was ignited and weighed as SiO_2. The results are given in table 1. These results give an apparent ratio of Zn:Si of 1:1.25.

Heat treatment. Exchanger was dried at different temperatures in a muffle furnace for four hours. Cation exchange capacity of one gram of each of the dried product was determined as described earlier. The products dried at temperatures 40°, 100°, 200° and 300 C had the capacities 2.30, 1.70, 1.30, 0.94 meq/g respectively. This shows a loss in capacity at higher temperatures.

Chelating properties. The fact that zinc silicate keeps a firm hold on the sorbed substances has been advantageously used to make it act like a chelating exchanger. The exchanger was kept immersed in an alcoholic solution of PAN for 24 hours to allow complete sorption of the latter. Washed first with alcohol and then with deionized water and dried at 40°C. The zinc-silicate-PAN product so obtained was then used for the separations and recovery of some of the metal ions. Alcohol and dilute solution of ammonium hydroxide do not cause release of PAN from the exchanger.

Distribution studies. Distribution coefficients of seven metal ions were determined by batch process on PAN-sorbed zinc silicate

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

The amount of exchanger was 0.5 g and total volume of equilibrating solution was maintained at 25 ml. Shaking was done for six hours. Au(III), Pt(IV) (12) and Ag(I) (13) were determined by spectrophotometric methods, whereas Co^{2+}, Cu^{2+}, Ni^{2+} and Fe^{3+} were estimated volumetrically by EDTA. The Kd

TABLE 4

Kd values of metal ions

Cations	Kd values, ml g^{-1}						
	DMW	NH_4OH 1M	NH_4OH 2M	NH_4OH 3M	NH_4OH 4M	NH_4OH 5M	NH_4OH 6M
Cu^{2+}	260.0	147.5	50.8	14.52	8.32	1.0	0.0
Ni^{2+}	280.0	18.0	9.2	2.60	0.0	0.0	0.0
Co^{2+}	560.0	110.0	72.0	45.70	45.7	45.7	45.7
Fe^{3+}	360.0	40.0	17.1	0.0	0.0	0.0	0.0
Pt^{4+}	0.9	0.8	0.8	0.8	0.9	0.9	0.9
	DMW	NH_4OH 0.001M	NH_4OH 0.005M	NH_4OH 0.01M	NH_4OH 0.05M	NH_4OH 0.1M	NH_4OH 0.5M
Ag^{+}	840	480	220	176	104	72	0.60
Au^{3+}	620	380	195	154	98	52	0.42

values of these ions were determined in deionized water and in solutions of different concentrations of ammonia. The results presented in table 4 indicate that zinc-PAN-silicate shows a selective sorption for Co^{2+}, Cu^{2+}, Fe^{3+} and Ni^{2+} whereas desorption for Ag(I), Pt(IV) and Au(III) ions. This paved the way for the easy separations of the two class of ions. The reason for selective sorption and desorption of certain types of metal ions can be attributed to the larger difference in the stability constants of the metal-PAN complexes. The elution is based on the stability constant

TABLE 5

Separations on zinc-silicate-PAN columns

	Mixture	Eluent	Eluate (ml)	Amount loaded	Amount found	% Error
1a	Pt(IV)	DMW	50	500 µg	493 µg	1.40
	Fe(III)	NH_4OH 6 mol.dm^{-3}	100	40 mg	40.25 mg	0.65
1b	Pt(IV)	DMW	50	500 µg	515 µg	3.00
	Fe(III)	NH_4OH 6 mol.dm^{-3}	80	500 µg	490.33 µg	1.93
1c	Pt(IV)	DMW	60	10 mg	9.28 mg	7.20
	Fe(III)	NH_4OH 6 mol.dm^{-3}	100	1 mg	1.03 mg	3.00
2	Au(III)	DMW	40	500 µg	510 µg	2.00
	Fe(III)	NH_4OH 6 mol.dm^{-3}	80	500 µg	510.12 µg	2.24
3a	Ag(I)	NH_4OH 0.1 mol.dm^{-3}	80	13.8 mg	14.0 mg	1.5
	Cu(II)	NH_4OH 6 mol.dm^{-3}	70	5.8 mg	6.0 mg	3.4
3b	Ag(I)	NH_4OH 0.1 mol.dm^{-3}	90	1.38 mg	1.42 mg	2.80
	Cu(II)	NH_4OH 6 mol.dm^{-3}	80	600 µg	615 µg	2.50
3c	Ag(I)	NH_4OH 0.1 mol.dm^{-3}	90	600 µg	608 µg	1.30
	Cu(II)	NH_4OH 6 mol.dm^{-3}	70	600 µg	610 µg	1.66

(TABLE 5 CONTINUED)

	Mixture	Eluent	Eluate (ml)	Amount loaded	Amount found	% Error
4a	Au(III)	DMW	40	475 µg	470 µg	1.05
	Cu(II)	NH_4OH 6 $mol.dm^{-3}$	70	4.1 mg	4.0 mg	2.46
4b	Au(III)	DMW	30	1 mg	1.02 mg	2.00
	Cu(II)	NH_4OH 6 $mol.dm^{-3}$	100	1.14 mg	1.09 mg	4.38

of metal-eluting ligand complex. Metal-eluting ligand having high stability constant will be eluted first.

Column separations. A glass column (length 43 cm, i.d. 0.39 cm^2) was filled to a height of 10 cm with two grams of the exchanger fully sorbed with PAN. The column was washed with 50 bed volumes of demineralized water and 10 bed volumes of buffer of pH 3.6. The sample solutions containing the metal ions desired to be separated was passed onto the column at a flow rate of 1 to 2 ml min^{-1}. Unlike Fe^{3+}, Ni^{2+}, Cu^{2+} and Co^{2+} which were retained by the exchanger, Ag(I), Au(III) and Pt(IV) passed out unsorbed. Quantitative separations of iron and platinum, iron and gold, copper and silver and copper and gold have been achieved. Table 5 shows a list of separations successfully achieved on a column of PAN sorbed zinc silicate. The order and the eluents are presented in figures 1, 2, 3 and 4.

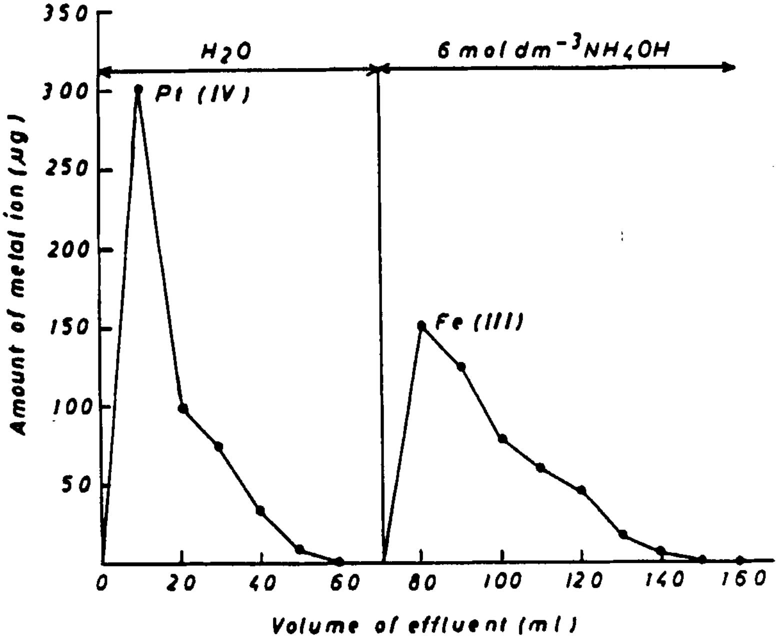

FIG. 1. SEPARATION OF Pt (IV) - Fe (III)

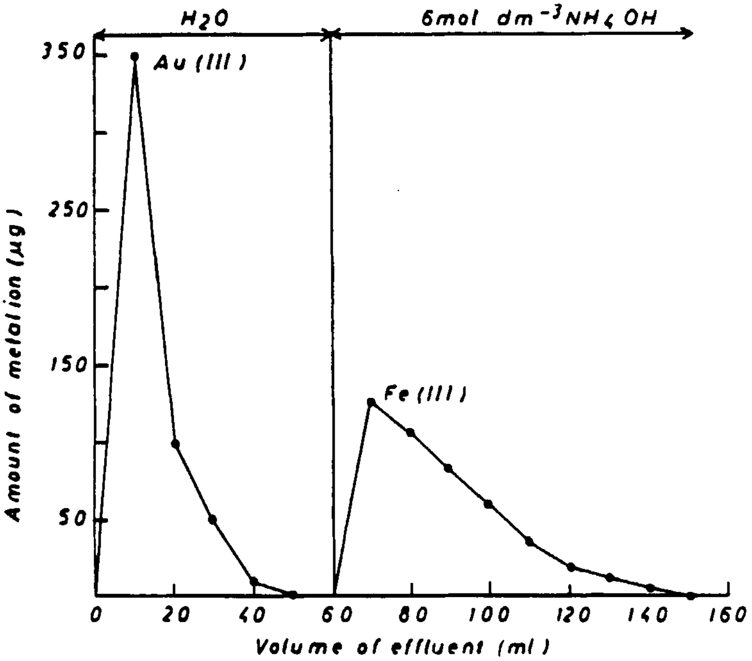

FIG.2 SEPARATION OF Au (III)- Fe (III)

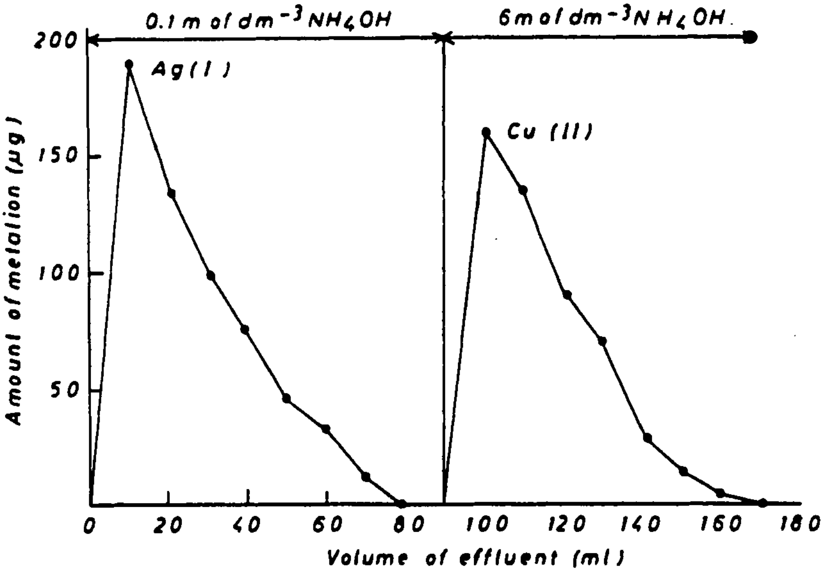

FIG.3 SEPARATION OF Ag(I) - Cu (II)

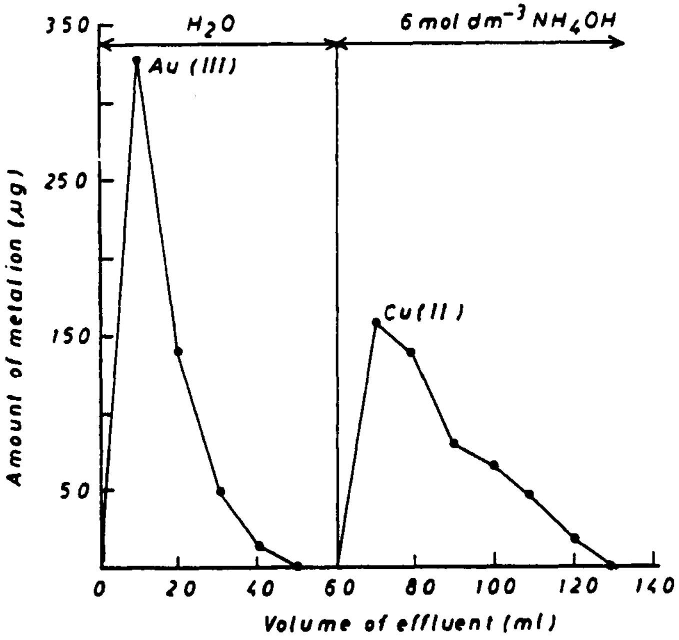

FIG. 4 SEPARATION OF Au(III)-Cu (II)

TABLE 6

Recovery of Pt(IV) and Au(III) ions at pH 3.6 from solutions containing 5 mg each of Co(II), Ni(II), Cu(II) and Fe(III)

Ions measured	Initial weight of ion present (mg)	Weight of ion eluted (mg)	Recovery %
Pt(IV)	1	0.99	99
Pt(IV)	5	4.80	96
Au(III)	1	0.99	99
Au(III)	5	5.06	101

Recovery of Pt(IV) and Au(III). Table 6 shows the successful recoveries of platinum and gold from solutions containing iron, cobalt, copper and nickel. In the presence of five fold excess of these metal ions, neither of them could be detected in the water eluate containing platinum and gold. The retained metal ions, Co^{2+}, Cu^{2+}, Ni^{2+} and Fe^{3+} were easily eluted out with 6M NH_4OH. This shows the importance of PAN-sorbed zinc silicate in the recovery of precious metal ions.

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