

Chelation Ion Chromatography on 1-(2-Pyridylazo)-2-naphthol Sorbed Stannic Silicate: Selective Separation of Cd²⁺, Hg²⁺ and Pb²⁺ from some Transition Metal Ions

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ABSTRACT

Selective separation of three of the most toxic metal ions Cd²⁺, Hg²⁺ and Pb²⁺ has been achieved on a column packed with 1-(2-pyridylazo)-2-naphthol (PAN) sorbed stannic silicate using nitric acid solution of pH 1 and 6 as eluents. Adsorption behavior of several metal ions like Al³⁺, Cr³⁺, Mn²⁺, Fe³⁺, Co²⁺, Ni²⁺, Cu²⁺, Zn²⁺, Cd²⁺, Hg²⁺ and Pb²⁺ on PAN sorbed stannic silicate from aqueous solution at different pH (from 1 to 6) was studied to calculate their distribution coefficients. In addition to the selective separation of Cd²⁺, Hg²⁺ and Pb²⁺ several binary separations of metal ions e. g., Hg²⁺ - Al³⁺, Pb²⁺ - Cr³⁺, Cd²⁺ - Cr³⁺ and Hg²⁺ - Cr³⁺ using aqueous solutions of pH 6 and pH 1 as eluents have been successfully achieved on PAN sorbed stannic silicate.

Keywords: stannic silicate; chelation ion chromatography; separation; 1-(2-Pyridylazo)-2-naphthol.

INTRODUCTION

The use of chelation ion chromatography to concentrate and separate transition and rare earth elements from common alkali and alkaline earth metals and from complex matrix components is receiving attention for a long time now as illustrated in a number of fundamental reviews by Sahni and Reedijk¹, Myasoedova and Savvin², Biernat et al.³, Torre and Marina⁴, Nickson et al.⁵, Garg et al.⁶ and Pereira and Arruda⁷. With the help of chelation ion chromatography metal ions of interest are being separated from complex matrices such as sea water and acid digested biological and geological samples.

Consequently, there is an interest in developing chelation resins of good stability, higher selectivity and higher capacity for given metal ions in ever increasing matrix complicity. The chelation ion exchangers are prepared by incorporating a complexing agent into an ion

exchange material. The selectivity of the chelation ion exchangers for metal ions depends on the functional group of the complexing agent. While some excellent metal ion separations have been obtained on conventional ion exchangers, selectively factors are lower.

The utility of chelation ion chromatography as a method for trace elemental analysis in complex environments and biological samples has been discussed in detail by Siriraks and Kingston⁸. A chromatographically useful packing material has been prepared by immobilizing 8-hydroxyquinoline on Porasil⁹. This material has been found useful in separating such similar ions as Co-Ni, Cd-Pb-Zn and La-Cd-Yb at trace levels employing both isocratic and gradient elution. Various chelating agents like ethylenediaminetriacetic acid, imminodiacetic acid and dimethyl glyoxime have

been used to prepare various useful chelation ion resins. Titan yellow loaded Amberlite IR-120 has been used for selective removal¹⁰ of Pb^{2+} and Hg^{2+} from a solution of Ca^{2+} , Zn^{2+} and Cu^{2+} . The use of high performance chelation ion chromatographic system incorporating a xylenol orange impregnated resin column for the combined preconcentration and separation of trace elements (Zn, Pb, Ni, Cu) in sea water has been developed¹¹.

Chelation Ion Chromatography on DMSO impregnated Silica Gel-G layers has been used for the separation of Cd^{2+} , W^{6+} and Zr^{4+} from transition metal ions¹². Separation and determination of metal ion content of pharmaceutical preparations by chelation ion chromatography on naphthol blue-black modified Amberlite IR-400 anion exchange resin has been studied by Nabi et al¹³. Separation of arsenic species in the presence of other metals has been achieved at ppb range with sodium bis(trifluoroethyl)dithiocarbamate chelation and supercritical fluid chromatography¹⁴.

Stannic silicate loaded with complexones Xylenol and 1,10-phenanthroline has been used as chelation ion exchanger¹⁵. The former was used for the separation of Th^{4+} from Cd^{2+} and Zn^{2+} and Cu^{2+} from Cd^{2+} and Zn^{2+} and the latter was used for the separation of Fe^{3+} from Fe^{2+} . Zn^{2+} and Ca^{2+} ions were quantitatively separated and determined in pharmaceutical preparations on strong acid cation exchanger loaded with neutral red¹⁶. It has also been used for the selective separation of Zn^{2+} and Zr^{6+} from a mixture of metal ions. Binary and selective separation of Hg^{2+} from metal ions viz. Fe^{3+} , Cu^{2+} , Al^{3+} and Ni^{2+} has been achieved on cresol red modified Amberlite IR-400 (Cl⁻ form) resin¹⁷. Selective separation of Zn^{2+} and Hg^{2+} from many other metal ions has been achieved on cation exchange resin Amberlite IR-120 modified by the sorption of 1-(2-pyridylazo)-2-naphthol (PAN)¹⁸ at pH 6. Recently, a wide range of chelation ion exchange resins have been prepared by Shah et al.¹⁹⁻²¹ which show different chelating ability for different metal ions.

The excessive release of metal ions into the natural environment from a number of sources like industries, waste streams, mining, combustion of fossil fuels, automobile emission and indiscriminate urbanization and industrialization has given rise to a serious environmental problem due to toxicity of several metal ions even at very low concentration. Hence, there is a need to continuously monitor the metal

ion concentration in the environment. Techniques such as Atomic Absorption Spectrometry (AAS), Inductively Coupled Plasma- Atomic Emission Spectrometry (ICP-AES), and Inductively Coupled Plasma-Mass Spectrometry (ICP-MS) are routinely used for accurate determination of metal ion concentration in all types of samples. Sometimes it is extremely important to remove sample matrix and/or preconcentrate metal ions of interest before analysis on AAS, ICP-AES and ICP-MS. For many years chelation ion chromatography has been used for the separation and preconcentration of metal ions in complex matrices like sea water, brine and acid decomposed animal, plant and geological samples.

Sigh and Raj²² have used PAN sorbed stannic silicate for the recovery of Pt^{4+} and Au^{3+} (1-5 mg) from dilute solutions in the presence of Co^{2+} , Ni^{2+} , Cu^{2+} and Fe^{2+} (5mg each) at pH 2. In addition quantitative binary separations like Co^{2+} - Ni^{2+} , Cu^{2+} - Ni^{2+} , Pt^{4+} - Ni^{2+} , Ag^{2+} - Cu^{2+} , Mn^{2+} - Zn^{2+} , Pb^{2+} - Cd^{2+} have been achieved using various eluents like 0.01M HCl, 0.05M EDTA, 4M NH_3 , 0.1M NH_3 and Demineralized water.

In the present study, the authors have used PAN sorbed stannic silicate for the selective separation of Cd^{2+} , Hg^{2+} and Pb^{2+} from some transition metal ions using only nitric acid solution of pH 1 and 6 as eluents. Cd^{2+} , Hg^{2+} and Pb^{2+} are among the most toxic metal ions and hence this method will find application in environmental monitoring and assessment.

EXPERIMENTAL

Reagents and chemicals:

Stannic chloride pentahydrate (Loba Chemicals) and sodium silicate (Merck India) used for synthesis of Stannic silicate ion-exchanger were Analytical Grade reagents. Solution of 1-(2-Pyridylazo)-2-naphthol (S.D. fine chemicals, India) was prepared in ethanol (1%). 0.1 M solutions of metal ions were prepared by dissolving corresponding metal nitrates/chlorides in double distilled water. All the salts of metal ions were analytical grade reagents.

Synthesis of stannic silicate

Stannic silicate was prepared by mixing 0.1M solution of stannic chloride pentahydrate and 0.1M solution of sodium silicate as per the method described elsewhere²³. The white precipitate formed was kept standing at room

temperature for 24 hours. The precipitate was filtered and dried at 60°C.

Preparation of 1-(2-pyridylazo)-2-naphthol (PAN) sorbed stannic silicate.

100 g of stannic silicate was treated with 500 ml of 100 ppm solution of 1-(2-pyridylazo)-2-naphthol (PAN) for 24 hours with intermittent shaking to ensure maximum adsorption. The procedure is in consonance with similar other studies carried out by Rawat et al.¹⁵ and Nabi et al.^{10,13,16,18} on modification of ion exchange resins with chelating agents. After separating from the solution the exchanger was washed with demineralized water until the supernatant liquid was free from excess reagent and finally dried at 40°C for 24 hours.

Adsorption of metal ions on modified stannic silicate

Effect of time

The effect of time on the amount of metal ions adsorbed was determined by batch equilibrium technique. 0.5 g of the modified exchanger was shaken on a temperature controlled SICO shaker with 2.5×10^{-2} M solution of a metal ion solution in a series of stoppered conical flasks for different time intervals viz. 5, 10, 15, 20, 25, 30, 35, 40, 45, 50 minutes. After shaking for the given time interval supernatant liquid was taken and the concentration of the unadsorbed metal ions determined by titration with EDTA. The amount of sorbed metal ions was then calculated from the difference of the amount of metal ions initially taken and amount found after shaking.

Distribution coefficients

Distribution coefficients of metal ions on modified stannic silicate were determined by batch equilibrium technique at room temperature. 0.5 g of the modified stannic silicate was equilibrated for one hour with 20 ml of 5.0×10^{-3} M solution of a metal ion at different pH ranging from 1 to 6 in separate flasks. The pH was maintained by the addition of HNO₃. After equilibration with intermittent shaking the solution was filtered and the filtrate analyzed for the amount of metal ions by titrimetry. The amount of the metal ions adsorbed was then calculated from the difference of amount of metal ions initially taken and the metal ions found in the filtrate. The distribution coefficient (K_d) is given by

$$K_d = \frac{\text{Amount of metal ions in one gram of ion exchanger}}{\text{Amount of metal ions in one mL of solution}}$$

Quantitative separation of metal ions in binary synthetic mixtures

The separation of metal ions was carried out by elution technique. 2.0 g of modified stannic silicate was packed in a glass column 0.6 cm in internal diameter and 30 cm in length, with glass wool support at the end. It was washed thoroughly with DMW a couple of times. 4 ml of the binary mixture of metal ions to be separated was poured on the top of the column and the solution was allowed to flow gently maintaining a flow rate of 2-3 drops per minute. The elution of metal ions was then carried out using appropriate mobile phase in the usual manner at a constant flow rate of 4 ml per minute. The eluent fractions were collected in separate flasks (at 10 ml interval) and analyzed for metal ion concentration by titration with EDTA. The separation of metal ions takes less than an hour in all the cases studied.

Selective separation of Cd²⁺, Hg²⁺ and Pb²⁺ from synthetic mixtures.

For selective separation of Cd²⁺, Hg²⁺ and Pb²⁺ synthetic solutions of metal ions containing Al³⁺, Mn²⁺, Fe³⁺, Co²⁺ and Ni²⁺ were used. The synthetic mixtures were prepared by mixing 1mg each of Al³⁺, Mn²⁺, Fe³⁺, Co²⁺ and Ni²⁺ in known volumes of distilled water. Known amounts of Cd²⁺, Hg²⁺ and Pb²⁺ were added to separate mixtures of metal ions. 4ml of the mixture of metal ions was poured on the top of the column and separation carried out in the same manner as described for the binary mixtures above. The process was repeated for all the three metal ions Cd²⁺, Hg²⁺ and Pb²⁺ separately.

RESULTS AND DISCUSSION

Chelating ion exchangers show higher selectivity than simple exchangers. It is why Stannic silicate has been modified with a chelating agent 1-(2-pyridylazo)-2-naphthol (PAN). Immediately after coming in contact with it, stannic silicate starts adsorbing 1-(2-pyridylazo)-2-naphthol (PAN) which is indicated by the colour change to yellow which deepens with time. However, 24 hours contact time was given to obtain complete adsorption of PAN onto stannic silicate.

Table I Distribution coefficients (K_d) of metal ions in aqueous solutions of different pH values on PAN sorbed stannic silicate

Metal ion	K_d					
	pH-6	pH-1	pH-2	pH-3	pH-4	pH-5
Al ³⁺	0.00	1.02	4.50	23.75	56.5	60.01
Cr ³⁺	0.00	0.00	7.05	13.30	25.53	41.02
Mn ²⁺	0.00	4.61	38.45	90.1	185.33	626.33
Fe ³⁺	8.11	14.59	30.52	110.26	279.94	493.85
Co ²⁺	10.15	73.71	80.36	296.11	390.00	651.93
Ni ²⁺	0.00	4.90	41.45	138.64	168.89	533.08
Cu ²⁺	2.66	8.98	94.35	389.42	447.30	-
Zn ²⁺	0.00	5.72	26.23	43.00	83.44	-
Cd ²⁺	0.00	7.65	114.20	365.43	449.60	1339.10
Hg ²⁺	0.00	6.54	72.15	193.90	247.19	1250.74
Pb ²⁺	1.47	22.60	225.17	394.30	585.08	1415.32

Table II Binary separation of metal ions on PAN sorbed stannic silicate column

S.No.	Mixture	Eluent	Volume of eluent [ml]	Amount loaded [mg]	Amount found [mg]	Error [%]
1	Al ³⁺	10 ⁻⁶ HNO ₃	70	0.540	0.534	1.11
	Hg ²⁺	10 ⁻¹ HNO ₃	80	4.012	3.911	2.55
2	Cr ³⁺	10 ⁻⁶ HNO ₃	80	1.039	3.967	1.12
	Pb ²⁺	10 ⁻¹ HNO ₃	80	1.270	1.251	1.60
3	Cr ³⁺	10 ⁻⁶ HNO ₃	80	1.039	1.036	0.28
	Cd ²⁺	10 ⁻¹ HNO ₃	100	2.248	2.180	3.11
4	Cr ³⁺	10 ⁻⁶ HNO ₃	80	1.039	1.019	1.96
	Hg ²⁺	10 ⁻¹ HNO ₃	80	4.012	3.951	1.51

Table III Selective separation of Cd²⁺, Hg²⁺ and Pb²⁺ from solutions containing one mg each of Al³⁺, Mn²⁺, Fe³⁺, Co²⁺ and Ni²⁺

Metal ion	Amount loaded [mg]	Amount found [mg]	Error [%]
Cd ²⁺	2.05	2.02	1.46
Hg ²⁺	2.76	2.67	3.26
Pb ²⁺	3.10	3.03	2.25

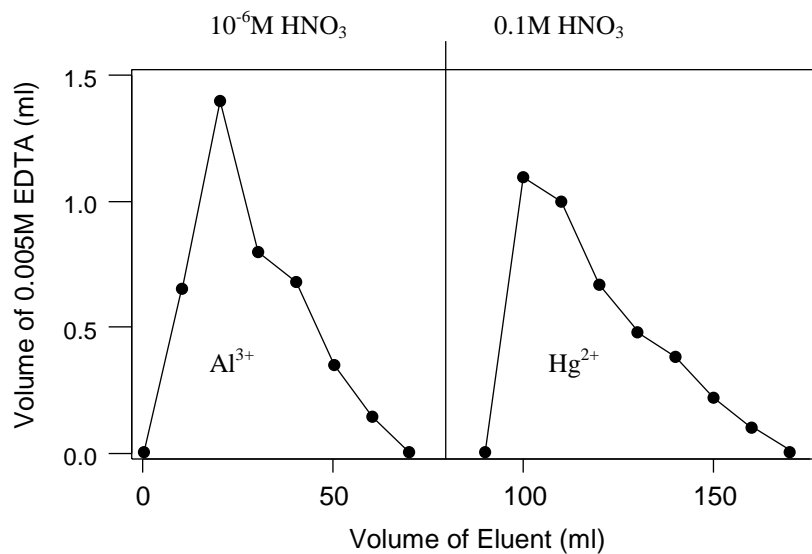


Figure 1 Separation of Al³⁺ and Hg²⁺ on PAN sorbed stannic silicate column

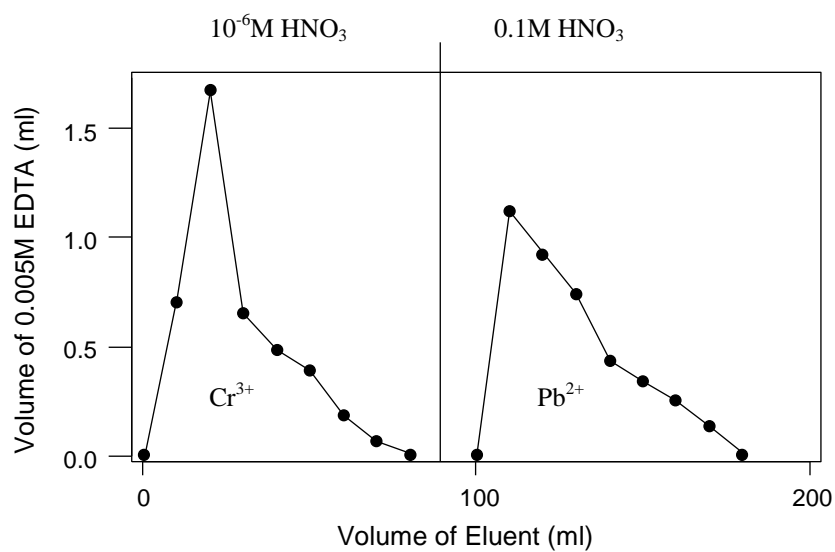


Figure 2 Separation of Cr³⁺ and Pb²⁺ on PAN sorbed stannic silicate

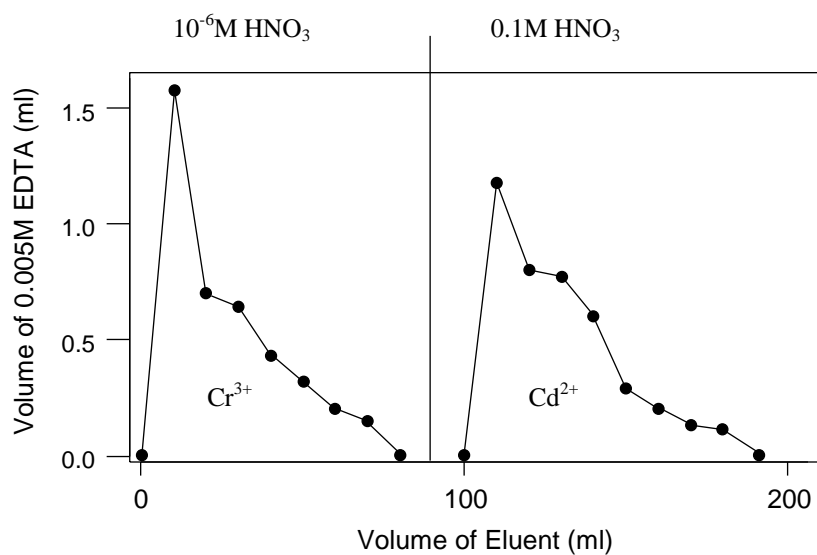


Figure 3 Separation of Cr^{3+} and Cd^{2+} on PAN sorbed stannic silicate

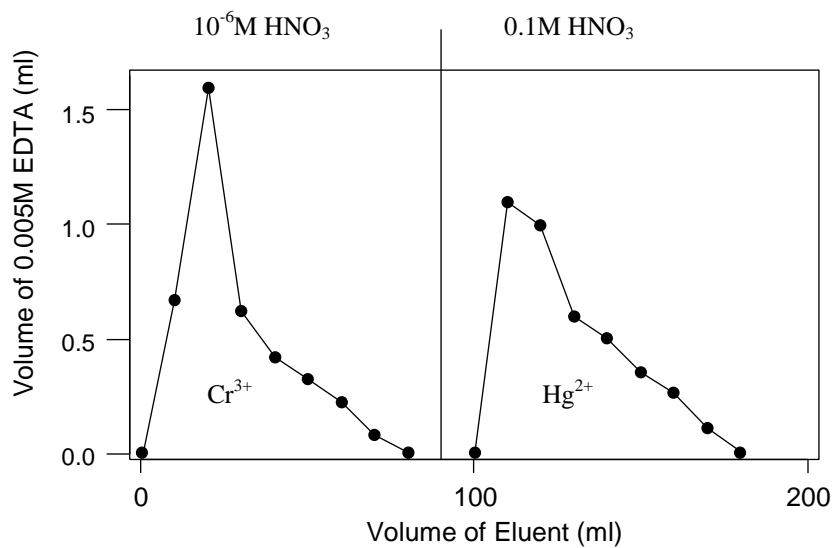


Figure 4 Separation of Cr^{3+} and Hg^{2+} on PAN sorbed stannic silicate

Stannic silicate which originally had sodium ion capacity of $0.5 \text{ meq} \cdot \text{g}^{-1}$ acquired chelation ion capacity after the adsorption of 1-(2-pyridylazo)-2-naphthol (PAN) which possesses complexing groups on it. To investigate the separation potential of modified Stannic silicate, adsorption behaviour of several metal ions from aqueous solution was studied at pH 1, 2, 3, 4, 5 and 6 (except for Cu^{2+} and Zn^{2+} in which precipitation is observed beyond pH 5). It has been found that the uptake of the metal ions increases with increase in contact time and becomes constant from 20 to 30 minutes for all the metals ions studied. Hence, one hour contact time was fixed for subsequent metal ion adsorption experiments. No fading of yellow colour of the modified ion exchanger was observed during adsorption experiments to indicate any leaching of PAN. pH of the metal ion solutions has shown a profound effect on the adsorption of the modified exchanger for different metal ions. The uptake of all the metal ions studied increases with the increase in pH and reaches a maximum at pH 6 and so does the K_d value. The K_d values calculated for various metal ions at different pH values are reported in Table 1. The K_d values of various metal ions on the modified Stannic silicate at pH-6 are in the following order: $\text{Pb}^{2+} > \text{Cd}^{2+} > \text{Hg}^{2+} > \text{Co}^{2+} > \text{Mn}^{2+} > \text{Ni}^{2+} > \text{Fe}^{3+} > \text{Al}^{3+} > \text{Cr}^{3+}$ with K_d values of Pb^{2+} , Cd^{2+} and Hg^{2+} being much higher, even more than ten times the K_d values of some other metal ions studied, making their chromatographic separation from these metal ions feasible. Table 2 lists some binary separation e.g. Hg^{2+} from Al^{3+} , Pb^{2+} from Cr^{3+} , Cd^{2+} from Cr^{3+} , Hg^{2+} from Cr^{3+} successfully achieved on a column packed with 1-(2-pyridylazo)-2-naphthol (PAN) sorbed stannic silicate, using aqueous solutions of pH 6 and pH 1 as eluents. Elution profiles (chromatograms) of binary separations achieved on 1-(2-pyridylazo)-2-naphthol (PAN) sorbed stannic silicate are given in figures 1 to 4. The much higher K_d values of Cd^{2+} , Pb^{2+} and Hg^{2+} than that of many other metal ions studied makes it possible to selectively separate them from a mixture of other metal ions. Table 3 gives the details of selective separation of Cd^{2+} , Pb^{2+} and Hg^{2+} from synthetic solutions containing Al^{3+} , Mn^{2+} , Fe^{3+} , Co^{2+} and Ni^{2+} .

CONCLUSIONS

1-(2-Pyridylazo)-2-naphthol sorbed stannic silicate preferentially adsorbs Cd^{2+} , Pb^{2+} and Hg^{2+} from an aqueous solution of some transition

metal ions. It has been successfully used for some important binary separations e.g. Hg^{2+} from Al^{3+} , Pb^{2+} from Cr^{3+} , Cd^{2+} from Cr^{3+} , Hg^{2+} from Cr^{3+} using aqueous solutions of pH 6 and pH 1 as eluents. Besides it can be used for the selective separation of Cd^{2+} , Pb^{2+} and Hg^{2+} from an aqueous solution of some other metal ions for further analysis-an important application in environmental pollution monitoring and assessment.

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