Metal ion chelation chromatography on dithizone sorbed stannic silicate : Binary separation of Cd^{2+}, Hg^{2+}, Pb^{2+} and Cr^{3+} from Fe^{3+} and Al^{3+}

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Abstract : Stannic silicate, a cation exchanger, has been modified by adsorption with dithizone. Adsorption behaviour of several transition and heavy metal ions like Al^{3+}, Cr^{3+}, Mn^{2+}, Fe^{3+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, Hg^{2+} and Pb^{2+} on the modified ion exchanger from aqueous solution at different pH (from 1-6) has been studied and their distribution coefficients (K_d) calculated. While Cd^{2+}, Hg^{2+}, Pb^{2+} and Cr^{3+} show very high adsorption on the modified exchanger, Fe^{3+} and Al^{3+} are adsorbed the least among the metal ions studied. On the basis of distribution coefficients binary separations of Cd^{2+}, Hg^{2+}, Pb^{2+} and Cr^{3+} from Fe^{3+} and Al^{3+} have been achieved on a chromatographic column packed with dithizone sorbed stannic silicate using nitric acid solution of pH 6 and pH 1 as eluents.

Keywords : Metal ion, dithizone, binary separation, chromatography, distribution coefficients.

Introduction

The excessive release of metal ions into the natural environment from a plethora of human activities and toxicity of some of them to all forms of life even at low concentration has necessitated the development of sensitive and selective methods for their determination in different sample types. Techniques such as Atomic Absorption Spectrometry, Inductively Coupled Plasma-Atomic Emission Spectrometry and Inductively Coupled Plasma-Mass Spectrometry 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 now 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. 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

ion exchangers 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, selectivity factors are lower.

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 has been receiving attention for a long time now as illustrated in a number of fundamental reviews by Sahni and Reedijk[1], Myasoedova and Savvin[2], Biernat et al.[3], Torre and Marina[4], Nickson et al.[5], Garg et al.[6] and Pereira and Arruda[7] . 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 Kingston[8]. A chromatographically useful packing material has been prepared by immobilizing 8-hydroxyquinoline on Porasil[9].

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 ethylenediaminotriacetic acid, imminodiacetic acid and dimethyl glyoxime have been used to prepare various useful chelation ion exchangers. Titan yellow loaded Amberlite IR-120 has been used for selective removal[10] 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 developed[11]. 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 ions[12]. 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 al.[13]. 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 chromatography[14]. Zn^{2+} and Ca^{2+} ions were quantitatively separated and determined in pharmaceutical preparations on strong acid cation exchanger loaded with neutral red[15]. It has also been used for the selective separation of Zn^{2+} and Zr^{6+} from a mixture of some other 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) resin[16]. 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)[17] at pH 6. Recently, a wide range of chelation ion exchange resins have been prepared by Shah et al.[18-21] which show different chelating ability for different metal ions. Trace transition metals (Fe^{3+}, Mn^{2+}, Cu^{2+}, Cd^{2+}, Co^{2+}, Zn^{2+} and Ni^{2+}) in environmental samples were analyzed by chelation ion chromatography using a mixed bed ion exchange column (a bifunctional quaternary ammonium-sulfonate ion exchanger) and pyridine-2,6-dicarboxylic acid and oxalic acid as eluents by Murgia et al.[22]. An ion chromatographic method for the separation of high valence metal cations including uranium, zirconium and hafnium from titanium, stannic, vanadium and ferric ions using a neutral polystyrene resin dynamically modified with dipicolinic acid has been developed by Cowan et al.[23]. Preconcentration/separation of Co^{2+}, Fe^{3+}, Pb^{2+}, Cr^{3+}, Cu^{2+} and Cd^{2+} ions using sodium dodecyl sulfate coated alumina modified with bis(5-bromo-2-hydroxy-benzaldehyde)-2-methyl-1,5-pentane diimine has been recently reported[24]. Naushad et al.[25] has successfully used neutral red modified strong acid cation exchange resin for the selective separation of Fe^{3+} from Al^{3+}, Cu^{2+}, Zn^{2+} and Ni^{2+}.

Stannic silicate, a simple cation exchanger with a sodium ion capacity of 0.5 meq g^{-1} has been used as a chelating ion exchanger after modification by adsorption with xylenol and 1,10-phenanthroline[26]. 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+}. Singh and Raj[27] 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+} (5 mg 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 on PAN sorbed stannic silicate. Recently, the authors of this paper achieved selective separation of toxic metal ions viz. Cd^{2+} and Pb^{2+} from a number of other transition metal ions on stannic silicate modified with Alizarin Red-S[28]. In an extension of work on modified stannic silicate, the authors of this paper have studied the potential of dithizone sorbed stannic silicate in the separation of toxic metal ions from transition metal ions. Dithizone sorbed stannic silicate was found useful in the binary separation of Cd^{2+}, Hg^{2+}, Pb^{2+} and Cr^{3+} from Fe^{3+} and Al^{3+}. The method will be useful in the separation/preconcentration of Cr^{3+}, Cd^{2+}, Hg^{2+} and Pb^{2+} from solutions containing high concentration of Fe^{3+} and Al^{3+}. This method will find application in environmental monitoring and assessment.

Experimental

Reagents and chemicals :

Stannic chloride pentahydrate (Loba Chemie) and sodium silicate (Merck, India) used for synthesis of stannic

silicate ion-exchanger were analytical grade reagents. Solution of dithizone (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 0.1 M solutions of stannic chloride pentahydrate and 0.1 M solution of sodium silicate as per the method described elsewhere[29]. The white precipitate formed was kept standing at room temperature for 24 h. The precipitate was filtered and dried at 60 °C.

Preparation of dithizone sorbed stannic silicate :

100 g of stannic silicate was treated with 500 ml of 100 ppm solution of dithizone for 24 h with intermittent shaking to ensure maximum adsorption. The procedure is in consonance with similar other studies carried out by Nabi *et al.*[10,13,15,17] and Rawat *et al.*[26] 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 h.

Adsorption of metal ion on dithizone sorbed 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 with 2.5×10^{-2} M solution of a metal ion in a series of stoppered conical flasks for different time intervals viz. 5, 10, 15, 20, 25, 30, 35, 40, 45, 50 min. After shaking for a given time interval supernatant liquid was taken and the concentration of the unsorbed metal ion determined by titration with EDTA. The amount of sorbed metal ion 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 $\times$ 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 HNO_3. 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

$$K_d = \frac{\text{Amount of metal ions in exchanger phase g}^{-1}}{\text{Amount of metal ions in solution phase mL}^{-1}}$$

Quantitative separation of metal ions in binary synthetic mixtures :

The separation of metal ions was carried out by elution technique. 2.0 g 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 min. The elution of metal ions was then carried out using nitric acid solution of pH 6 and pH 1 as mobile phase in the usual manner at a constant flow rate of 18–20 drops per min. The eluent fractions were collected in separate flasks (at 10 ml interval) and analyzed for metal ion concentration by titration with EDTA and Atomic Absorption Spectrometry. AAS was particularly used to detect the presence or absence of a metal ion in collected eluent fractions. The Fe^{3+} (or Al^{3+}) ions were eluted first using 10^{-6} M HNO_3 solution while Cr^{3+} (or $Cd^{2+}/Hg^{2+}/Pb^{2+}$) ions were strongly retained by the modified exchanger (having high K_d value at pH 6). Once all the Fe^{3+} ions were completely eluted a solution of 0.1 M HNO_3 was passed through the column which elutes Cr^{3+} ions; the K_d values of all the metal ions being very low at pH 1.

Results and discussion

Chelating ion exchangers show higher selectivity than simple exchangers. Excellent selective separations of some metal ions have been achieved on stannic silicate modified with chelating agents like xylenol[26], 1,10-phenanthroline[26], PAN[27] and Alizarin Red-S[28]. In the present study stannic silicate has been modified by adsorption with dithizone. Immediately after coming in con-

tact with it, stannic silicate starts adsorbing dithizone which is indicated by the colour change to gray which deepens with time. However, 24 h contact time was given to obtain maximum adsorption of dithizone onto stannic silicate. Stannic silicate which originally had the sodium ion capacity of 0.5 meq g^{-1} acquired chelation ion capacity after the adsorption of dithizone 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 1-6 (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 20-30 min for all the metals ions studied. Hence, one hour contact time was fixed for subsequent metal uptake experiments. 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 Cr^{3+}, Cd^{2+}, Hg^{2+} and Pb^{2+} on the modified stannic silicate at pH 6 are much higher than that of Fe^{3+} and Al^{3+} making feasible their chromatographic separation from Fe^{3+} and Al^{3+}. Moreover, K_d values at pH 1 are very low for all the metal ions studied. Table 2 lists some binary separation e.g. Fe^{3+}-Hg^{2+}, Fe^{3+}-Pb^{2+}, Fe^{3+}-Cd^{2+}, Fe^{3+}-Cr^{3+}, Al^{3+}-Pb^{2+}

and Al^{3+}-Cd^{2+} successfully achieved on a column packed with dithizone sorbed stannic silicate, using aqueous so-

Table 2. Binary separation of metal ions on dithizone sorbed stannic silicate

Sl. no.	Mixture	Eluent (M, HNO₃)	Volume of eluent (ml)	Amount loaded (mg)	Amount found (mg)	Percent error
1	Fe^{3+}	10^{-6}	60	1.116	1.111	0.45
	Hg^{2+}	10^{-1}	90	4.012	3.902	2.74
2.	Fe^{3+}	10^{-6}	60	1.116	1.076	2.04
	Pb^{2+}	10^{-1}	60	4.144	3.916	5.82
3.	Fe^{3+}	10^{-6}	60	1.116	1.107	0.81
	Cd^{2+}	10^{-1}	70	2.248	2.158	4.00
4.	Fe^{3+}	10^{-6}	60	1.116	1.102	1.25
	Cr^{3+}	10^{-1}	70	1.039	0.098	5.00
5.	Al^{3+}	10^{-6}	100	0.540	0.536	0.74
	Pb^{2+}	10^{-1}	60	4.144	4.102	1.01
6.	Al^{3+}	10^{-6}	100	0.540	0.519	3.89
	Cd^{2+}	10^{-1}	70	2.248	2.189	2.62

Fig. 1. Separation of Fe^{3+} and Hg^{2+} on dithizone sorbed stannic silicate.

Table 1. Distribution coefficients (K_d) of metal ions in aqueous solutions of different pH values on dithizone sorbed stannic silicate

Metal ion	K_d					
	pH 1	pH 2	pH 3	pH 4	pH 5	pH 6
Al^{3+}	2.3	4.4	83	108	170	187
Cr^{3+}	0.0	4.4	79.4	170	392	1190
Mn^{2+}	0.0	3.2	71.1	126	218	575
Fe^{3+}	0.0	24	150	245	93.3	133
Co^{2+}	7	77.6	105	202	460	960
Ni^{2+}	5.19	15.7	54	137	307	802
Cu^{2+}	3.95	7.1	226	360	626	–
Zn^{2+}	0.0	0.0	32	105	126	–
Cd^{2+}	0.0	20	198	267	531	1102
Hg^{2+}	2.3	21	240	381	721	1293
Pb^{2+}	1.7	17.1	188	210	493	1026

Fig. 2. Separation of Fe^{3+} and Pb^{2+} on dithizone sorbed stannic silicate
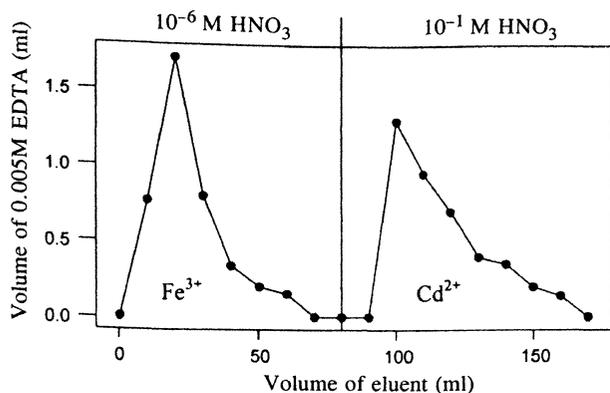
Fig. 3. Separation of Fe^{3+} and Cd^{2+} on dithizone sorbed stannic silicate.
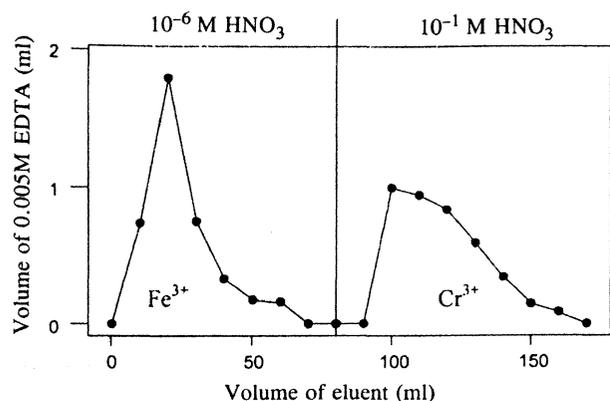
Fig. 4. Separation of Fe^{3+} and Cr^{3+} on dithizone sorbed stannic silicate.

lutions of pH 6 and pH 1 as eluents. While Fe^{3+}/Al^{3+} ions were eluted first using 10^{-6} M HNO_3 solution, $Cr^{3+}/Cd^{2+}/Hg^{2+}/Pb^{2+}$ ions were eluted by a solution of 0.1 M HNO_3. Elution profiles (chromatograms) of binary separations achieved on dithizone sorbed stannic silicate are given in Figs. 1 to 4. The method will be useful in the separation/preconcentration of Cr^{3+}, Cd^{2+}, Hg^{2+} and Pb^{2+} from solutions containing high concentration of Fe^{3+} and Al^{3+}.

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