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Synthesis and Application of Ion Selective Chelating Resin Derived from Guar

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Guar gum (a polysaccharide derived from the seed of guar plant, *Cyamoposis tetragonalobus*) a hydrophilic polysaccharide matrix has been used for preparation of a new chelating resin. The preferential complexing tendency of different metal ions towards chelating agents anchored on a polymer has been used for separation of transition metals. The 5-amino salicylic acid group was anchored on the guar backbone in dioxane medium. This ion selective chelating resin has been used in column chromatographic separation of copper(II) and iron(III).

Key words: Ion selective chelating resin, 5-amino salicylic acid, column chromatography, polysaccharide, guar gum.

INTRODUCTION

Complex equilibria and ion exchange chromatography are closely related. The merging of these disciplines has contributed significantly to inorganic analysis[1, 2]. The use of complex ion formation in ion exchange chromatography allows the separation of metals, which, without complex ion formation, would be very difficult or impossible to separate. A number of chelating ion exchange resins[3, 4] have been produced by resin manufacturers to overcome this problem and so encourage the application of ion exchange[5] to a broader range of process solutions[6]. Using high capacity cation and anion exchange resins with metal complexing eluents, the separation of many transition and post-transition metals was accomplished. Guar polyions have been used in ion-exchange chromatography of many biological materials and metal ions.

The preferential complexing tendency of a chelating agent anchored on a polymer is used for separation of transition metals[7]. Some water soluble guar based polymeric metal ions precipitated were reported from our laboratory as toxic metal ion scavengers[8]. We have considered that cross-linking[9] of the guar polymer matrix shall yield insoluble resins suitable for use in a column.

Guar[10] being hydrophilic in nature is preferred as a base polymer for the preparation of cation exchangers. Cyanuric chloride reacts with guar at low temperature (5–10°C) and gets attached to —CH_2OH. The two free chlorine atoms at alternate positions are then reacted with 5-amino salicylic acid to form a guar triazine 5-amino salicylic acid conjugate. The polymer bound salicylic acid has been used in column chromatographic separation of copper(II) and iron(III).

EXPERIMENTAL

All the chemicals used were of high purity commercially available reagents.

IR spectra were recorded using Schimadzu IR 440 spectrophotometer. Elemental analysis was done by Carlo Erba Strumentenzione Model 1106. Metal ions were estimated, using a Schimadzu AA-630-12 atomatic absorption spectrophotometer.

The derivatised guar was prepared with the same method as described elsewhere. The guar triazine 5-amino salicylic acid (referred as GTASA hereafter) was analysed (Table-1). Its cation exchange capacity was determined using standard method[11] and was found to be 0.30 meq/g of dry resin. The capacity of reprocessed GTASA was found to be 0.31 meq/g of dry resin. Standard solutions of copper(II) sulphate and ferric ammonium sulphate were prepared. 0.2 M acetic acid and 0.2 M sodium acetate solutions were used to prepare buffers of various pH.

15–20 cm long glass column of uniform diameter (0.74—1 cm) was used. A slurry of GTASA was prepared in doubly distilled water and was poured down the column. The height of the resin in the column was around 6 to 8 cm. Individual metal ions were loaded on the column one at a time and were eluated at different pH. Similarly a mixture of copper(II) and iron(III) was loaded and the different bands on the column were eluated by eluent having suitable pH. The quantity of individual metal ions was then determined in the eluate by atomic absorption spectrophotometry and iodimetrically.

The distribution coefficient (K_d) was found for copper and iron at equilibrium in GTASA (Table-2).

Determination of Distribution Coefficient: K_d values were calculated using standard method[12] and are recorded in Table-2.

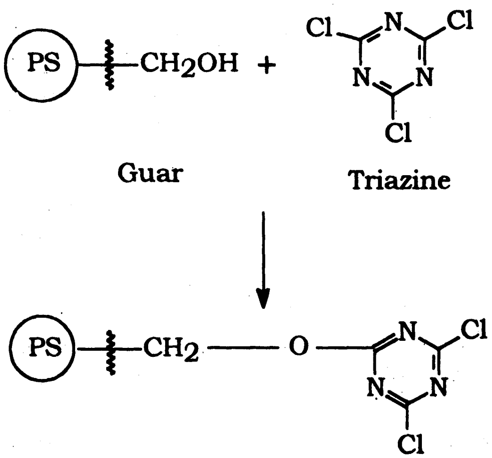
RESULTS AND DISCUSSION

Synthesis and structure of resin: The ligand bound polymer was prepared as in Scheme 1. Its capacity found by standard method is 0.30 meq/g.

The elemental analysis (Table-1) showed that only one chlorine of cyanuric chloride was replaced by salicylic acid and the other chlorine was hydrolyzed to form a hydroxyl group. In the IR spectra of chelating polymer a medium intensity broad band envelope at 3610–3470 cm^{-1} was observed and is ascribed to phenyl hydroxy group; a band at 3280 cm^{-1} is assigned to ν(N—H) and one at 1645 cm^{-1} is assigned to ν(C=O). Since the polymer is of the Na-salt form, the formation of intrahydrogen bond is negligible.

TABLE-1
ANALYTICAL DATA OF POLYMER BOUND CHELATING AGENTS

Sodium salt of (GTASA)	Analysis (%)		
	C	H	N
Found	44. 14	2.67	18.72
Calculated	44.01	2.52	18.65



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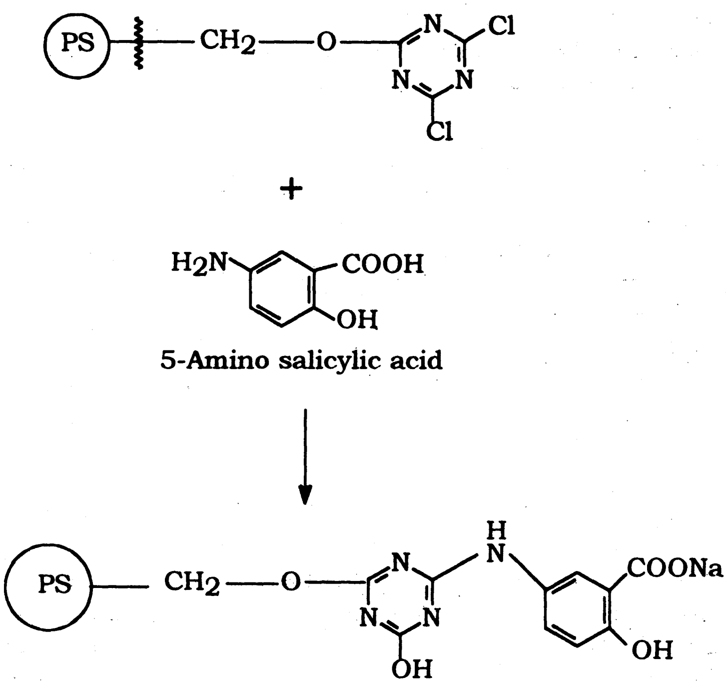

II

Guar triazine -5-Amino Salicylic acid

TABLE 2
DISTRIBUTION COEFFICIENT OF METAL IONS ON EQUILIBRIUM AT DIFFERENT pH

S.No.	pH of the solution	$K_d = \frac{\text{Amt. of metal ion in resin phase/g resin}}{\text{Amt. of metal ion in solution phase/mL}}$	
		Cu^{2+}	Fe^{3+}
1.	3.42	1.89	42.84
2.	4.45	38.21	36.66
3.	5.57	93.53	17.74

The stability constant of Fe(III) salicylate is higher than that of Cu(II). The GTASA binds iron(III) in preference to copper. By examining Table-3, we observe that both these metals can be quantitatively separated within the experimental concentration range.

It could be speculated that it is easier for copper and iron ions to complex with pendant O—CH_2OH group in guar or —OH attached to triazine ring in GTASA than with —COOH and —OH of salicylic acid. Dare and Kumar showed that the uptake of Cu^{2+} is considerably higher in functionalized than in untreated polymeric materials. Plane guar does not retain copper(II) or iron(III) ions when loaded on a column. The extent of binding of various metal ions by GTASA can be estimated from the difference between the initial and final concentrations of respective metal ions. The values so calculated are given in Table 3.

TABLE-3
AMOUNT OF Cu^{2+} AND Fe^{3+} LOADED ON DIFFERENT COLUMNS AND IN ELUATE FROM THE COLUMN

S. No.	Cu^{2+} (mg)				Fe^{3+} (mg)			
	Amt. loaded	Recovery	S.D.	C.V.	Amt. loaded	Recovery	S.D.	C.V.
1.	6.30	6.29	0.007	0.112	0.56	0.55	0.007	1.20
2.	9.45	9.43	0.014	0.149	0.84	0.83	0.007	0.82
3.	12.60	12.59	0.007	0.056	1.40	1.38	0.007	0.50

S.D. = Standard deviation; C.V. = Coefficient of variation; Number of determinations = 5.

Data in Table-4 show that the separation of iron(III) and copper(II) is very effective in low concentration and at controlled pH. With the change in pH of eluent, the separation of these ions is quantitative. Copper and iron are separated at pH 2.3 and 1.0, respectively (Table-4). Copper is eluated very quickly (10 min/estimation) but iron is eluated with difficulty (2 h/estimation), the reason being that iron salicylate is quite a stable complex as compared to copper complex. The eluates of individual metal ions are collected separately and estimated for the metal contents. Both by atomic absorption sepctrophotometry and by conventional methods the results are quite satisfactory.

TABLE-4
SEPARATION OF METAL IONS

Eluent 1. Dil. $HClO_4$ of pH = 2.3 for Cu^{2+}. *Eluent 2.* Dil. $HClO_4$ of pH = 1.0 for Fe^{3+}.

S. No.	Amt. of Cu^{2+} and Fe^{3+} in mixture loaded on column (mg)		Amount of Cu^{2+} and Fe^{3+} in eluate (mg)					
	Cu^{2+}	Fe^{3+}	Cu^{2+}	S.D.	C.V.	Fe^{3+}	S.D.	C.V.
1.	3.15	0.280	3.14	0.007	0.225	0.26	0.014	5.27
2.	1.89	0.392	1.88	0.007	0.375	0.39	0.014	3.58

Number of determinants = 5.

The method of separation of metal ions is very simple, easy and can be proposed as a standard method. The GTASA resin can be regenerated and used again and again. The reactivation is done by alternate treatment with an acid ($HClO_4$) and NaOH of standard strength.

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