

Thiosalicylic acid-immobilized Amberlite XAD-2: metal sorption behaviour and applications in estimation of metal ions by flame atomic absorption spectrometry

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Received 18th August 2000, Accepted 26th September 2000
First published as an Advance Article on the web 3rd November 2000

Thiosalicylic acid (TSA)-modified Amberlite XAD-2 (AXAD-2) was synthesized by coupling TSA with the support matrix AXAD-2 through an azo spacer. The resulting chelating resin was characterized by elemental analyses, thermogravimetric analysis (TGA) and infrared spectra. The newly designed resin quantitatively sorbs Cd^{II} , Co^{II} , Cu^{II} , Fe^{III} , Ni^{II} and Zn^{II} at pH 3.5–7.0 when the flow rate is maintained between 2 and 4 ml min^{-1} . The HCl or HNO_3 (2 mol l^{-1}) instantaneously elutes all the metal ions. The sorption capacity is 197.5, 106.9, 214.0, 66.2, 309.9 and 47.4 $\mu\text{mol g}^{-1}$ of the resin for cadmium, cobalt, copper, iron, nickel and zinc, respectively, whereas their preconcentration factor is between 180–400. The breakthrough volume of HCl or HNO_3 for elution of these metal ions was found to be 4–8 ml. The limit of detection (LOD) for Cd^{II} , Co^{II} , Cu^{II} , Fe^{III} , Ni^{II} and Zn^{II} was 0.48, 0.20, 4.05, 0.98, 1.28 and 3.94 $\mu\text{g l}^{-1}$, respectively, and the limit of quantification (LOQ) was found to be 0.51, 0.29, 4.49, 1.43, 1.58 and 4.46 $\mu\text{g l}^{-1}$, respectively. The loading half time, $t_{1/2}$, for the cations was found to be less than 2.0 min, except for nickel for which the value was 13.1 min. The determination of each of these six cations is possible in the presence of other five, if their concentration is up to 4 times. All six metals were determined in river water (RSD \approx 0.7–7.7%) and tap water samples (RSD \approx 0.3–5.7%). The estimation of Co was made in the samples of multivitamin tablets (RSD $<$ 2.3%). The results agree with those quoted by manufacturers.

Introduction

Chelating resins are important metal ion collectors suitable for metal ion enrichment prior to determination by AAS or ICP-AES, as they can provide better selectivity than ion-exchangers by controlling the pH. Chelex-100^{1–3} is one such matrix available commercially. Amberlite XAD-2 (styrene-divinylbenzene copolymer) is a promising support,^{4–18} used to develop several chelating resins in the recent past by immobilizing chelating ligands on it. Amberlite XAD-4, 7, 8 and 16,^{19–23} silica gel^{24,25} and cellulose²⁶ are some other important supports used for immobilization of ligands. The ligands are generally coupled through a methylene⁵ or an azo⁶ spacer onto the matrix Amberlite XAD-2 to design the chelating resin. Alizarin Red-S,⁶ salicylic acid,⁷ pyrocatechol violet,⁸ 8-hydroxyquinoline,⁹ *o*-aminophenol,¹¹ calmagite,^{12,13} chromotropic acid,¹⁴ tiron,¹⁵ dithiocarbamate¹⁷ and *o*-vanillinthiosemicarbazone¹⁸ are some of the ligands immobilized on this support. However, thio ligands are poorly¹⁸ immobilized on Amberlite XAD-2. It was therefore thought worthwhile to couple thiosalicylic acid (TSA) with Amberlite XAD-2. The combination of ‘soft’ and ‘hard’ donor sites present in TSA is expected to result in a resin of wider applicability and high capacity, as complexes of both ‘hard’ and ‘soft’ metal ions would be stabilized. The resulting matrix, therefore, shows a preconcentration factor of up to 400 for some metal ions. The results of these investigations are described in the present paper.

Experimental

Reagents and solutions

Analytical-reagent grade chemicals were used unless otherwise stated. Stock solutions (1 g l^{-1}) of metal ions were prepared by

dissolving appropriate amounts of analytical-reagent grade CdI_2 , $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$, $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, $(\text{NH}_4)_2\text{SO}_4 \cdot \text{FeSO}_4 \cdot 6\text{H}_2\text{O}$, $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ and $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ in deionized water acidified with 5 ml of the corresponding acid. Aerial oxidation of ferrous ions was used to prepare a solution of Fe^{III} . Complexometric titration with EDTA²⁷ was used to standardize the metal ion solutions. The working solutions of the metal ions were obtained by dilution of the stock solutions with doubly distilled water. The solutions were adjusted to a particular pH using 0.1 mol l^{-1} HCl and NaOH. Acetate²⁷ and phosphate²⁷ buffers were used to adjust the pH in the ranges 3.5–6.0 and 6.8–9.0, respectively, wherever suitable. Amberlite XAD-2 resin (surface area, 330 $\text{m}^2 \text{g}^{-1}$, pore diameter, 90 Å and bead size, 20–60 mesh) was procured from Aldrich (Milwaukee, USA). Thiosalicylic acid (Aldrich, Milwaukee, USA) was used as received. The water samples from the Ganges (Rae Bareli, India) and Gomti (Lucknow, India) rivers and municipal water supply (New Delhi, India) were collected, acidified with 2% HNO_3 immediately, filtered and stored in glass bottles. Amberlite XAD-2 was cleared as described previously.¹¹

Instruments

A flame atomic absorption spectrometer (Electronic Corporation of India Ltd, Hyderabad, India, Model, 4129) employing an air-acetylene flame (air and acetylene flow rates: 10 l min^{-1} and 2 l min^{-1} , respectively) was used for atomic absorption spectrometric measurements. The wavelengths (nm) used for monitoring Cd, Co, Cu, Fe, Ni and Zn are 228.8, 240.0, 324.8, 248.3, 232.0 and 213.9, respectively. Elemental analyses were carried out on a Perkin Elmer (Rotkreuz, Switzerland) elemental analyser, Model 240C, and thermogravimetric analyses (TGA) were carried out on a Dupont (Wilmington, Delaware, USA) 2100 thermal analyser. A Nicolet (Madison, USA) FT-IR

spectrometer, Model Protégé 460, was used to record IR spectra (in KBr) in the range 400–4000 cm^{-1} . The pH was measured with an Elico (Hyderabad, India) pH meter (Model LI-120 digital). The flow of solution through the column was maintained using a peristaltic pump (Watson-Marlow Model 101/U/R, Falmouth, UK). The sorption–desorption studies with all metal ions were generally carried out on columns of 1 cm diameter (Pharmacia, Bromma, Sweden). A mechanical shaker equipped with an incubator (Hindustan Scientific, New Delhi, India), with a speed of 200 strokes min^{-1} was used for metal ion–chelating resin equilibration.

Modification of Amberlite XAD-2 with thiosalicylic acid

The published procedure^{14,15} was used for the nitration of Amberlite XAD-2 beads. The nitrated Amberlite XAD-2 was reduced to an amino polymer by a reported method.^{14,15} The following procedure was used to diazotize the amino polymer and couple it with TSA.

The amino polymer was treated with 2 mol l^{-1} HCl and subsequently washed with doubly distilled water to remove excess of HCl. The hydrochloride of the amino resin was suspended in 200 ml of ice-cold water and reacted with 1 mol l^{-1} HCl and NaNO_2 at -5°C until the reaction mixture began to give a violet colour with starch iodide paper. The resulting diazotized polymer was filtered, maintaining the cold condition, and reacted with thiosalicylic acid (15 g dissolved in 250 ml of 10% NaOH solution) at 0 to -5°C for 24 h. The resulting dark brown coloured beads were filtered, washed and air-dried. Fig. 1 depicts the repeat unit of thiosalicylic acid-modified Amberlite XAD-2.

Recommended procedure for separation and preconcentration

The batch and column methods were both employed for preconcentrating the metal ions. Their details are as follows.

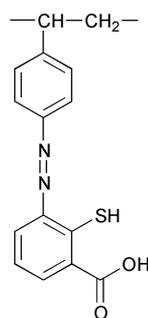


Fig. 1 Thiosalicylic acid immobilized Amberlite XAD-2.

Column method. Thiosalicylic acid-immobilized Amberlite XAD-2 (1 g) was swollen fully in doubly distilled water for 24 h so that its volume became ≈ 1.2 times that of the dry form. It was packed in a glass column (1.0 \times 10.0 cm) and treated with 50 ml of 4 mol l^{-1} HCl or HNO_3 and washed with doubly distilled water until free from acid. A suitable aliquot of the solution containing Cd^{II} , Co^{II} , Cu^{II} , Fe^{III} , Ni^{II} or Zn^{II} in the concentration range of 0.0025–1.0 $\mu\text{g ml}^{-1}$ was passed through this column after adjusting its pH to the optimum value (Table 1) at a flow rate of 2–4 ml min^{-1} . The metal ions from the resin bed were desorbed with 2 mol l^{-1} HNO_3 (10–25 ml) and the eluates were aspirated into the flame of a FAAS instrument, standardized prior to the determination. The dilution with doubly distilled water was made before aspiration in the case of concentrated eluates.

Batch method. A solution (100 ml) containing 0.1–250 $\mu\text{g ml}^{-1}$ of Cd^{II} , Co^{II} , Cu^{II} , Fe^{III} , Ni^{II} or Zn^{II} was placed in a glass stoppered bottle (250 ml) after adjusting its pH to the optimum value (Table 1). Thiosalicylic acid-modified Amberlite XAD-2 (0.4 g) was added to it and the bottle was stoppered and shaken for 30 min. The resin was filtered, washed with doubly distilled water, shaken with 2 mol l^{-1} HNO_3 (10–25 ml) for 20 min and again filtered. The filtrate was aspirated into the flame of a pre-standardized FAAS instrument.

Results and discussion

The beads of Amberlite XAD-2 on loading with TSA change their colour from pale violet to rusty brown, but remain virtually intact. The results of elemental analyses of the dried beads agree with the values calculated by presuming the stoichiometry of its repeat unit to be $\text{C}_{15}\text{H}_{12}\text{N}_2\text{O}_2\text{S}\cdot\frac{3}{2}\text{H}_2\text{O}$ (calculated: C, 57.80%; H, 4.82%; N, 9.00%; found: C, 58.42%; H, 5.15%; N, 7.63%). The thermogravimetric analysis (TGA) curve of the chelating resin shows mass loss in two steps. In the first step, a mass loss of 8.42% up to 125 $^\circ\text{C}$ seems to be due to sorbed water, whereas in the second step (up to 535 $^\circ\text{C}$) mass loss is 41.44%. The TGA and elemental analyses together suggest that nearly one and a half water molecules per repeat unit is sorbed. The IR spectrum of the modified resin TSA-AXAD-2 was compared with that of untreated Amberlite XAD-2. There are two additional bands at 1615 and 1700 cm^{-1} which may be assigned to azo ($-\text{N}=\text{N}-$) and carboxylic acid ($>\text{C}=\text{O}$) stretching vibrations, respectively. The IR spectrum of the metal ion-free chelating resin was compared with those of the metal ion-saturated resin. A red shift (8–15 cm^{-1}) in the bands of the azo group and carbonyl group of carboxylic acid is exhibited in comparison to those of the metal-free resin. This suggests that chelation of metal ions through $-\text{SH}$ and $-\text{COOH}$ or $-\text{N}=\text{N}-$ (azo) groups is probably responsible for metal sorption. The availability of two chelation

Table 1 Optimum conditions for sorption and desorption of metal ions

Experimental parameter	Metal ion					
	Cd^{II}	Co^{II}	Cu^{II}	Fe^{III}	Ni^{II}	Zn^{II}
pH	4.0–4.5	4.0–4.5	3.5–5.0	3.5–4.0	4.5–7.0	4.0–7.0
Flow rate/ ml min^{-1}	2–5	2–4	2–5	2–5	2–3	2–5
HNO_3/HCl concentration for desorption/ mol l^{-1}	0.05–2.00/ 0.10–2.00	0.05–2.00/ 0.05–1.00	0.50–2.00/ 0.20–2.00	2.00–4.00/ 1.00–4.00	0.50–2.00/ 0.50–2.00	0.50–2.00/ 0.20–3.00
Sorption capacity of resin/ $\mu\text{mol g}^{-1}$	197.5	106.9	214.0	66.2	309.9	47.4
Loading half time, $t_{1/2}/\text{min}$	<1	1.7	<1	1.1	13.1	<1
Average recovery (%)	97	98	96	96	92	95
Standard deviation ^a	0.032	0.028	0.020	0.049	0.054	0.028
Relative standard deviation (%) ^a	1.64	1.43	1.04	2.56	2.94	1.50

^a For six determinations of 2 $\mu\text{g ml}^{-1}$.

sites on the resin probably results in its high metal ion sorption capacity.

Optimum conditions for sorption and desorption

The column was packed and cleaned as described in the recommended procedure mentioned above in the Experimental section. A set of solutions was taken for each cation. The pH of each set was varied in the range 2.0–8.0 and the recommended procedure applied. The recovery for all the six cations as a function of pH is shown in Fig. 2. The optimum pH ranges for maximum recoveries are given in Table 1. The acetate and phosphate buffer solutions (2–5 ml) used to maintain the pH of metal ion solutions in the range 3.0–6.0 and 6.8–8.0, respectively, do not affect the sorption and are suitable for pH adjustments. Other optimum conditions determined in a similar way are given in Table 1. Acid concentrations of $>4 \text{ mol l}^{-1}$ were not studied for desorption, as the partial neutralization needed before measurement with AAS would reduce the preconcentration factor. The sorption capacity (per g of resin) for each metal ion was determined by the column and batch methods. The resin was saturated with metal ions and the total metal sorbed was estimated with FAAS after stripping it off from the resin with acid. The values of sorption capacity determined by the two methods are consistent (variation 1.0–2.5%). The results are given in Table 1. The capacity for different metal ions probably varies due to their size, degree of hydration and the stability constants of their complexes with thiosalicylic acid.

Calibration curve for working ranges

The calibration curves were drawn after setting various parameters of FAAS (*viz.* wavelength, slit-width, lamp current) for metal ions at an optimum level and employing optimum preconcentration parameters. The curves were found to be linear for working ranges ($\mu\text{g ml}^{-1}$) given in the parentheses: Cd (0.5–2.5), Co (0.1–12.0), Cu (0.5–8.0), Fe (0.5–15.0), Ni (0.5–15.0) and Zn (0.1–2.0). The linear equation along with regression (r^2) are as follow: $\text{Cd}^{\text{II}}, A = 0.1227C + (-0.0051), r^2 = 0.9975$; $\text{Co}^{\text{II}}, A = 0.0166C + (-0.0060), r^2 = 0.9996$; $\text{Cu}^{\text{II}}, A = 0.0674C + (-0.0097), r^2 = 0.9979$; $\text{Fe}^{\text{III}}, A = 0.0259c + (+0.0045), r^2 = 0.9972$; $\text{Ni}^{\text{II}}, A = 0.0196c + (+0.0021), r^2 = 0.9996$; and $\text{Zn}^{\text{II}}, A = 0.1764c + (+0.0104), r^2 = 0.9965$, where A is the absorbance corresponding to concentration C ($\mu\text{g ml}^{-1}$) for the metal ion. The statistical calculations are based on the average of triplicate readings for each standard solution in the given range.

Flow rate for metal extraction

The optimum flow rates (controlled with a peristaltic pump) for maximum loading of metal ions onto thiosalicylic acid-

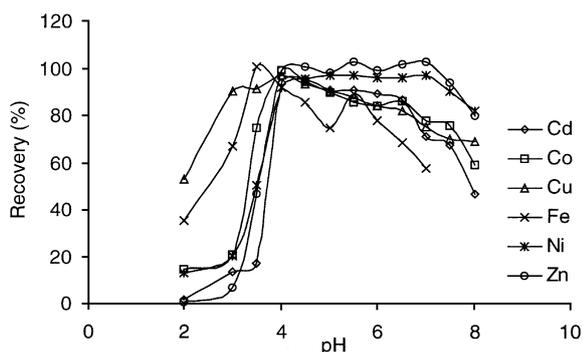


Fig. 2 Effect of pH on sorption of metal ions.

modified Amberlite XAD-2 are in the range 2–5 ml min^{-1} . Flow rates slower than 2 ml min^{-1} were not studied to avoid a longer time of analysis. Similarly for desorption, a flow rate of 1.5–2.5 ml min^{-1} was found to be suitable.

Preconcentration limit, enrichment factor and breakthrough volume for elution

The enrichment factor was studied by taking 10 μg of each metal in a volume varying between 0.1–4.0 dm^{-3} and applying the recommended procedure. The recoveries (%) and the enrichment factor achieved at the lowest concentration limit are given in Table 2. The largest volume suitable for quantitative recovery (also called the breakthrough volume) and the corresponding concentration are given in Table 2. The efficacy of the eluent (2 $\text{mol l}^{-1} \text{HNO}_3$) was studied for different volumes (1–10 ml). It was found that 5, 7, 4, 8, 5 and 5 ml of acid was sufficient for quantitative recovery of the six metal ions respectively. Therefore, 10 ml of 2 $\text{mol l}^{-1} \text{HNO}_3$ was used for elution so that the method could be applied for simultaneous elution of all the metal ions from the resin column.

Re-usability of the resin

The re-usability of the resin was tested by loading the metal ions several times on a column from a solution having a concentration 40 $\mu\text{g ml}^{-1}$ at a flow rate of 2–3 ml min^{-1} and eluting by the recommended procedure. It was found that the sorption capacity after 12 cycles of sorption and desorption did not vary more than 2% for any metal ion. Therefore, multiple use of the resin is feasible. Similar results are shown for the batch method also. The sorption capacity of 1 g of the present chelating resin does not change when it is treated with 100 ml of 6 $\text{mol l}^{-1} \text{HNO}_3$ or 0.1 $\text{mol l}^{-1} \text{NaOH}$ solution for 2 h.

Separation of metal ion from electrolytes

The effect of the electrolytes NaBr, NaCl, NaF, NaNO_3 , Na_3PO_4 and Na_2SO_4 and cations Ca^{II} and Mg^{II} on the sorption of all the six metal ions was studied. A set of solutions of electrolytes having different concentrations was used. A solution containing 50 μg of metal ions was added to each solution of the set (total volume was made up to 100 ml) and the recommended procedure was applied. Na_3PO_4 interferes with Cd, Co, Ni and Zn. Tolerance limits for all the electrolytes are given in Table 3. This indicates that TSA-AXAD-2 can be successfully applied to saline water with reasonable recovery. Similarly, the effect of Mg^{II} and Ca^{II} on the sorption was studied. Their tolerance limits are also given in Table 3.

Metal ion sorption kinetics

A 0.4 g mass of chelating resin beads was shaken with 100 ml of a solution containing 20 mg of metal for different times

Table 2 Parameters at the concentration limit

Metal ion	Volume of sample solution/ml	Concentration/ ng ml^{-1}	Preconcentration factor	Breakthrough volume of eluent/ml	Recovery ^a (%)
Cd^{II}	2000	20	200	5	97
Co^{II}	1800	5	180	7	98
Cu^{II}	2000	20	200	4	96
Fe^{III}	4000	2.5	400	8	96
Ni^{II}	2000	5	200	5	92
Zn^{II}	2000	20	200	5	95

^a In a volume of 10 ml.

varying from 1 to 180 min, and the recommended procedure was applied. The variation of sorption as a function of time for all the six metal ions is shown in Fig. 3. The loading half time, $t_{1/2}$, required to attain 50% saturation of the resin was found to be less than 2.0 min for all metals, except Ni, for which it was 13.1 min. The reasonably fast kinetics of the resin-metal ion interaction for most of the metal ions at optimum pH reflects a good accessibility of the chelating sites of the modified resin for metal ions.

Limit of detection and quantification

The limit of detection (LOD) values [defined as (blank + 3σ), where σ is standard deviation of blank determination] are 0.48, 0.20, 4.05, 0.98, 1.28 and $3.94 \mu\text{g l}^{-1}$ for Cd, Co, Cu, Fe, Ni and Zn, respectively. The limit of quantification (LOQ = blank + 10σ) values are found to be 0.51, 0.29, 4.49, 1.43, 1.58 and $4.46 \mu\text{g l}^{-1}$, respectively.

Determination of Cd, Co, Cu, Fe, Ni and Zn in tap water samples

The applicability of the present resin was tested for tap water samples. The pH of 2 l of water sample (acidified with 2% HNO_3) was adjusted to the optimum level (Table 1) and the

Table 3 Tolerance limit of electrolytes

Metal ion	Electrolyte or metal ion/mol l ⁻¹							
	NaBr	NaCl	NaF	NaNO ₃	Na ₂ SO ₄	Na ₃ PO ₄	Ca ^{II}	Mg ^{II}
Cd ^{II}	0.002	0.050	I ^a	0.020	0.010	0.001	0.002	0.001
Co ^{II}	0.100	0.200	I	0.400	0.100	I	0.002	0.002
Cu ^{II}	0.050	0.500	0.002	0.100	0.020	0.010	0.500	0.200
Fe ^{III}	0.020	0.040	0.001	0.500	0.050	0.010	0.010	0.002
Ni ^{II}	0.010	0.200	I	0.020	0.010	I	0.004	0.500
Zn ^{II}	0.005	0.100	I	0.500	0.010	0.001	0.002	0.001

^a I = interferes.

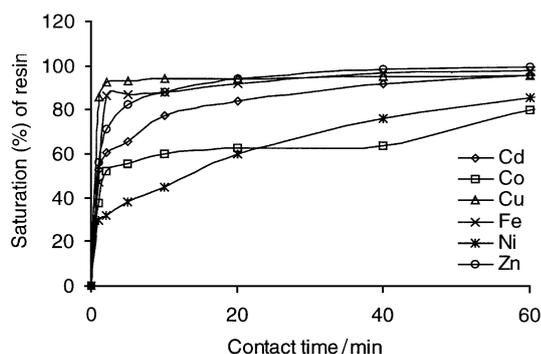


Fig. 3 Kinetics of metal ion sorption on TSA-AXAD-2.

Table 4 Determination of metal ions in water samples; $n = 6$

Origin of sample	Method	Metal ions/ $\mu\text{g l}^{-1}$											
		Cd	RSD (%)	Co	RSD (%)	Cu	RSD (%)	Fe	RSD (%)	Ni	RSD (%)	Zn	RSD (%)
Ganges river, Kanpur	Direct ^a	0.49	7.7	22.35	2.3	77.16	0.7	52.42	0.86	8.06	3.4	16.95	5.2
	SA ^a	0.51	6.5	18.28	3.1	75.88	1.0	48.86	2.0	9.26	3.2	14.46	3.9
Gomti river, Lucknow	Direct ^a	1.22	6.2	21.40	2.0	61.45	0.9	6.98	1.4	72.16	1.1	14.18	2.7
	SA ^a	0.85	6.4	18.13	1.5	56.75	1.8	5.64	2.2	65.28	0.9	11.35	4.4
Tap water, New Delhi	Direct ^a	0.93	1.8	0.59	3.4	7.75	1.7	4.59	2.3	1.42	5.7	27.81	0.3
	SA ^a	0.86	3.5	0.55	5.4	7.87	0.9	4.35	2.1	1.35	2.5	27.63	0.4

^a Direct: recommended procedure is directly applied, SA: standard additions method.

recommended procedure (column) was applied. After standard additions of each of the six metal ions (5.0–250.0 μg) to 2 l of water sample, the recommended procedure was adopted for metal extraction and estimation. The results are given in Table 4 with the corresponding RSD.

Determination of metal ions in river water samples

A sample solution (1 l) with and without standard additions (5.0–250.0 μg) was passed through the chelating resin (after pH adjustments) and all the six metal ions were determined as described in the recommended procedure. The results are given in Table 4 and indicate the suitability of the present resin for preconcentration of these six metal ions from river water samples. The values obtained by the standard additions method are somewhat lower than those obtained by direct determination in some cases, but the difference is within the acceptable limit at such a low concentration.

Determination of cobalt in pharmaceutical samples

The cobalt content in a multivitamin tablet with tradename polybion (E. Merck, India) was analyzed by digesting 20 tablets (6.56 g) in a beaker with 25 ml of concentrated HNO_3 and slowly increasing the temperature to 240 °C until a residue was left. The residue was dissolved in 20 ml of concentrated HNO_3 after cooling and was slowly evaporated on a steam bath until a residue remained again. This was dissolved in 100 ml of distilled water and concentrated HNO_3 was added dropwise with gradual stirring until a colourless solution was obtained. After adjusting the pH of the solution to 4, Co was estimated using the recommended procedure. The cobalt content was found to be $0.636 \mu\text{g g}^{-1}$ (RSD 2.3% for 6 determinations); the certified value is $0.654 \mu\text{g g}^{-1}$.

Comparison with other metal ion collectors

The sorption capacity of thiosalicylic acid-immobilized Amberlite XAD-2 is compared with those of other important matrices in Table 5. This resin exhibits better than or comparable capacity values to a large number of the metal-matrix combinations. For sorbing zinc, the TSA-AXAD-2 resin exhibits a capacity lower than those of chromotropic acid-¹⁴ and tiron-loaded¹⁵ Amberlite XAD-2. Dithizone-loaded poly-(vinylpyridine)³² shows better sorption capacities for Cu, Ni and Zn in comparison to thiosalicylic- and tiron-acid immobilized Amberlite XAD-2 for Fe. However, the preconcentration factors for the six metal ions with the TSA-AXAD-2 resin are better than or comparable to all the important chelating resins (Table 6). The short loading time ($t_{1/2}$) is another advantage. The working pH range (4.0–6.0) for all the metal ions is slightly acidic and therefore the possibility of their hydrolysis is very small, which probably results in low RSD values. The matrix effects with TSA-AXAD-2 are low, as

Table 5 Comparison of sorption capacities

Immobilized ligand	Metal ion/ $\mu\text{mol g}^{-1}$					
	Cd	Co	Cu	Fe	Ni	Zn
<i>Support: Amberlite XAD-2</i>						
Thiosalicylic acid	197.5	106.9	214.0	66.2	309.9	47.4
Alizarin Red-S ⁶	1.10				2.36	7.81
Salicylic acid ⁷						17.5
Pyrocatechol violet ⁸	11.2				10.5	21.5
<i>o</i> -Aminophenol ¹¹	30.42	58.0	53.0		55.20	44.96
Calmagite ¹²			1.59			
Chromotropic acid ¹⁴	83.18	65.16	133.8	58.01	103.4	147.6
Tiron ¹⁵	84.51	110.2	220.3	100.2	214.6	169.7
<i>o</i> -Vanillinthiosemicarbazone ¹⁸		13.3				22.9
1-(2-Pyridylazo)-2-naphthol ³⁴					1.87	
<i>Support: Amberlite XAD-7</i>						
Xylenol Orange ¹⁶	17.79	44.12	25.17	28.65	44.30	27.53
Glyoxaldithiosemicarbazone ²¹			19.7			
Dimethylglyoxal bis(4-phenyl-3-thiosemicarbazone) ²¹			20.9			
<i>Support: Silica gel</i>						
Acid Red 88 ²⁴	11.7	15.1	12.1	3.9	11.3	16.2
Salicyldoxime ²⁸		60.0	80.0	50.0	40.0	40.0
3-Methyl-1-phenyl-4-stearoyl-5-pyrazolone ³¹		45.0	42.99		48.98	
1-(2-Thiazolylazo)-2-naphthol ³⁵			2600			24.99
<i>Support: Polyurethane foam</i>						
2-(2-Benzothiazolylazo)- <i>p</i> -cresol ³⁶		1200				
<i>Support: Poly(vinylpyridine)</i>						
Dithiazone ³²			510.0		590.0	650.0

Table 6 Comparison of preconcentration factors

Immobilized ligand	Metal ion					
	Cd	Co	Cu	Fe	Ni	Zn
<i>Support: Amberlite XAD-2</i>						
Thiosalicylic acid	200	180	200	400	200	200
Alizarin Red S ⁶	40				40	40
Salicylic acid ⁷						180
Pyrocatechol violet ⁸	50				18	60
<i>o</i> -Aminophenol ⁸	50	100	50		65	40
Calmagite ¹²			50			
Chromotropic acid ¹⁴	100	150	100	120	200	200
Tiron ¹⁵	48	56	200	80	150	180
<i>o</i> -Vanillinthiosemicarbazone ¹⁸			90			140
1-(2-Pyridylazo)-2-naphthol ³⁴					50	
<i>Support: Amberlite XAD-7</i>						
Xylenol Orange ¹⁶	50	100	50	200	100	100
Dimethylglyoxal bis(4-phenyl-3-thiosemicarbazone) (DMBS) ²¹	100		100			
8-(Benzenesulfonamido)quinoline ²⁹	10					10
<i>Support: Silica gel</i>						
Salicyldoxime ²⁸		40	40	40	40	40
3-Hydroxy-2-methyl-1,4-naphthoquinone ³⁰		10	10	10		10
3-Methyl-1-phenyl-4-stearoyl-5-pyrazolone ³¹		40	40		40	
<i>Support: activated carbon</i>						
8-Hydroxyquinoline ³³	100					
Cupferron ³³	100					
<i>Support: Polyurethane foam</i>						
2-(2-Benzothiazolylazo)- <i>p</i> -cresol ³⁶		2.5				
<i>Support: Polyacrylonitrile</i>						
Aminophosphoric and dithiocarbamate ³⁷	200	200	200			

shown from the vitamin and water analysis results. The concentration of acid required for stripping off the metal ions is not very high, which probably makes the repeated use of the resin feasible.

Acknowledgement

The authors thank the Council of Scientific and Industrial Research (India) for financial support.

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