

Characterization of a Chelating Resin Functionalized via Azo Spacer and Its Analytical Applicability for the Determination of Trace Metal Ions in Real Matrices

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ABSTRACT: A selective flame atomic absorption spectrometric method has been developed for the determination of trace amount of metal ions after preconcentration on salicylic acid (SA) loaded Amberlite XAD-4 resin (AXAD-4) at suitable pH. The chelating resin AXAD-4-SA was characterized based on FTIR, thermal and chemical stability, and hydrogen ion capacity. The sorption capacity was found to be 245.0, 156.2, 155.0, 145.0, 125.0, 122.5, and 70 $\mu\text{mol g}^{-1}$ for Cu(II), Cr(III), Zn(II), Cd(II), Mn(II), Ni(II), and Co(II), respectively with $t_{1/2} < 15$ min. All the metals could be eluted by 5 mL of 4 mol L^{-1} HCl/ HNO_3 resulting in high preconcentration factor of 200–360 up to a low preconcentration limit of 5.5–10 $\mu\text{g L}^{-1}$. The accuracy and

precision of the developed method was checked by analyzing standard reference materials. The experimental values were not statistically significant from the certified values with $< 5\%$ RSD. The detection limits were found to be 0.42, 0.57, 0.63, 0.77, 0.94, 0.96, and 1.41 $\mu\text{g L}^{-1}$, respectively. The analytical utility of the AXAD-4-SA for preconcentration and determination of metal ions was explored by analyzing river, canal, sewage, and tap water by direct as well as standard addition method. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 123: 3448–3458, 2012

Key words: chelating resin; flame atomic absorption spectrometry; preconcentration; natural water; toxic metals

INTRODUCTION

Heavy metals constitute a major category of persistent, bioaccumulative, and toxic (PBT) chemicals that do not readily break down in the environment, not easily metabolized, and may accumulate in human or ecological food chains through consumption. Hence, once released to the environment, may present increasing long-term toxic effects to public health even if the release was of a small amount and pose a significant threat to public health through occupational as well as environmental exposures. The toxicities of heavy metals may be caused by the inhibition and reduction of various enzymes, complexation with certain ligands of amino acids, and substitution of essential metal ions from enzymes.^{1–3} Hence, their determination in real samples is important, especially in the environment monitoring and assessment of occupational and environmental exposure to toxic metals. However, most of the toxic metal ions in real matrices are in very low concentrations and occur together with much higher concentrations of compounds likely to cause interferences during the analysis even with frequently used sophisticated

instrumental techniques for trace metal determination such as inductively coupled plasma atomic emission spectrometry, electrothermal atomic absorption spectrometry, etc. without sample enrichment and cleanup.^{4,5} Preconcentration by solid-phase extraction (SPE) addresses these two problems. It can extend the detection limits and remove interfering constituents thereby improving the precision and accuracy of the analytical results. Flame atomic absorption spectrometric (FAAS) with relatively lower detection limit has been demonstrated^{6–8} to be a very effective technique in combination with preconcentration procedures. The main advantage of this technique is the possibility of using a relatively simple detection system with flame atomization instead of a flameless technique, which require more expensive equipment and are usually much more sensitive to interferences from macro components of various natural matrices.⁹ The use of chelating resin in SPE as metal ion extractants has attracted researchers in the field of separation science.^{10–12} The possibility to extract selectively a number of analytes over a wide pH range, quantitative sorption and elution, kinetically faster sorption and desorption mechanisms, good retention capacity, high preconcentration factor, and regeneration of resins over many cycles with good reproducibility in the sorption characteristics are frequently quoted as an advantage.¹² Activated carbon,¹³ polymeric fibers,¹⁴ Ambersorb,¹⁵ inorganic ion-exchanger,¹⁶ alumina,¹⁷

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and silica gel¹⁸ have been used to preconcentrate trace metal ions. However, they suffer from lack of selectivity, which leads to high interference of other existing species with the analyte metal ion and chemical stability.¹⁹ Amberlite XAD series resins with polystyrene-divinyl benzene copolymer matrix have proved themselves as efficient support for anchoring chelating ligands due to uniform pore size distribution, high surface area, and excellent chemical and physical stability.²⁰ Resin of moderate to high porosity increases the accessibility of the ligands as well as the metal ions for the chelating site. Selective chelating resin with high metal ion uptake capacity may be designed by immobilizing a small sized polydentate ligand moiety onto Amberlite XAD resins either through surface sorption or through chemical modification. Chemical modification involves the insertion of an appropriate functional group (linkage/spacer group) such as $-\text{N}=\text{N}-$, $-\text{CH}_2-$, $-\text{N}=\text{C}-$ on the surface of polymeric support and then immobilization of a particular ligand by a condensation reaction or coupling reaction. Chelating resin prepared by chemical linkage exhibits better resistance to the leaching of the ligands. High selectivity may be attributed to their function as chelate formation, ion exchange and physical sorption. Salicylic acid (SA) is a commercial ligand with a carboxylic and a phenolic function which can act as electron pair donors reacting with most of hard and intermediates cations.^{21,22} Salicylic acid (SA) is a ligand with a carboxylic and phenolic functional group, which forms chelates with a number of metal ions.²² It has already been used, for example, for the spectrophotometric determination of copper,²³ aluminum,^{24,25} and iron.²⁶ Certain chelating resins like Amberlite XAD-2-SA,²⁷ Amberlite XAD-4-SA (grafting via a ketone bridge),²⁸ and Silica gel-SA²⁹ have been synthesized and characterized but their applications with analytical figures of merit have not been explored.

Therefore, it was thought worthwhile to functionalize Amberlite XAD-4 with SA by coupling through azo spacer. The chelating resin was used for the preconcentration of Cu(II), Cr(III), Zn(II), Cd(II), Mn(II), Ni(II), and Co(II) from environmental and various other real matrices prior to their determination by FAAS and was found to have superior preconcentration and sorption characteristics for metal ions compared to other SA functionalized chelating resins. The proposed method was validated by analyzing standard reference materials (SRMs) (both environmental and biological) and by performing recovery studies.

EXPERIMENTAL

Instruments

An atomic absorption spectrometer, GBC 932+ (Dandenong, Australia) was employed for the determina-

tion of metal ion concentration. The wavelengths (slit widths) used for Cu(II), Cr(III), Zn(II), Cd(II), Mn(II), Ni(II), and Co(II) were 324.8 (0.7), 357.9 (0.7), 213.9 (0.7), 228.8 (0.7), 279.5 (0.2), 232.0 (0.2), and 240.7 (0.2) nm, respectively, while maintaining the lamp current at 25, 12, 15, 10, 12, 15, and 30 mA, respectively (Zn(II), Cd(II), and Mn(II) have been determined in the Advanced laboratory, Department of Botany). An Elico-LI-120 (Hyderabad, India) digital pH meter was used for pH measurements. A thermostated mechanical shaker-NSW-133 (New Delhi, India) was used for carrying out equilibrium studies at 200 strokes min^{-1} . Infrared (IR) spectra were recorded on a Fourier Transform-IR Spectrometer from Spectro Lab-Interspec 2020 (Newbury, UK) using KBr disc method. A Shimadzu TG/DTA simultaneous measuring instrument-DTG-60/60H (Kyoto, Japan) was used for thermogravimetric analysis (TGA) and differential thermal analysis (DTA). The CHN analysis was carried out on Carlo Erba-EA1108 (Milan, Italy) elemental analyzer in sophisticated analytical instrument facility of Central Drug Research Institute (Lucknow, India). A column (1 × 10 cm) fitted with sintered disc, for dynamic studies, was obtained from J-SIL Scientific Industries (Agra, India).

Reagents and solutions

All solutions were prepared in triply distilled water. Stock solutions of nitrate salts of Cu(II), Cr(III), Zn(II), Cd(II), Mn(II), Ni(II), and Co(II) (supplied by Central Drug House (P), New Delhi, India) at the concentration of 1000 mg L^{-1} in 1% HNO_3 were standardized by complexometric titration³⁰ before use. The working solutions of the metals were prepared by appropriately diluting the stock solutions. Buffer solutions were used for pH adjustment. For this, solutions containing suitable amounts of sodium sulfate-sodium bisulfate for pH 2, acetic acid-ammonium acetate for pH 4–6, and ammonia-ammonium chloride for pH 8–10 were prepared in distilled water. Fulvic acid powder and soluble humates containing 75% humic acid and 10% potassium were received as a gift from Nutri-Tech Solutions, (Yandina, Australia). AXAD-4 as 20–60 mesh particle size (40 Å mean pore size) with 725 $\text{m}^2 \text{g}^{-1}$ of surface area and SA were procured from Sigma-Aldrich chemie GmbH (Steinheim, Germany). SRMs such as vehicle exhaust particulates NIES 8, human hair NIES 5, tea leaves NIES 7 were obtained from the National Institute of Environmental Studies (Ibaraki, Japan). rompin hematite JSS (800-3) and zinc base die-casting alloy C NBS 627 were provided by the Iron and Steel Institute of Japan (Tokyo, Japan) and the National Bureau of Standards, U.S. Department of Commerce, (Washington, DC), respectively. A multivitamin capsule (bearing the

commercial name Maxirich) was procured from Cipla Limited (Mumbai, India) and infant milk substitute, IMS, (commercially available as Lactogen 1) was obtained from Nestle India Limited (New Delhi, India). Hydrogenated oil (locally known as vanaspati ghee) was obtained from the local market, Aligarh.

Pretreatment of samples

Natural and sewage water samples

The water samples namely river water (collected from the Ganga, Narora, India), canal water (collected from Kasimpur, Aligarh, India), sewage water (collected from area in the vicinity of local nickel electroplating industry, Aligarh), and tap water (collected from University campus) were immediately filtered through Millipore cellulose membrane filter (0.45 μm pore size), acidified to $\text{pH } 2 \pm 0.01$ with HNO_3 , and stored in precleaned polyethylene bottles.

Digestion of standard environmental, biological, and metal alloy samples

To dissolve the environmental SRM (vehicle exhaust particulates-NIES 8), 0.5 g of the sample was dissolved by adding 10 mL of concentrated nitric acid (15.5 mol L^{-1}), 10 mL of concentrated perchloric acid (12.2 mol L^{-1}), and 2 mL of concentrated hydrofluoric acid (22.4 mol L^{-1}) in a 100 mL in a Teflon beaker. The solution was evaporated to near dryness, redissolved in minimum volume of 2% HCl, filtered and made up to 50 mL volume in a calibrated flask. The sample solutions of biological SRMs such as human hair (NIES 5) and tea leaves (NIES 7) were prepared as proposed by the International Atomic Energy Agency.³¹ A 50 mg of each of the samples was agitated with 25 mL of acetone, and then washed three times with distilled water and with 25 mL of acetone. The contact time of the cleaning medium with the sample was 10 min. The samples were finally dried for 16 h at $100 \pm 0.2^\circ\text{C}$. Then each of the samples was dissolved in 10–20 mL of concentrated nitric acid. After adding 0.5 mL of 30% H_2O_2 , the solution was boiled to dryness. The residue obtained was dissolved in minimum amount of 2% HCl and made up to a 50 mL volume in a calibrated flask.

To dissolve the standard reference alloys (JSS 800-3), rompin hematite and zinc based die-casting alloy C (NBS 627), and an amount of 25 mg of the sample was taken into a beaker and dissolved in 10–50 mL of aqua-regia. The solution was boiled to near dryness. Finally, the residue was dissolved in minimum volume of 2% HCl and filtered through Whatman filter paper No. 1. The residue was washed with two 5 mL portions of hot 2% HCl. The aqueous layer

was evaporated to dryness. The residue was redissolved in 5 mL of 2% HCl and made up to 50 mL with distilled water.

Digestion of multivitamin capsule and food samples (infant milk substitutes and hydrogenated oil)

Five multivitamin capsules (5.64 g) were taken in a beaker containing 25 mL of concentrated HNO_3 and digested by slowly increasing the temperature of the mixture to $120 \pm 0.2^\circ\text{C}$. The mixture was further heated till a solid residue was obtained. It was allowed to cool and then dissolved in 20 mL of concentrated HNO_3 . The solution was gently evaporated on a steam bath until a residue was left again. It was subsequently mixed with 50 mL of distilled water and concentrated HNO_3 was then added and then was added drop wise until a clear solution was obtained on gentle heating.

Powdered IMS food sample (200 mg) was heated in a beaker containing mixture of concentrated H_2SO_4 (20 mL) and HNO_3 (10 mL) until a clear solution was obtained. It was allowed to cool and most of the acid was neutralized with NaOH. The total volume was made up to 50 mL and kept as stock.

Hydrogenated oil (2 g) was taken in a beaker and dissolved in 15 mL of concentrated nitric acid with heating. The solution was cooled, diluted and filtered. The filtrate was made up to 50 mL with distilled water after adjusting its pH to the optimum value.

Preparation of chelating resin (AXAD-4-SA)

SA functionalized Amberlite XAD-4 resin (AXAD-4-SA) was prepared through azo spacer as reported earlier.³² The synthesis was carried out according to the following sequence: nitration, amination, diazotization, and azotisation (Scheme 1).

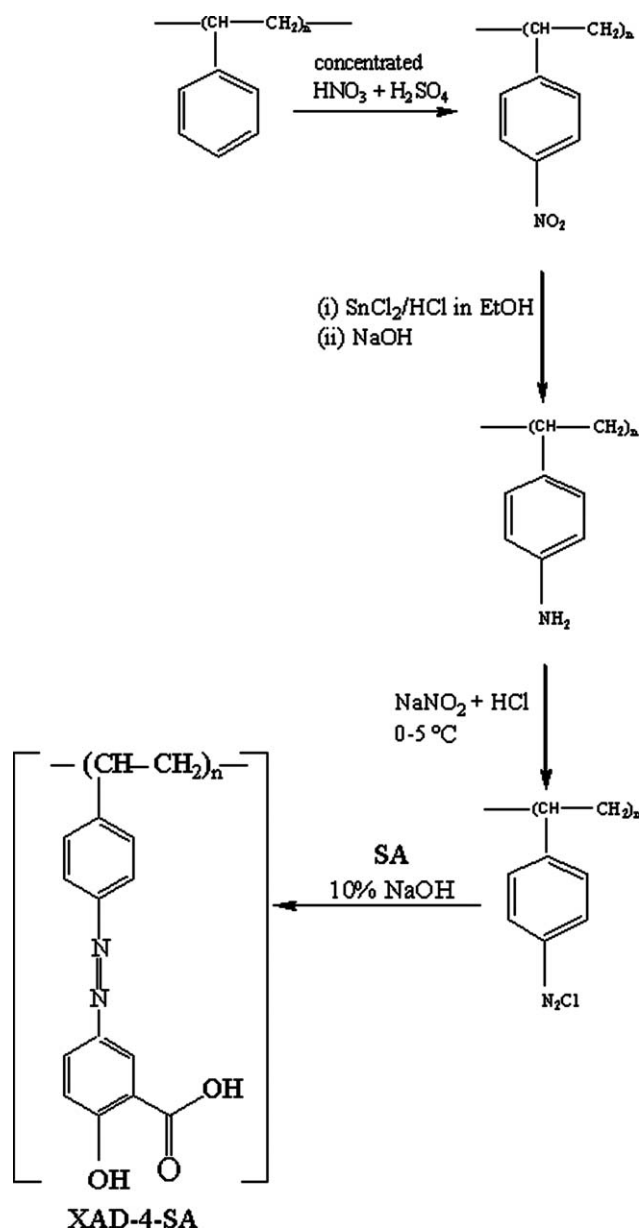
Characterization of the AXAD-4-SA

Stability

The resin (0.5 g) was stirred in 25 mL of acid ($0.1\text{--}5.0 \text{ mol L}^{-1}$ of HCl and HNO_3) and alkaline solution ($0.1\text{--}5.0 \text{ mol L}^{-1}$ of NaOH) for 48 h, then filtered off and washed with distilled water. Its resistance to chemical changes was tested by checking its sorption capacity. The effect of temperature was investigated by subjecting the resin to TGA and DTA in the nitrogen atmosphere at heating rate of $10^\circ\text{C min}^{-1}$.

Hydrogen ion capacity

For hydrogen ion capacity, an accurately weighed (0.5 g) resin was first treated with 4.0 mol L^{-1} HCl and then filtered off, washed with distilled water to



Scheme 1 Synthesis of AXAD-4-SA.

make it free from acid, and dried at 100°C for 6 h. The acidic form of the resin was equilibrated with 30.0 mL of 0.1 mol L⁻¹ NaOH solution for 6 h at 25 ± 0.2°C and then the excess alkali was estimated with 0.1 mol L⁻¹ hydrochloric acid solution.

Recommended procedure for sorption and desorption studies of metal ions

Batch "static" method

A weighed amount of AXAD-4-SA in Erlenmeyer flask (100 mL) was equilibrated with 50 mL of metal solution of suitable concentration maintained at constant pH at 25 ± 0.2°C for 2 h. The resin was filtered and the sorbed metal ions were desorbed by shaking

with the appropriate solution of eluting agents and subsequently analyzed by FAAS.

Column "dynamic" method

Asample An amount of AXAD-4-SA was soaked in water for 24 h and then poured before packing into a glass column. The resin bed was buffered with 5 mL of the buffer solution of corresponding pH. A solution of metal ions of suitable concentration was passed through the column, which was prebuffered at optimum pH with 5 mL of the buffer solution, at an optimum flow rate. After the sorption operation, recovery experiments were performed. For this purpose, The column was washed before allowing a certain volume of eluting agent to percolate through the bed of loaded resin whereby the sorbed metal ions get eluted and for their subsequent determination by FAAS.

RESULTS AND DISCUSSION

Characterization of AXAD-4-SA

To study the extent of product formation, elemental analysis was carried out at each stage of the reaction scheme (Scheme 1). The nitrogen content of the nitrated resin and the subsequent reduced product was found to be 9.38% (6.71 mmol g⁻¹) and 11.76% (8.40 mmol g⁻¹), respectively. Elemental analysis of AXAD-4-SA gave C 63.36%, H 4.56%, and N 10.12%, which are in agreement with calculated values for C₁₅H₁₂N₂O₃·H₂O as C 62.48%, H 4.93%, and N 9.77%.

The resin was subsequently characterized by IR spectral data. The FT-IR spectrum of AXAD-4-SA (Fig. 1) has prominent bands at 1680, 1645, 1486, and 1387 cm⁻¹ due to carboxylate, —N=N—, OH (bending), and phenolic group vibrations, respectively. This supports the immobilizing of SA onto Amberlite XAD-4 resin. The absence of broadening of the hydroxyl band in the spectra of the metal loaded resin proves the absence of hydrogen bonding that indicates the participation of —OH group in the coordination process. The red shifts of the two peaks namely hydroxyl and carboxylic by 10–15 cm⁻¹ for metal loaded resin further suggest that chelation with SA functionality is responsible for the sorption of metal ions by AXAD-4 resin, whereas the —N=N— band remained unchanged. The resin shows good chemical stability with no loss of capacity up to 5 mol L⁻¹ of HCl/HNO₃/H₂SO₄ used for stripping of metal ions. It can withstand alkaline medium up to 4 mol L⁻¹ NaOH. At concentrations higher than 4 mol L⁻¹ of NaOH, the sorption capacity gets reduced by 3.5%. According to TGA, (Fig. 2) the resin was found to be stable up to 200°C with no significant loss of weight other than the loss due to sorbed water (5.72%). Weight loss of 14.47% up to 382.71°C in TGA was supported by an

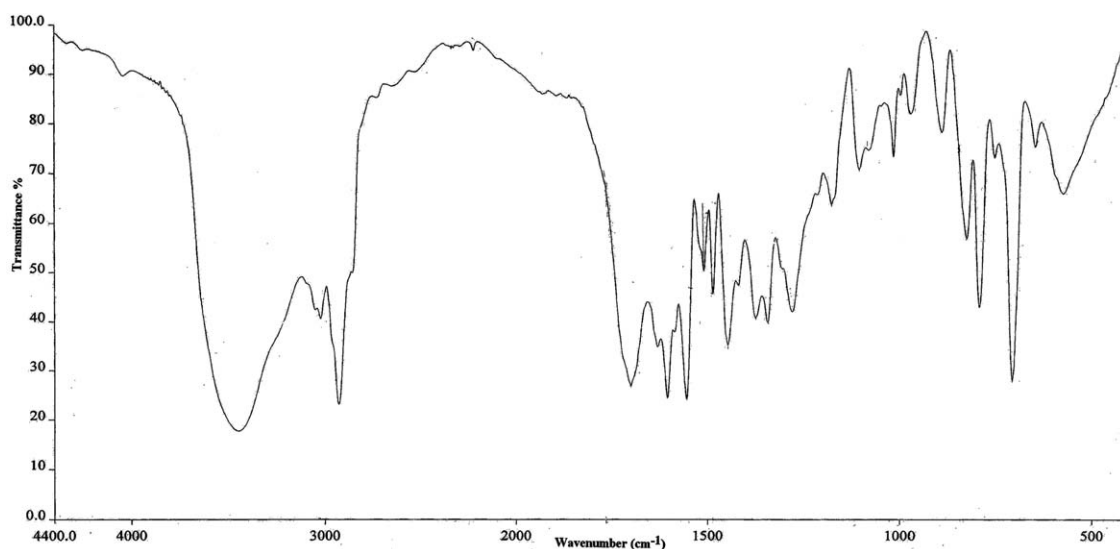


Figure 1 FT-IR Spectra of AXAD-4-SA.

endothermic peak in the DTA curve indicate the loss of functional group due to the degradation of SA reagent in the chelating resin.

The water regain capacity was found to be $11.45 \text{ mmol g}^{-1}$. This value reflects the high hydrophilicity of the resin, which is satisfactory for column operation. The overall hydrogen ion capacity was found to 7.15 mmol g^{-1} of resin, which may be contributed by the two replaceable hydrogen ions of the hydroxyl and the carboxylic moieties. Theoretically, if 3.7 mmol of the reagent constituted per gram of the resin, the hydrogen ion capacity, due to the hydroxyl and carboxylic groups should have been 7.40 mmol g^{-1} , which agrees with the experimental value.

Optimum experimental parameters

To optimize sorption of metal ions, the multivariate approach was followed to establish all the parameters. Each optimum condition was established by varying one of them and following the recommended procedure.

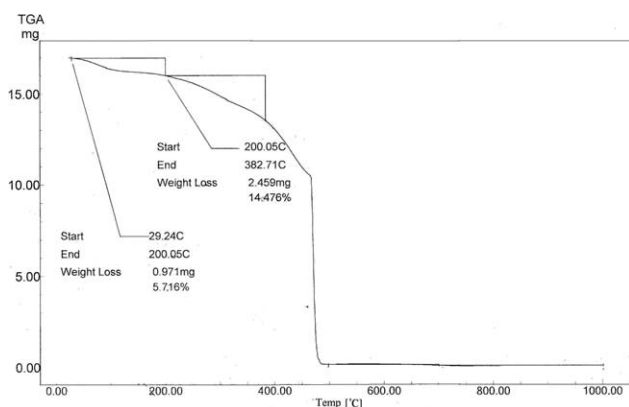


Figure 2 TGA Curve of AXAD-4-SA.

Effect of pH for metal ion uptake

Optimum pH of metal ion uptake was determined by static method. Excess of each metal ion (50 mL ; $100 \mu\text{g mL}^{-1}$) was shaken with 0.2 g of resin for 120 minutes. The pH of metal ion solution was adjusted prior to equilibration over a range of pH 2–10 (± 0.01) with the corresponding buffer system. The pH > 10 was not studied to avoid precipitation due to the formation of metal hydroxide. The effect of pH on the sorption of metal ions on AXAD-4-SA is shown in Figure 3. As the complex formation is strongly pH dependent, careful adjustment of proper pH for the reagent was necessary. All the metal ions studied exhibited higher sorption capacity at pH 5.5–8.0 (± 0.01) except for Cu(II), which shows high sorption at $\text{pH } 10 \pm 0.01$. Hence, $\text{pH } 5.57 \pm 0.01$

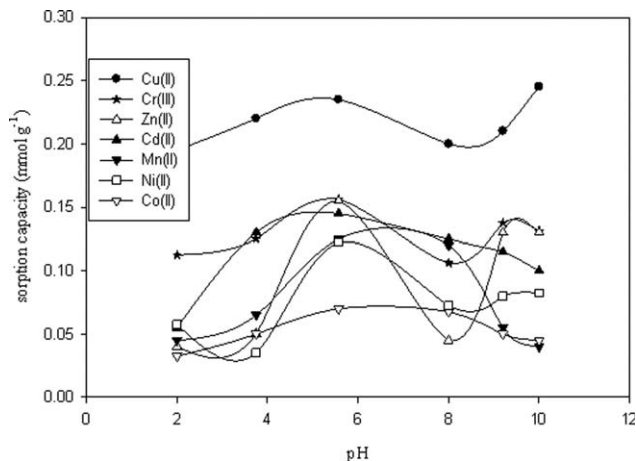


Figure 3 Dependence of sorption capacity on the pH of the solution (Batch method parameter: 50 mL , solution; $100 \mu\text{g mL}^{-1}$, metal ions; 0.2 g , resin).

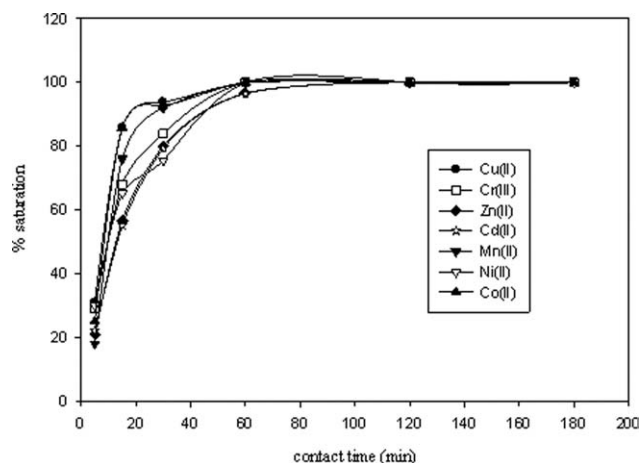


Figure 4 Kinetics of sorption of metal ions on AXAD-4-SA (Batch method parameter: 50 mL, solution; 100 $\mu\text{g mL}^{-1}$, metal ions; 0.2 g, resin).

was adjusted in all further experiments for all metals except Cu(II), which was adjusted at $\text{pH } 10 \pm 0.01$.

Sorption kinetics and loading halftime

The rate of loading of metal ions on the resin was determined by static method. Fifty milliliter of each metal ion solution ($100 \mu\text{g mL}^{-1}$) was shaken with 0.2 g of the resin in a thermostat shaker for preselected intervals of time. The loading halftime, $t_{1/2}$, that is, the time required to reach 50% of the resins total loading capacity was evaluated from the resulting isotherm. From the kinetics of sorption for each metal (Fig. 4), it was observed that 50 min was enough for the sorbent to reach the saturation level for all the metals. The sorption rate constant k can be calculated using the following equation:⁸ $-\ln(1 - F) = kt$, where $F = Q_t/Q$ and Q_t is the sorption amount at sorption time t and Q the sorption amount at equilibrium. Putting the value of Q_t at $t_{1/2}$

TABLE I
Kinetics and Batch Capacity of Sorption of Metal Ions on AXAD-4-SA (Batch Method Parameter: 50 mL, Solution; 0.2 g, Resin)

Metal ion	Loading halftime $t_{1/2}$ (min)	Rate constant k (min^{-1}) $\times 10^{-2}$	Batch capacity ($\mu\text{mol g}^{-1}$)
Cu(II)	10	6.93	245.0
Cr(III)	10	6.93	156.2
Zn(II)	15	4.62	155.0
Cd(II)	15	4.62	145.0
Mn(II)	12	5.77	125.0
Ni(II)	12	5.77	122.5
Co(II)	12	5.77	70.0

in the above equation, we may get the corresponding value of k for every metal ion (Table I).

Effect of resin amount on the sorption capacity

To investigate the effect of the amount of the resin on the sorption of metal ions, an excess of the metal ion solution corresponding to $150 \mu\text{g mL}^{-1}$ was equilibrated with varying amounts of resin buffered at the suitable pH. The retention of the metal ions per gram of the resin increased with the increase in the amount of the resin. An almost constant and maximum sorption capacity was observed after 0.2 g of the resin.

Effect of flow rate for sorption and elution

The flow rate for the sorption of metal ions was changed within $1\text{--}10 \text{ mL min}^{-1}$, and the results showed that the flow rate has no effect on the sorption of metal ions up to 4 mL min^{-1} , and in the higher flow rates ($>4 \text{ mL min}^{-1}$) the sorption of metal ions decreased at least 20%. The eluent flow rate had no effect on the stripping of metal ions up to 3 mL min^{-1} , and the recovery was quantitative.

TABLE II
Elution of Metal Ions From the AXAD-4-SA (Column Parameter: 3 mL min^{-1} , Elution Flow Rate; 0.2 g, Resin)

Type	Stripping agent		Mean recovery for five replicates (%)						
	Concentration mol L^{-1}	Volume (mL)	Cu(II)	Cr(III)	Zn(II)	Cd(II)	Mn(II)	Ni(II)	Co(II)
HCl	2	5	25	15	18	41	70	28	25
	4	5	99	29	52	96	99	92	40
H ₂ SO ₄	1	5	21	32	17	33	45	25	51
	2	5	24	36	26	40	48	35	58
HNO ₃	1	5	56	42	29	36	24	51	38
	2	5	88	48	34	62	32	97	61
	4	5	39	98	98	69	35	95	97
HCOOH	1	5	41	34	29	35	25	38	40
	2	10	54	40	33	39	28	43	49
CH ₃ COOH	2	5	10	8	13	9	21	18	25
	4	10	12	14	13	10	25	18	26
HClO ₄	2	5	34	24	38	20	16	28	41
	4	10	42	27	39	26	18	28	48

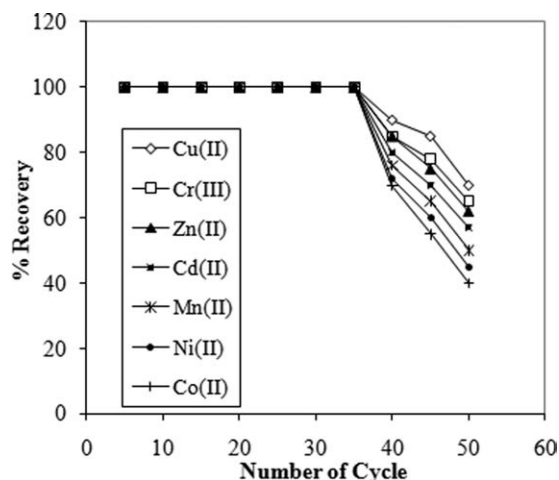


Figure 5 Regenerability of AXAD-4-SA for different metals (Column parameters: 3 mL min⁻¹, elution flow rate; 50 μg mL⁻¹, metal ions; 0.2 g, resin).

Hence, such fast flow rate makes it superior to the previously reported works employing SA as the chelating ligand.²⁷ [Saxena et al., 1995].

Types of eluting agents

To investigate the most efficient eluting agent, varying concentration of different volumes of HNO₃, HCl, and H₂SO₄ were tried. Other acids such as formic acid, acetic acid, and perchloric acid were also investigated. Distilled water was found to be unsuitable for the purpose of elution as <0.5% recovery was achieved indicating that the metal ions were retained by the resin by some strong bonding forces. Among the mineral acids, 4 mol L⁻¹ HCl was found to give >98% recovery of Cu(II), Ni(II), Cd(II), and Mn(II) with 5 mL, respectively, while 4 mol L⁻¹ HNO₃ could give >99% recovery of Zn(II), Co(II), and Cr(III). Table II depicts the results.

Resin reusability test

For the reusability of the resin, the loading solution of the metal ions taken several times on a column having a concentration of 50 μg mL⁻¹ at a flow rate of 3 mL min⁻¹ and eluting by the appropriate eluting agent. The capacity of the modified resin was found to be apparently constant (<3%) after the repeated use of more than 35 cycles of sorption and desorption as shown in Figure 5.

Study of interferences

Various cations and anions, which are inevitably associated with heavy metals, may interfere in the latter's determination through precipitate formation, redox reactions, or competing complexation reactions. To assess the analytical applicability of the resin to real samples, common chemical species such as sodium citrate, sodium tartrate, sodium oxalate, humic acid, fulvic acid, NO₃⁻, CO₃²⁻, NH₄⁺, SO₄²⁻, PO₄³⁻, Cl⁻, K⁺, and Na⁺ were checked for any interference in the sorption of these metals. Very few literatures^{33,34} have considered the interference of these humic substances, which are generally present in natural waters at μg mL⁻¹ to ng mL⁻¹ levels and form complexes with various heavy metals.³⁵⁻³⁷ The tolerance limit is defined here as the species concentration causing a relative error smaller than ±5% related to the preconcentration and determination of the analytes. The tolerance limit for each metal (Table III) is found to be much higher than that reported in other literature.²⁷

Adsorption isotherm

To determine the sorption capacity of the resin, test solutions of Cu(II), Cr(III), Zn(II), Cd(II), Mn(II), Ni(II), and Co(II) weighing in the range 100–50,000

TABLE III
Tolerance Limit of Foreign Species (in Binary Mixtures) on Sorption of Metal Ions (Column Parameter: 50 mL, Solution; 5 μg, Metal ion; 0.2 g, Resin)

Foreign species	Tolerance limit of metal ions (μg mL ⁻¹)						
	Cu(II)	Cr(III)	Zn(II)	Cd(II)	Mn(II)	Ni(II)	Co(II)
NaCl	20,000	15,000	20,000	20,000	20,000	20,000	20,000
Na ₂ SO ₄	10,000	10,000	10,000	10,000	10,000	10,000	10,000
NaNO ₃	15,000	10,000	15,000	10,000	15,000	15,000	10,000
Na ₂ PO ₄	500	300	500	250	400	400	400
NH ₄ Cl	20,000	15,000	15,000	10,000	15,000	15,000	15,000
Sodium citrate	250	300	300	300	250	400	350
Sodium oxalate	85	80	70	100	80	100	100
Sodium potassium tartrate	65	50	100	150	120	90	100
CH ₃ COONa	10,000	8000	10,000	7000	6000	12,000	10,000
CaCl ₂	20,000	10,000	15,000	10,000	10,000	20,000	20,000
MgCl ₂	20,000	10,000	15,000	15,000	15,000	20,000	20,000
Humic acid	40	55	60	60	65	65	65
Fulvic acid	35	40	45	45	50	50	45

TABLE IV
Langmuir Isotherm Constants for Sorption of Metal Ions
(Column Parameters: 4.0 mL min⁻¹, Sorption Flow Rate;
0.2 g, Resin)

Metal ions	b (L mg ⁻¹)	q_m (mg g ⁻¹)	R^2	Standard deviation ($N = 5$)
Cu(II)	0.0327	15.36	0.9989	0.3622
Cr(III)	0.0539	8.01	0.9992	0.2310
Zn(II)	0.0515	10.16	0.9997	0.3016
Cd(II)	0.0870	16.12	0.9983	0.4324
Mn(II)	0.0153	6.66	0.9986	0.2118
Ni(II)	0.0191	7.02	0.9999	0.1948
Co(II)	0.0152	4.12	0.9982	0.3133

μg were taken in batches containing 0.2 g of chelated resin and recoveries were investigated. Langmuir isotherms were plotted to determine the resin capacity in accordance to the literature.³⁸ The Langmuir adsorption isotherm is described by the equation given as,

$C_e/q_e = 1/q_m b + C_e/q_m$, where q_e is the amount of metal sorbed per unit weight of the resin (mg g⁻¹) at equilibrium, C_e is the final concentration in the solution (mg L⁻¹), q_m is the maximum sorption at monolayer coverage (mg g⁻¹), and b is the sorption equilibrium constant, which is related to the energy of sorption. A plot of C_e/q_e versus C_e shows linearity and hence, the Langmuir constants, q_m and b , can be calculated from the slope and intercept of the plot (Table IV). From the plots obtained for each metal, the amount of maximum total metal (q_m) sorbed on 1.0 g of resin is calculated. The maximum sorption capacity calculated from the Langmuir isotherm (Fig. 6) indicated that the resin retained Cu(II) more strongly than the other metal ions under study. The higher surface area of AXAD-4 resin complemented

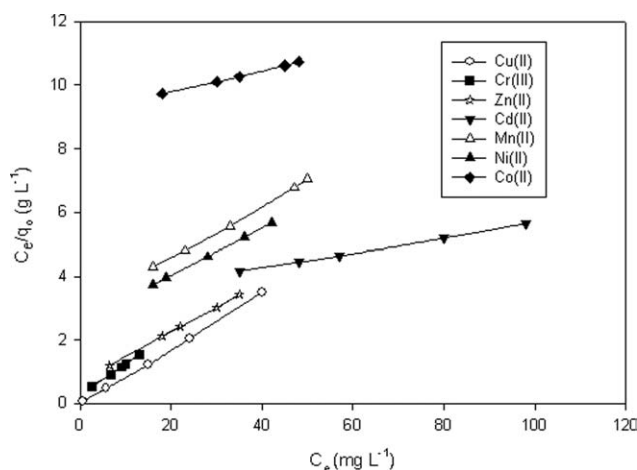


Figure 6 Langmuir sorption isotherms depicting the sorption behaviors of metal ions onto AXAD-4-SA (Column parameters: 4 mL min⁻¹, sorption flow rate; 0.2 g, resin).

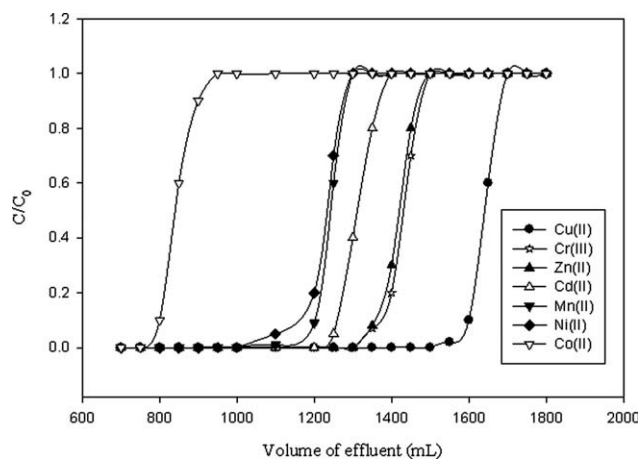


Figure 7 Breakthrough curves for sorption of metal ions: C/C_0 is the concentration ratio of the effluent to influent (Column parameters: 4 mL min⁻¹, sorption flow rate; 0.5 g, resin).

by highly efficient incorporation of SA may be the contributing factors for higher sorption. This fact is also supported by the high hydrophilicity of AXAD-4-SA, which facilitates better surface contacts with the metal ions in aqueous solutions.

Preconcentration factor and breakthrough capacity

The limit of preconcentration was determined by increasing the volume of metal ion solution and keeping the total amount of loaded metal ion constant at 10 μg . The breakthrough volume corresponds to the volume at which the effluent concentration of metal ions from the column is about 3–5% of the influent concentration. The breakthrough volume was determined by the dynamic procedure. The overall capacity, breakthrough capacity and the degree of utilization was determined by the literature method were also determined.³⁹ Figure 7 gives the breakthrough curves for all the metal studied. The overall sorption capacity calculated on the basis of total saturation volume was compared with the corresponding breakthrough capacities for each metal. The closeness of the dynamic capacity to the total sorption capacity reflects the applicability of the column technique for preconcentration. Quantitative collection of metal ions was possible from solutions of concentration in the order of 5.5–10.0 $\mu\text{g mL}^{-1}$ with a recovery up to 98% resulting in a preconcentration factor of 200–360 (Table V). The preconcentration factor of Zn is higher than previously reported literature.²⁷

METHOD VALIDATION AND APPLICATIONS

The accuracy of this method was evaluated from the results of the analysis of various SRMs including environmental, biological, and alloy samples

TABLE V
Preconcentration and Breakthrough Profiles of Metal Ions on AXAD-4-SA (Column Parameter: 4 mL min⁻¹, Sorption Flow Rate; 3 mL min⁻¹, Elution Flow Rate; 0.5 g, Resin)

Metal ions	Preconcentration studies			Breakthrough studies			Degree of column utilization
	Total volume (mL)	Concentration limit (ng mL ⁻¹)	Preconcentration factor	Overall sorption capacity (μmol g ⁻¹)	Breakthrough capacity (μmol g ⁻¹)	Breakthrough volume (mL)	
Cu(II)	1800	5.50	360	245.0	214.3	1700	0.87
Cr(III)	1600	6.25	320	156.2	123.1	1500	0.78
Zn(II)	1600	6.25	320	155.0	122.0	1500	0.78
Cd(II)	1500	6.45	300	145.0	119.5	1400	0.82
Mn(II)	1400	7.14	280	125.0	110.0	1300	0.88
Ni(II)	1400	7.14	280	122.5	106.2	1300	0.86
Co(II)	1000	10.00	200	70.0	60.1	950	0.85

applying recommended column procedure. Calculated Student's *t* (t-test) values for respective metal ions were found to be less than the critical Student's *t*-value of 2.78 at 95% confidence level for *N* = 5 (Table VI). Hence, the mean values were not statistically significant from the certified values indicating that the method could be applied successfully for the analysis of real samples constituting different matrices.

Using optimum conditions, the precision of the method was evaluated. Six successive sorption and elution cycles of 10 μg of each metal ion taken in 100 mL (eluted in 5 mL of 4 mol L⁻¹HCl/HNO₃) were performed following the recommended procedure. It was found that the mean percentage recoveries of all the metal ions studied were 97.8–100.7% at 95% con-

fidence level. The RSD values were calculated to be below 5%. The results of water analysis with RSD <5% support the applicability of the method.

Applicability of the present method for preconcentration and determination of metal ions was accomplished by analyzing 500 mL of each water sample following recommended column procedure (direct method). The metal ion determinations were also confirmed using the method of standard additions from various real water (500 mL) samples, which were spiked with known amount (5 μg) of individual metal ions. Recommended column procedure was then applied to determine the total metal ion contents (Standard Additions Method, S.A). The close agreement of the results found by direct with that found by standard addition method (Table VII)

TABLE VI
Analysis of Metal Ions in Standard Reference Materials (Column Parameter: 50 mL, Solution; 4 mL min⁻¹, Sorption Flow Rate; 3 mL min⁻¹, Elution Flow Rate, 0.2 g, Resin)

Samples	Certified value (μg g ⁻¹)	Found by proposed method μg g ⁻¹ (RSD) ^a	Calculated Student's "t" value ^b
Vehicle exhaust particulates NIES 8 ^c	Cd:1.1, Co:3.3, Cu: 67, Ni: 18.5	Cd:1.06 (4.3), Co:3.2 (2.8), Cu:64.5 (3.4), Ni: 17.8 (3.2)	1.96, 2.49, 2.54, 2.74
Human hair NIES 5	Mn:5.2, Zn:169, Cu:16.3, Ni:1.8	Mn:5.0 (4.0), Zn:163.8 (2.9), Cu: 15.9 (2.8), Ni: 1.7 (4.8)	2.23, 2.44, 2.00, 2.74
Tea leaves NIES 7	Mn:700, Zn:33, Cu:7.0, Ni:6.5	Mn:690.0 (1.9), Zn:31.6 (3.8), Cu:6.7 (4.5), Ni:6.2 (4.3)	1.70, 2.60, 2.22, 2.51
Rompin hematite, JSS (800-3) ^d	Mn:2200, Cu:640, Zn: 1030	Mn:2185.5 (1.1), Cu:630.2 (1.9), Zn:1019.4 (1.4)	1.34, 1.83, 1.66
Zinc base die-casting alloy C NBS 627 ^e	Cu:1320, Cd:51, Mn: 140, Ni: 29	Cu:1310.2(1.2), Cd:49.1(4.1), Mn: 134.9(3.5), Ni: 27.5(4.6)	1.39, 2.11, 2.41, 2.65

^a Relative standard deviation, *n* = 5.

^b At 95% confidence level.

^c National Institute of Environmental Studies (NIES).

^d Iron and Steel Institute of Japan (JSS).

^e National Bureau of Standards (NBS).

TABLE VII

Determination of Metal Ions in Natural Water After Preconcentration by AXAD-4-SA Column (Column Parameter: 500 mL, Solution; 4 mL min⁻¹, Sorption Flow Rate; 3 mL min⁻¹, Elution Flow Rate, Amount of Resin 0.5 g)

Samples	Method	Metal ion found by proposed method $\mu\text{g L}^{-1}$ (\pm confidence limit ^a)						
		Cu(II)	Cr(III)	Zn(II)	Cd(II)	Mn (II)	Ni (II)	Co(II)
Canal water	Direct	15.2 \pm 0.90	5.7 \pm 0.58	7.2 \pm 0.33	N.D. ^b	3.6 \pm 0.27	6.4 \pm 0.36	5.3 \pm 0.44
	S.A. ^c	15.7 \pm 0.81	6.1 \pm 0.59	7.5 \pm 0.46	1.2 \pm 0.12	3.5 \pm 0.27	6.5 \pm 0.38	5.2 \pm 0.36
Tap water	Direct	11.9 \pm 0.85	9.7 \pm 0.69	15.4 \pm 1.18	N.D. ^b	10.3 \pm 0.74	5.8 \pm 0.31	7.5 \pm 0.46
	S.A.	12.1 \pm 0.99	10.2 \pm 0.83	16.3 \pm 1.29	1.1 \pm 0.12	10.4 \pm 0.80	5.9 \pm 0.35	7.5 \pm 0.54
Sewage water	Direct	10.2 \pm 1.16	6.5 \pm 0.66	4.1 \pm 0.26	4.6 \pm 0.20	5.1 \pm 0.29	11.8 \pm 0.87	6.4 \pm 0.62
	S.A.	10.5 \pm 1.01	6.8 \pm 0.64	4.5 \pm 0.26	4.6 \pm 0.21	5.2 \pm 0.28	11.9 \pm 0.94	6.5 \pm 0.75
River water	Direct	19.6 \pm 1.80	4.9 \pm 0.25	6.9 \pm 0.56	2.8 \pm 0.16	6.6 \pm 0.27	4.4 \pm 0.27	3.1 \pm 0.25
	S.A.	20.4 \pm 1.11	5.3 \pm 0.25	7.5 \pm 0.57	2.9 \pm 0.15	6.8 \pm 0.33	4.5 \pm 0.31	3.3 \pm 0.31

^a Confidence limit, C.L = $\bar{x} \pm \frac{ts}{\sqrt{N}}$, $n = 3$ at 95% confidence level.

^b N.D.= not detected.

^c S.A. = Standard addition.

indicates that the reliability of this method for metal analyses in water samples of various matrices without significant interference.

A blank run was performed applying recommended column procedure with 100 mL of aqueous solution prepared by adding suitable buffer (excluding metal ions) and finally eluting the same in 5 mL before subjecting it to FAAS determination. The detection limits, evaluated as three times the standard deviation (s) of the blank signal, were found to be 0.42, 0.57, 0.63, 0.77, 0.94, 0.96, and 1.41 $\mu\text{g L}^{-1}$ for Cu(II), Cr(III), Zn(II), Cd(II), Mn(II), Ni(II), and Co(II), respectively.

The proposed method has also been applied for the determination of metal ions in multivitamin formulation and food samples (IMS and vanaspati ghee). The observed results obtained were found to be accurate and in close agreement with the reported value (Table VIII).

CONCLUSION

The chelating ability of SA has been used in developing chelating sorbents for the purpose of separation and preconcentration of trace metal ions. The results reflect its promising nature for trace metal ion analysis in various natural water resources, environmental, and biological samples. The main advan-

tages of this procedure are the simple and fast preparation of the chelating resin and no requirement of organic solvents in the metal elution step. The excellent ability for the exclusion of alkali and alkaline earth elements on the AXAD-4-SA resin makes it desirable for use in the separation and preconcentration of trace elements because their presence often interfere in the subsequent FAAS determination. The results obtained demonstrated good reproducibility. Moreover, the use of a column preconcentration technique allows for the assessment of low trace metal concentrations, even by less sensitive determination methods such as FAAS. As compared to other previous works²⁷⁻²⁹ employing chelating resins using SA as the chelating ligand, this work covers more experimental parameters (such as breakthrough volume, Langmuir isotherm, matrices (including humic and fulvic acids) for interference studies, and has been found to be superior in various aspects, such as flow rate, preconcentration factor, half-loading time, and sorption capacity. This work also reports lower LOD (Limit of detection) that makes it more feasible for the preconcentration and determination of trace metal ions. Preconcentration by this material (AXAD-4-SA) from river water samples do not require any prior digestion of the samples. It can be successfully applied for the analysis of both environmental and biological samples as

TABLE VIII

Determination of Metal Ions in Capsule and Food Samples (Column Parameter: 50 mL, Solution; 4 mL min⁻¹, Sorption Flow Rate; 0.2 g, Resin)

Samples	Reported value ($\mu\text{g g}^{-1}$)	Found by proposed method $\mu\text{g g}^{-1}$ (RSD) ^a
Maxirich (Cipla)	Cu : 398.2; Zn : 442.5	Cu : 390.3 (2.7), Zn : 440.6 (3.3)
Lactogen 1(Nestle)	Cu : 2.9; Zn : 37.0	Cu : 2.8 (1.9), Zn : 35.8 (2.5)
Vanaspati ghee	Ni : 0.45	Ni : 0.40 (2.3)

^a Average of five determinations.

indicated by the high precision and absence of systematic errors.

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