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Macromolecular Chelator-Amberlite XAD-16 Anchored with 2,3-Dihydroxypyridine (DHP) for Enrichment of Metal Ions before their Determination by Flame Atomic Absorption Spectrometry

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Abstract: 2,3-Dihydroxypyridine (DHP) was loaded onto Amberlite XAD-16 via azo linker and the resulting resin AXAD-16-DHP explored for enrichment of Zn(II), Mn(II), Ni(II), Pb(II), Cd(II), Cu(II), Fe(III), and Co(II) in the pH range 4.0–6.5. The sorption capacity was found in the range 120–512 μmol g^{-1} and the preconcentration factor from 200 to 300. Tolerance limits for foreign species are reported. The kinetics of sorption is fast, as $t_{1/2}$ is generally ≤ 2 min. The chelating resin can be reused for fifty cycles of sorption-desorption without any significant change ($\leq 2.0\%$) in its sorption capacity. The limit of detection values (blank + 3s) are 2.90, 3.80, 5.17, 7.02, 1.91, 1.63, 4.59, and 5.02 μg L^{-1} for Zn, Mn, Ni, Pb, Cd, Cu, Fe, and Co respectively. The corresponding limit of quantification (blank + 10 s) values are 5.30, 6.20, 8.38, 9.54, 4.22, 4.17, 8.62, and 9.86 μg L^{-1}, respectively. The enrichment on AXAD-16-DHP coupled with monitoring by flame atomic absorption spectrometry (FAAS) is used to determine these metal ions in river and synthetic water samples, Co in vitamin tablets, and Zn in milk samples. AXAD-16-DHP has been found to perform better than DHP loaded cellulose and Amberlite XAD-2.

Keywords: 2,3-Dihydroxypyridine, Amberlite XAD-16, metal ion, preconcentration FAAS, polymers

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INTRODUCTION

The preconcentration/separation steps improve the detection limit and selectivity of determination by flame AAS. Several methods are known for preconcentration and separation of metal ions at trace/micro level and used according to the nature of the sample, the concentration of the analyte, and the measurement technique employed (1). Ion exchange (2), co-precipitaion (3–6), solvent extraction (7), and solid phase extraction (SPE) (8–19) are important among them but SPE with chelating matrices has rapidly grown in the recent past and coupled with FAAS and ICP-AES, it is frequently used. Chelating matrices generally have ligands immobilized on inert surfaces like silica gel (10, 11), cellulose (12–14) and organic co-polymers (17, 18, 21, 22). Amberlite XAD-2 is a commercially available co-polymer which is functionalized with a variety of ligands to design promising macromolecular chelators (18, 22, 24–28). Recently Aldrich (USA) has introduced Amberlite XAD-16 which has a higher surface area than that of Amberlite XAD-2, but in chemical essence is similar to it. Chelating matrices of very high sorption capacities (29, 30) are designed using Amberlite XAD-16. It was therefore thought worthwhile to load a small size ligand 2,3-dihydroxypyridine (DHP) onto Amberlite XAD-16 via azo-coupler and investigate the resulting chelating matrix (AXAD-16-DHP) for enrichment of Zn, Mn, Ni, Pb, Cd, Cu, Fe, and Co. The results of these investigations are reported in this paper. FAAS methods coupled with the enrichment with AXAD-16-DHP were developed for the eight metal ions and applied to determine Co in vitamin samples, Zn in milk samples, and all the metal ions in water samples. Earlier, DHP has been anchored on cellulose (13) and Amberlite XAD-2 (28) but the performance of the present matrix AXAD-16-DHP has been found to be superior in comparison to both, at least for Ni, Cd, Pb, and Cu.

EXPERIMENTAL

Instruments

Flame atomic absorption spectrometer (FAAS) of Perkin-Elmer Instruments, Shelton, USA (model Aanalyst 100) equipped with air-acetylene flame was used for monitoring Zn, Mn, Ni, Pb, Cd, Cu, Fe, and Co at wavelengths 213.9, 279.8, 231.1, 217.0, 228.8, 324.8, 248.8, and 240.7 nm, respectively. 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 a digital pH meter (Toshniwal Instruments, Ajmer, India). Thermogravimetric analysis (TGA) was carried out on a Dupont (Wilmington, Delaware, USA) 2100 thermal analyser and Perkin Elmer (Rotkreuz, Switzerland) elemental analyser, Model 240C, was used for elemental analyses. The flow of solution through the column was controlled using a peristaltic pump (Watson-Marlow Model 101/U/R, Falmouth, UK). Sorption and desorption of metal ions on the chelating matrix were generally carried out using columns of 1 cm in diameter and 10 cm in length (Pharmacia, Bromma, Sweden) equipped with adjustable frits. A mechanical shaker equipped with an incubator (Hindustan Scientific, New Delhi, India) (Speed 200 strokes min^{-1}) was used for batch equilibration.

Reagents

Amberlite XAD-16 (specific surface area $800\,\text{m}^2\,\text{g}^{-1}$ and bead size, 20–60 mesh) and 2,3-dihydroxypyridine (DHP) were obtained from Aldrich (Milwaukee, USA) and used as received. The stock solutions of metal ions ($1\,\text{g}\,\text{L}^{-1}$) were prepared from analytical reagent-grade metal salts as described earlier (20, 21) and standardized before use (22). The working solutions of the metal ions were made by suitable dilution of the stock solutions with doubly distilled water. 0.1 M HCl and NaOH, 0.1 M acetic acid-acetate buffer (pH 4 and 5), 0.1 M phosphate buffer (pH 6 and 7) and 0.1 M ammonia-ammonium chloride buffer (pH 8 and 9) were used to adjust the pH of the solutions, wherever suitable. Water samples from the Ganges river (Haridwar, India), Yamuna river (New Delhi, India), and tap water (New Delhi, India) were collected, acidified with 2% HNO_3, filtered, and stored in glass bottles. The glassware was washed with chromic acid and soaked in 5% HNO_3 overnight and cleaned with doubly distilled water before use.

Synthesis of DHP Loaded Amberlite XAD-16 (AXAD-16-DHP)

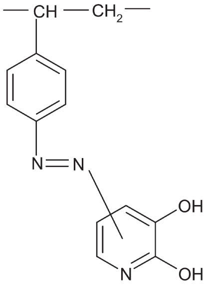
The nitrated beads of Amberlite XAD-16 were prepared and reduced to amino resin by published procedures (21, 22) for Amberlite XAD-2. The amino resin was suspended in 200 mL of ice-cold water and diazotized with 1 M HCl and 1 M $NaNO_2$ solution at -5°C until the reaction mixture started to change the color of iodide paper to violet. The diazotized polymer was filtered under ice-cold conditions (diazotized compounds disintegrate at higher temperature) and reacted with DHP (in 2% NaOH) at 0 to 5°C for 24 h. The resulting brownish crimson colored beads were filtered and washed with 4 M HCl and doubly distilled water successively and finally air dried.

Recommended Column Method for Preconcentration and Determination of Metal Ions

AXAD-16-DHP (1.0 g) swollen for 24 h was packed in a glass column C10/10 (Pharmacia, 10 cm × 10 mm), between frits, using the method recommended by the manufacturer (23). The column was treated with 4 M HCl or HNO_3 (50 mL) and washed with doubly distilled water until free from acid. A suitable aliquot of the sample solution containing Zn(II), Mn(II), Ni(II), Pb(II), Cd(II), Cu(II), Fe(III), or Co(II) in the concentration range 0.0050–1.0 μg mL^{-1} was passed through the column after adjusting its pH to optimum value (Table 1) at a flow rate of 1–5 mL min^{-1}, controlled with a peristaltic pump. The column was washed with distilled water to remove free metal ions. The bound metal ions were stripped from it with HCl or HNO_3 (10–25 mL) of optimum concentration given in Table 1, passed at flow rate of 1–4 mL min^{-1}. The metal ions in the eluate were determined by FAAS, standardized previously [after dilution with double distilled water if concentration exceeded the working range of FAAS].

Recommended Batch Method for Preconcentration and Determination of Metal Ions

A sample solution (100 mL) containing 0.1–32.5 μg mL^{-1} of Zn, Mn, Ni, Pb, Cd, Cu, Fe, or Co was placed in a glass stoppered bottle (250 mL) after adjusting its pH to the optimum value. AXAD-16-DHP (0.1 g) was added. The bottle was stoppered and shaken for 30 min on a mechanical shaker. The resin was filtered and the metal ions were stripped from the resin beads by treating them with HCl or HNO_3 of suitable strength given in Table 1. The resin was filtered off and the filtrate was aspirated into the flame of pre-standardized FAAS, after suitable dilution, if required.



I

RESULTS AND DISCUSSION

Characterization of Sorbent

The AXAD-16-DHP (**I**) was characterized by ^{13}C CPMAS NMR, FT-IR, TGA and elemental analyses. In its ^{13}C CPMAS NMR (Fig. 1) the signal at 158.8 ppm is due to C-OH of DHP. The signal at 40.5 ppm is due to CH_2 of polymer. The CH signals at 59 to 80 ppm are weak. The signals between 165 and 186 ppm appear due to C=O (as DHP exists in tautomeric form), C=N/C-N of pyridine ring and two C-N=N-groups. Its FT- IR spectrum

Table 1. Optimum conditions for the sorption and desorption of metal ions

	Metal ions							
Experimental parameter	Zn(II)	Mn(II)	Ni(II)	Pb(II)	Cd(II)	Cu(II)	Fe(III)	Co(II)
pH range	4.0–5.5	4.0–5.0	4.5–6.0	3.5–4.5	4.5–6.0	4.5–6.5	4.5–5.5	5.0–6.5
Flow rate (mL min^{-1})	1.0–5.0	2.0–4.0	1.0–5.0	2.0–4.0	1.0–5.0	2.0–5.0	2.0–4.0	1.0–5.0
HCl/HNO_3 concentration for desorption (M)	1.0–3.0	1.5–4.0	1.5–3.0	1.0–2.0[a]	1.5–3.0	1.0–3.0	1.0–3.5	1.5–3.0
Sorption capacity of resin (μmol g^{-1})	195	120	265	182	175	512	160	140
Average recovery (%)	98.6	97.4	97.2	99.4	97.6	98.4	99.7	97.0
Standard deviation[b]	0.0403	0.0114	0.0192	0.0148	0.0114	0.0894	0.0151	0.0158
Relative standard deviation (%)	4.09	1.17	1.97	1.49	1.16	0.91	1.52	1.63

[a] Only HNO_3 was used for desorption.

[b] For five determinations of 0.25 μg mL^{-1} metal ion (0.5 μg mL^{-1} for Pb).

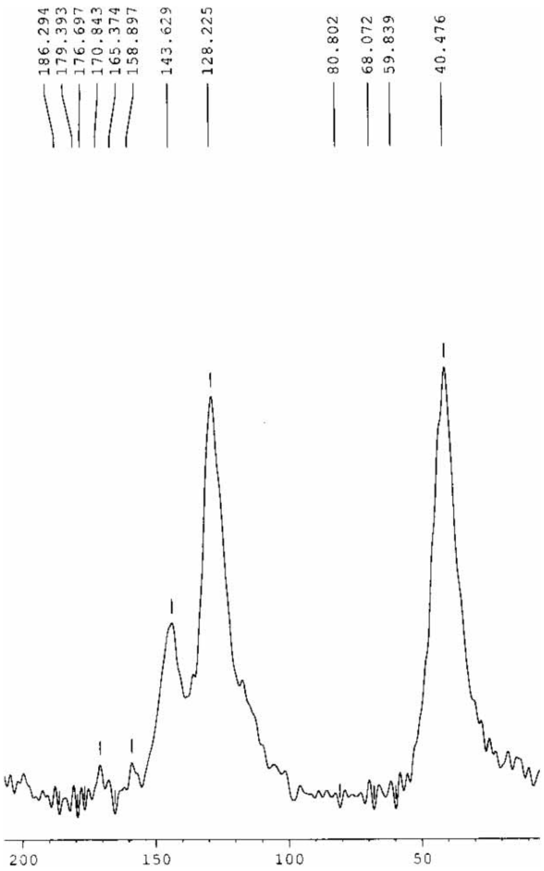


Figure 1. ^{13}C CPMAS spectra of AXAD-16-DHP.

(Fig. 2) has bands at 1262 (C-O stretching, in plane), 1500 (-N═N-stretching), 1546, 1527 (phenyl ring vibrations) and 1622 cm^{-1} (O-H stretching), which support the immobilization of DHP on Amberlite XAD-16. The surface area of Amberlite XAD-16-DHP was found to be 420.7 m^2 g^{-1}. The weight loss in TGA (Fig. 3) of AXAD-16-DHP was ~13.65% at 200°C. It indicates approximately two water molecules per repeat unit. Elemental analyses: Found C 63.80, H 4.31, N 17.01%. Calc. (For I + 20% divinyl benzene): C, 76.40; H, 5.77; N, 17.82%. These data suggest that nearly 80% of the Amberlite XAD-16 matrix is functionalized.

Optimum Conditions for Sorption and Desorption

The multivariate approach was used to optimize the working conditions for sorption of the eight metal ions on the column packed with the Amberlite

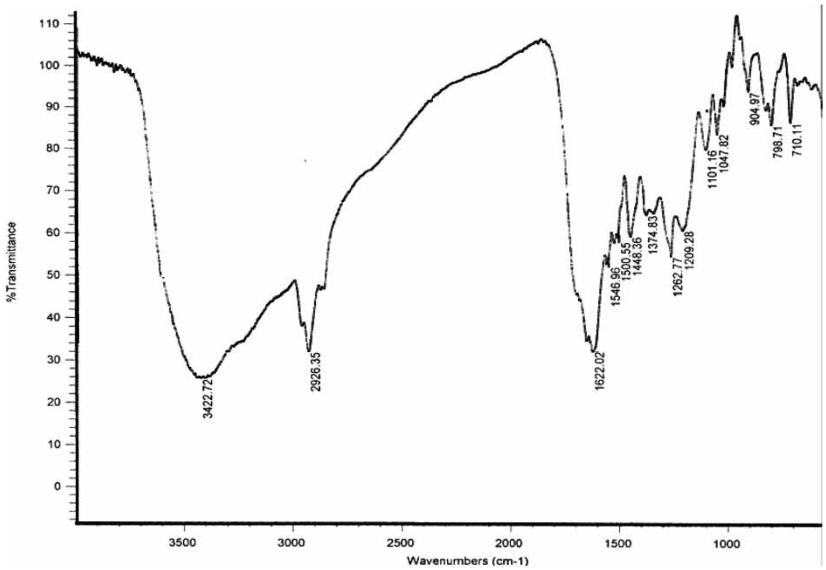


Figure 2. IR spectra of AXAD-16-DHP.

XAD-16-DHP (pH and flow rate) and their desorption (acid concentration, volume of eluent). Each optimum condition (Table 1) was rechecked after standardizing the all other working conditions. A typical optimization of pH for sorption of Cu on a resin column is as follows. A set of solutions (volume: 100 mL), each containing 0.25 μg mL^{-1} of Cu was taken. The pH of the solutions of the set was adjusted to different values in the range 2.0–9.0. The enrichment of the Cu(II) from these solutions was studied by the recommended column procedure and optimum pH range established is given in Table 1 (pH profiles shown in Fig. 4). The effect of pH was also studied by using the recommended batch method and the results were found to be consistent with those of the column method. The use of 4–10 mL of acetate/phosphate/ammonia buffer to adjust the pH does not affect the sorption behavior. The metal ions are not significantly desorbed ($<2\%$) by distilled water; therefore chelation contributes predominantly to the retention of metal ions.

The degree of metal ion sorption on a column packed with Amberlite XAD-16-DHP (1 g) was studied at various flow rates of the metal ion solution controlled with a peristaltic pump. The optimum flow rate for loading of all these metal ions is between 1.0–5.0 mL min^{-1}. A flow rate <1.0 mL min^{-1} was not employed to avoid the longer time of analysis. At flow rate >5.0 mL min^{-1}, there was a decrease in the percentage of sorption, probably because the metal ions do not equilibrate sufficiently with the resin. HCl and HNO_3 (at flow rates between 1.0 and 4.0 mL min^{-1}) were found to be the most suitable for stripping off the bound metal ions. The concentration of

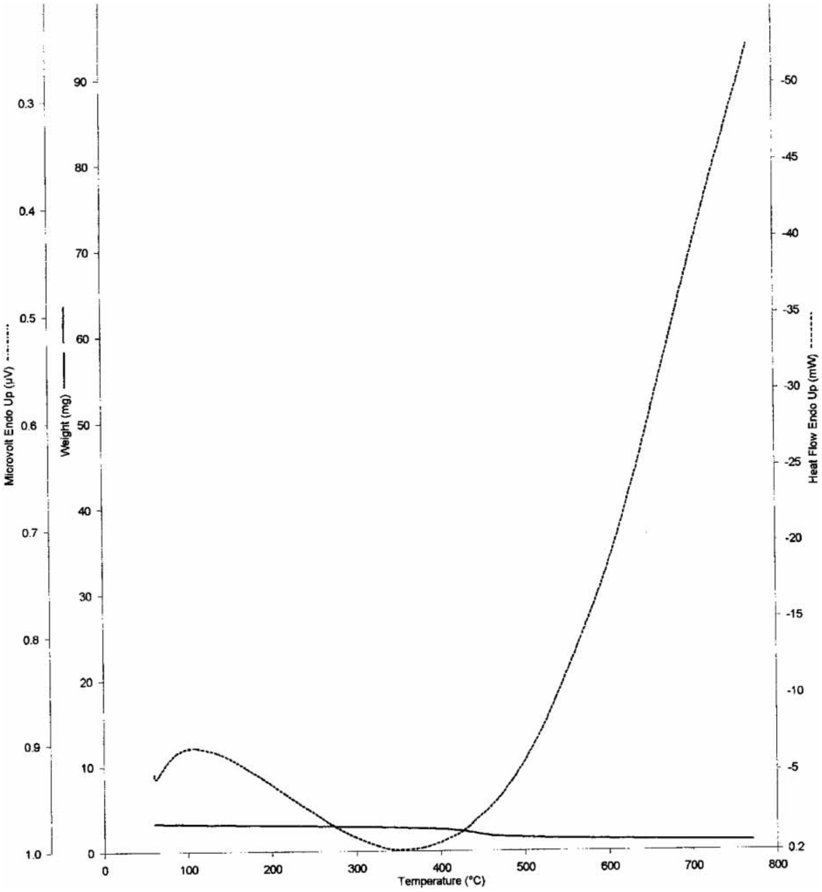


Figure 3. TGA of Amberlite XAD-2-DHP.

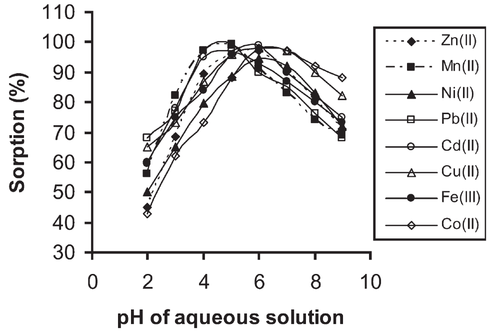


Figure 4. Effect of pH on sorption of Zn(II), Mn(II), Ni(II), Pb(II), Cd(II), Cu(II), Fe(III), and Co(II) onto Amberlite XAD-16-DHP.

these acid solutions and their volume for desorption (recovery >96.0%) of metal ions from the AXAD-16-DHP column was optimized by eluting the column with 10–25 mL of HCl/HNO_3 (1 to 4 M) at an optimum flow rate. The concentrations are given Table 1. The 10 mL of 1.5 M HCl was found suitable for quantitative recovery (96.3–99.6%) of all the metal ions (concentration $\leq 1\ \mu g\ mL^{-1}$), except Pb for which 1.0 M HNO_3 (10 mL) was required for 99.7% recovery.

Sorption Properties of Sorbent

The kinetics of sorption was studied by batch method. Amberlite XAD-16-DHP (0.5 g) was shaken with 50 mL of solution containing 40 $\mu g\ mL^{-1}$ of one of the eight metal ions for different equilibration times (2, 5, 10, 15, 20, 25, 30, 35, 40 min, and 5 h) under optimum conditions including pH (Table 1). The concentration of metal ions loaded onto the matrix as well as present in the supernatant solution was determined with FAAS after appropriate dilution. The variation of sorption as a function of time for all the metal ions is shown in Fig. 5. Shaking for 2 min was found to be sufficient for more than 50% sorption of all the metal ions except Co and Cd for which 5 min equilibration was needed.

Amberlite XAD-16-DHP (1 g) was saturated with Zn, Mn, Ni, Pb, Cd, Cu, Fe, or Co ion solution (concentration: 50 $\mu g \ldots mL^{-1}$) by equilibrating it with that on a mechanical shaker under optimum conditions (Table 1). The resin was filtered and washed with distilled water. The metal ions loaded on it were desorbed with 100 mL of 1.5 M HCl/1.0 M HNO_3 and determined with a pre-standardized FAAS to calculate the capacity. The filtrate after removing the resin was diluted suitably (to bring the metal ion concentration in the working range) and also subjected to flame AAS determination to further verify the capacity value. The results are reported in Table 1. The capacity for Cu was found to be highest. The sorption capacity values were also determined by column method and found to be consistent with the batch method values (variation <1.6%).

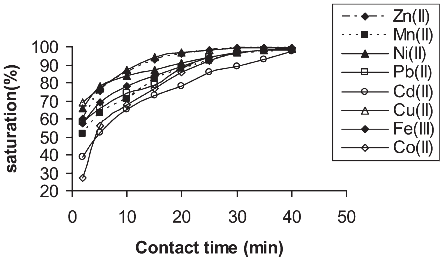


Figure 5. Kinetics of the sorption of metal ions on Amberlite XAD-16-DHP.

The stability of Amberlite XAD-16-DHP was studied in acid (1.0–6.0 M HCl/HNO_3) by batch method. The resin was shaken with acid solutions of varying concentrations for 6 h, filtered, washed with distilled water until free from acid, air-dried, and subjected to sorption capacity determination by batch method. The capacity values were found to be similar to those of untreated one (variation $\leq 2.0\%$). Thus present resin can withstand acid concentration up to 6 M. It can also be reused for fifty cycles of sorption-desorption, without any significant change ($<1.0\%$) in the sorption capacity.

The enrichment factor was determined by increasing the dilution of metal ion solution while keeping the total amount of loaded metal ion fixed at 15 μg for Fe, 20 μg for Zn or Ni, and 25 μg for Mn, Pb, Cd, Cu, or Co and applying the recommended column procedure. The feed volume and preconcentration factors are given in Table 2 with recoveries at the lowest concentration level. The limit of detection values [(blank + 3 s), where s is standard deviation of the 10 blank determinations] are 2.90, 3.80, 5.17, 7.02, 1.91, 1.63, 4.59, and 5.02 $\mu g\, L^{-1}$ for Zn, Mn, Ni(II), Pb, Cd, Cu, Fe, and Co respectively and corresponding limit of quantification (blank +10 s) values are 5.30, 6.20, 8.38, 9.54, 4.22, 4.17, 8.62, and 9.86 $\mu g\, L^{-1}$, respectively.

The effects of NaCl, NaBr, $NaNO_3$, Na_2SO_4, Na_3PO_4, NaI, Ca(II), Mg(II), and humic acid and some common complexing agents on the sorption efficiency of Zn, Mn, Ni, Pb, Cd, Cu, Fe, and Co (25 μg each) onto AXAD-16-DHP were studied using the recommended column method under the optimum conditions given in Table 1. They were added to the metal ion solution before applying the recommended column procedure. Tolerance limits given in Table 3 suggest that common anions, alkali, and alkaline earth metal ions do not adversely affect the sorption on the present resin when present in moderate amounts. Humic acid and other organic acids viz EDTA, ascorbic, citric, and tartaric acid can coexist with metal ions at low concentration levels only (Table 3) during their enrichment. Species is considered to interfere when it lowers the

Table 2. Enrichment factors and enrichment limits of metal ions

Metal ion	Total volume (mL)	Concentration (ng mL^{-1})	Final volume (mL)	Recovery (%)	Preconcentration factor
Zn(II)	3000	6.7	10	99.2	300
Mn(II)	2000	12.5	10	98.5	200
Ni(II)	2000	10.0	10	99.1	200
Pb(II)	3000	8.33	10	99.7	300
Cd(II)	2500	10.0	10	97.5	250
Cu(II)	3500	7.14	10	99.5	300
Fe(III)	3000	5.0	10	98.3	300
Co(II)	2000	12.5	10	96.3	200

Table 3. Tolerance limit of electrolytes, Ca(II) and Mg(II) and other species

Foreign species	Metal ion							
	Zn(II)	Mn(II)	Ni(II)	Pb(II)	Cd(II)	Cu(II)	Fe(III)	Co(II)
NaNO$_3$[a]	0.9	0.3	0.014	0.25	0.003	0.009	0.45	0.080
NaCl[a]	0.20	0.006	0.012	0.008	0.2	0.040	0.010	0.007
NaBr[a]	0.026	0.065	0.018	0.014	0.72	0.034	0.08	0.02
Na$_3$PO$_4$[a]	I	0.002	0.004	0.001	0.003	0.009	0.006	0.007
Na$_2$SO$_4$[a]	0.012	0.008	0.003	0.09	0.04	0.43	0.14	0.080
NaI[a]	0.4	0.004	0.005	0.085	0.028	0.055	0.120	0.35
Humic acid[b]	15	13	18	8	10	22	19	12
Ascorbic acid[c]	0.22	0.32	0.65	0.42	0.85	0.09	0.65	0.34
Citric acid[c]	0.25	1.20	0.42	0.69	1.4	2.2	0.95	0.32
EDTA[c]	0.003	0.001	0.006	0.18	0.010	0.24	0.015	0.010
Tartaric acid[c]	1.2	0.4	0.8	1.28	0.75	0.09	0.18	0.46
Ca(II)[a]	0.045	0.008	0.035	0.019	0.060	0.42	0.065	0.90
Mg(II)[a]	0.002	0.010	0.55	0.20	0.003	0.30	0.22	1.55

[a] $\mathrm{M\ L^{-1}}$.
[b] $\mu\mathrm{g\ mL^{-1}}$.
[c] $\mathrm{mM\ L^{-1}}$ and I = interfere.

recovery of metal ions more than 3% in comparison to the value observed in its absence. Each reported tolerance/interference is in the preconcentration and not in the determination by FAAS, as checked with the help of reagent matched standard solutions.

The sorption capacity of a chelating matrix depends on many factors, which include the nature of the ligand, the surface area of the supporting matrix, the amount of the ligand immobilized, hydrophilic/hydrophobic character of the support, and its porosity. Consequently its rationalization is not easy except the qualitative one. The present chelating matrix exhibits higher sorption capacity than those of Amberlite XAD-2 based systems (Table 5) barring few exceptions viz. thiosalicylic acid loaded Amberlite XAD-2 (Ni and Cd) and Tiron loaded Amberlite XAD-2 (Mn). The sorption capacities of the present resin are also comparable to those of silica gel/cellolose based matrices for most of the metal ions. In comparison to DHP loaded Amberlite XAD-2 the present matrix exhibits better sorption capacities for all the metal ions. The sorption capacities of the present matrix for Ni, Cd, Pb, and Cu are better than those of cellulose loaded with DHP. The sorption capacities reported for N-(3,4-dihydroxy)-benzyl-4-amino-3-hydroxynaphthalene-1-suphonic acid (30) anchored

Table 4. Comparison of sorption capacities (μmol g^{-1})

Immobilized ligand	Zn	Mn	Ni	Cd	Pb	Cu	Fe	Co
Support: Amberlite XAD-16								
2,3-Dihydroxypyridine (present matrix)	195	121	265	175	183	512	160	140
N-(3,4-dihydroxy)benzyl-4-amino-3-hydroxy-naphth-alene-1-sulphonic acid (30)			1210	760	880	2050		780
2-{[1-(3,4-Dihydroxy phenyl) methylidene] amino}benzoic acid (29)	198	178	269	128	97	468	515	221
Amberlite XAD-2								
Thiosalicylic acid (2)	47		310	198	89	214	66	106
Chromotropic acid (18, 24)	148		103	83	186	134	58	65
Pyrocatechol (18, 25)	28		53	41	105	93	74	23
o-Aminophenol (26)	45		55	30	16	53		58
Tiron (27)	170	182.	215	84	60	220	100	110
Pyrogallol (17)	69	82	70	4	32	71	83	70
Quinalizarin (21)	22	17		15	26	50		28
2,3-Dihydroxypyridine (DHP) (28)	176	91	220	150	66	407	90	87
Silica gel								
Resacetophenone (10)	191		254	58	67	186	273	365
8-Hydroxy quinoline (11)	177		255	92	158	448	386	205
Cellulose								
2,3-Dihydroxypyridine (13)	315		208	70	83	343	431	146
Pyrocatechol (12)	85		140	116	104.	186	109	160
8-Hydroxyquinoline (14)	349		178	114	94	630	256	206

Amberlite XAD-16 are exceptionally high, whereas the preconcentration factors are not (Table 6). The two sets of chelating sites present in the same ligand molecule may be responsible for these high values of sorption capacities. 2-{[1-(3,4-Dihydroxyphenyl)methylidene]amino}benzoic acid loaded Amberlite XAD-16 (29) has somewhat better sorption capacities than the present matrix, except for Pb and Cd. This may be due to the multidentate nature of ligand loaded. The higher surface area of the Amberlite XAD-16 in comparison to Amberlite XAD-2 is also partly responsible for the high sorption capacities of chelating matrices based on former as a support. The preconcentration factors of the present matrix are comparable or superior to those of many other matrices (Table 6). On comparing with DHP loaded Amberlite XAD-2, it has been found that the present matrix shows better preconcentration factors except for Ni. In comparison to DHP loaded cellulose the present matrix shows far superior preconcentration factors.

Table 5. Comparison of preconcentration factors

Immobilized ligand	Zn	Mn	Ni	Cd	Pb	Cu	Fe	Co
Support: Amberlite XAD-16								
2,3-DHP (present matrix) N-(3,4-dihydroxy)benzyl	300	200	200	250	300	350	300	200
4-Amino,3-hydroxynaphth alene-1-suphonicacid (30)			333	267	234	300		300
2-{[1-(3,4-Dihydroxyphenyl) methylidene] amino}benzoic acid (29)	300	250	100	250	250	300	450	167
Amberlite XAD-2								
Thiosalicylic acid (20)	200		200	200	100	200	400	180
Chromotropic acid (18, 24)	200		200	100	200	100	120	150
Pyrocatechol (18, 25)	100		200	200	200	100	80	200
o-Aminophenol (26)	40		65	50	40	50		100
Tiron (27)	180	64	150	48	25	200	80	56
Pyrogallol (17)	160	120	120	40	25	65	140	65
Quinalizarin (21)	100	65		50	50	100		40
2,3-Dihydroxypyridine (DHP) (28)	250	200	250	200	300	250	100	150
Amberlite XAD-7								
8-(Benzene sulfonamide quinoline) (31)	10			10				
Silica gel								
Resacetophenone (10)	150		200	250	250	250	200	300
8-Hydroxyquinoline (11)	200		200	150	250	300	300	250
Cellulose								
2,3-DHP (13)	200		125	200	200	250	300	100
Pyrocatechol (12)	180		75	250	200	300	300	100
8-Hydroxyquinoline (14)	250		90	250	200	300	300	100

Applications of the Enrichment and Determination

Determination of Metal Ions in Water Samples

AXAD-16-DHP was used to preconcentrate and determine the eight metal ions in samples collected from the Ganges (Haridwar), Yamuna (New Delhi) rivers and municipality water supply (New Delhi). The metal ions were estimated with and without (referred as direct determination) standard addition by passing 1000 mL of water sample (spiked with 5.0–10.0 μg of each of the seven metal ions in case of standard addition method) through the column packed with 1.0 g of resin after adjusting the pH to an optimum value (Table 1) and determining the metal ion as described in the recommended column procedure using 10 ml of eluent. The results are given in Table 6. The

Table 6. Determination of metal ion in water samples

		Metal ion (μg dm^{-3}) (RSD)							
Origin of sample	Method	Zn	Mn	Cd	Ni	Pb	Cu	Fe	Co
Yamuna river, New Delhi	Direct	5.7 (2.2)	4.3 (8.2)	—	6.7 (1.9)	11.0 (4.1)	38.7 (1.4)	68.7 (1.4)	—
	S.A.	5.6 (1.9)	4.2 (5.9)	—	6.8 (3.5)	10.8 (3.1)	38.5 (1.7)	68.5 (1.7)	—
Ganges river, Haridwar	Direct	5.9 (7.1)	2.8 (5.9)	6.9 (2.4)	4.7 (5.1)	3.9 (5.8)	32.3 (1.2)	47.0 (1.8)	13.4 (1.4)
	S.A.	5.8 (3.7)	2.9 (3.2)	6.8 (4.5)	4.8 (3.8)	3.8 (4.3)	32.2 (1.6)	47.2 (1.7)	13.3 (1.1)
Tap water, New Delhi	Direct	—	16.8 (1.2)	1.7 (7.4)	3.9 (3.2)	17.0 (2.1)	9.1 (3.7)	42.0 (1.1)	14.3 (2.1)
	S.A.	—	16.9 (1.6)	1.6 (8.7)	4.0 (2.8)	17.2 (1.3)	9.0 (2.6)	41.8 (1.7)	14.2 (4.3)

Direct: Recommended procedure directly applied.

S.A. Standard addition method.

RSD is for four determinations.

concentrations reported in Table 6 as estimated by standard addition (SA) method are the values obtained by subtracting the amount of metal added for spiking from the total metal recovered. The closeness of results of the direct and the SA method indicates the reliability of the present results of metal analyses in water samples and suitability of AXAD-16-DHP for metal enrichment from water samples.

Determination of Co in Pharmaceutical Samples

Ten tablets (weighing 3.25 g) of Polybion (Merck, Mumbai, India) were digested with 25 mL of concentrated HNO_3 by slowly increasing the temperature of the mixture to 400 K, until a solid residue was obtained. The residue was cooled, dissolved in 20 mL of concentrated HNO_3, and the solution gently evaporated on a steam bath until a residue was left again. It was mixed with 50 mL of distilled water and concentrated HNO_3 added drop wise until a clear solution was obtained on gentle heating. The pH of the resulting solution was adjusted to optimum level (Table 1) by adding 10 mL of the phosphate buffer and its Co content was estimated by the recommended column procedure. The average amount of Co (4 determinations) was found to be 1.94 $\mu g\ g^{-1}$ of tablet (RSD of 3.87%). The reported value of Co in the tablet is 1.96 $\mu g\ g^{-1}$. There is good matching between experimentally observed and reported values for the Co content (good recovery), which indicates that the excipients of the tablet do not adversely affect the present procedure.

Determination of Zn in and Milk Sample

A sample of powdered milk (1.0 g) was digested with a mixture of concentrated H_2SO_4 (20 mL) and HNO_3 (8 mL) till a clear solution was obtained. It was allowed to cool and most of the acid was neutralized with NaOH. The pH of the solution was adjusted to optimum value (Table 1) and the volume made up to 1000 mL. The solution was passed through the AXAD-16-DHP column under optimum conditions. The zinc ions were eluted from the column using 25 mL of 1.5 M HCl and determined using FAAS. The average amount of Zn (4 determinations) was found to be 37.18 $\mu g\ g^{-1}$ of milk powder (RSD 4.14%). The reported value of Zn in the milk sample is 38 $\mu g\ g^{-1}$.

Analysis of Synthetic Water Samples

To check the validity and accuracy of the present matrix coupled with flame AAS for metal ion monitoring, the recommended procedure was applied to determine the copper and iron content in synthetic water samples (1000 mL) having a composition similar to certified water samples SLRS-4 (National Research Council, Ottawa, Ontario, Canada). The averages of four determinations of copper and iron were found to be 1.76 and 102.0 $\mu g\ mL^{-1}$ respectively (RSD 3.03 and 3.38% respectively). Amounts ($\mu g\ mL^{-1}$) taken in the synthetic sample were: Cu, 1.81 and Fe, 103.

CONCLUSION

Amberlite XAD-16 on loading 2,3-dihydroxypyridine results in a matrix which shows good sorption capacities (120–512 $\mu mol\ g^{-1}$) and the preconcentration factors (200 to 300) for the enrichment of Zn(II), Mn(II), Ni(II), Pb(II), Cd(II), Cu(II), Fe(III), and Co(II) in the pH range 4.0–6.5. The $t_{1/2}$ is generally ≤ 2 min. The chelating resin can be reused for fifty cycles of sorption-desorption without any significant change ($\leq 2.0\%$) in its sorption capacity. The quanitificatiom limits possible with the resin are between 4.17–9.86 $\mu g\ L^{-1}$. AXAD-16-DHP has been found suitable for determining ions in river and synthetic water samples, Co in vitamin tablets and Zn in milk samples with RSD values $\leq 8.7\%$. In comparison to Amberlite XAD-2 based matrices the sorption capacities of AXAD-16-DHP are higher, probably the difference is contributed by a larger surface area of Amberlite XAD-16.

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