Research Article

Preconcentration and Flame Atomic Absorption Spectrometric Determination of Cu(ll), Ni(ll), Co(ll) and Mn(ll) in Environmental Samples using 6-aminopyridin-2-yliminomethylnapthalen-2-ol

A. Saranga Pani[1*], M. Ramamohan Reddy[2], R. Kishore Kumar[1] and N. V. S. Naidu[2]

[1]Department of Chemistry, S. V. Arts College, Tirupati, India -517502
[2]Enviro analytical Laboratories, Department of Chemistry, S. V. University, Tirupati, India -517502

Abstract

A facile separation and preconcentration procedure were established for the determination of trace amounts of Cu(II), Ni(II), Co(II) and Mn(II) in water samples using Amberlite XAD-1180 functionalized with a new chelating ligand, 6-aminopyridin-2-yliminomethylnapthalen-2-ol (APIMN). The sorbed elements were subsequently eluted with 10mL of 2 M HNO_3 and the elutes were analyzed by FAAS. The influences of the analytical parameters including pH, amount of adsorbent, eluent type and volume, flow-rate of the sample solution, volume of the sample solution and matrix interference effect on the retention of the metal ions have been studied. The optimum pH for the sorption of above mentioned metal ions was about 6.0. The sorption capacity of the resin was determined. The limit of detections was found to be 2.2, 2.6, 3.0 and 3.2 $\mu g\ mL^{-1}$ for Cu(II), Ni(II), Co(II) and Mn(II) respectively by applying a preconcentration factor 72. Recoveries under optimum conditions were found to be 94.0 to 99.0 % at the 98 % confident level. The proposed method was successfully applied for the determination of Cu(II), Ni(II), Co(II) and Mn(II) in environmental samples. The results were obtained are good agreement with reported method.
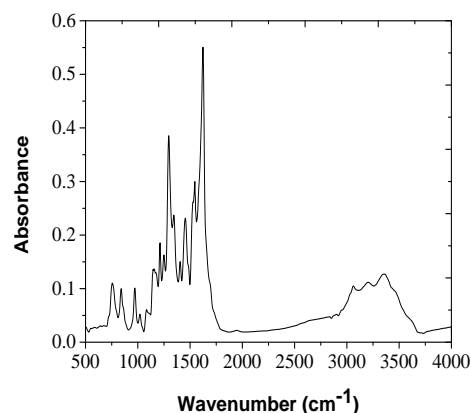
*Correspondence
A. Saranga Pani
E-mail: rayanuthalakishore@gmail.com

Introduction

The bioaccumulation of heavy metal ions in living cells can cause several progressive diseases such as, kidney deficiencies, lung problems, bone lesions, nervous system damages, hypertension and cancer in humans and animals [1-3]. Sensitive and accurate determination of metals at trace level is one of the important points of the analytical chemistry [4-5]. Although the sensitive and accurate determination of trace elements is by some instrumental techniques such as inductively coupled plasma mass spectrometry, (ICP-MS) [6-7], inductively coupled plasma optical emission spectrometry (ICP-OES) [8], graphite furnace atomic absorption spectrometry (GFAAS) [9] and flame atomic absorption spectrometry (FAAS) [10–12] are routinely used for the quantification of trace metals in the environmental samples. Compared with other techniques, Flame atomic absorption spectrometry (FAAS) is relatively simple and available technique in many laboratories for trace metal determinations [13–15]. However, the determinations of trace elements at microgram per liter concentration levels by FAAS are often difficult, not only because of its insufficient sensitivity, but also because of matrix effects. To solve this problem, separation–preconcentration procedures are often involved prior to analysis by FAAS. For this purpose, numerous separation and

preconcentration procedures have been developed for trace metal ion determination in various matrices. These methods include liquid–liquid extraction [16], ion exchange techniques [17], co-precipitation [18], cloud point extraction [19-20] and solid phase extraction [21-22] etc., the later is preferred due to its simplicity for the trace metal ions preconcentration by the researchers.

Solid phase extraction (SPE) is the most common pre-treatment method for sample matrix simplification and pre-concentration of trace amounts of analyte in samples. Compared with traditional liquid–liquid extraction method, SPE has the following advantages: (i) high preconcentration factor; (ii) simple operation; (iii) rapid phase separation; (iv) can be combined with different detection techniques and (v) time saving and cost saving [23]. Several solid phase materials such as activated carbons [24], Chromosorb 105 [25], cotton [26], surfactant-coated alumina [27] and silica gel [28] were employed for the separation and preconcentration of the metal ion in the various environmental samples. Several papers have been reported for the determination of metal ions in various environmental samples [29-32]. Chelating reagents like ammonium pyrrolidine dithiocarbamates (APDC) and sodium diethyl dithiocarbamates (Na-DDC) are generally used for complexation and extraction of trace metal ions into an organic solvent. Use of APDC and Na-DDC has certain disadvantages like poor sensitivity, less stability and low recoveries.

In this work, we have developed a facile, sensitive and novel analytical method for the separation and preconcentration of Cu(II), Ni(II), Co(II) and Mn(II) in environmental samples. The column was loaded with functionalized Amberlite XAD-1180 by covalent coupling of synthesized ligand 6-aminopyridin-2-yliminomethylnapthalen-2-ol (APIMN). The sorbed elements were eluted with 10 mL of 2 M HNO_3 and eluates were analyzed by FAAS. Optimum experimental conditions were investigated with respect to a standard solution of the matrix, in order to examine the possibility of obtaining the maximum extraction efficiency with minor sample treatment and minimal experimental conditions. Under these conditions the preconcentration factor was found to be **76 for 500 mL** of sample solution. The precision, as the percent relative standard deviation and the method detection limits were studied. The proposed method was successfully applied to the river and sea water samples, and its accuracy was tested by using a certified reference material.

Materials and Methods

Apparatus

Flame Atomic absorption spectrophotometer (FAAS, Model AA 6300, Shimadzu, Japan) with air-acetylene flame and hollow cathode lamps were used for the analysis of Cu(II), Ni(II), Co(II) and Mn(II) . The instrumental parameters recommended by the manufacturer were represented in **(Table 1)**. Fourier Transform Infrared (FT-IR) spectrometer (Thermo-Nicolet FT-IR, Nicolet IR-200, USA), Gemini-200 Varian, Switzerland and Avance - 300 Bruker, Switzerland were used for NMR studies used to characterize the new chelating compound and Elico (LI-129) pH meter was used for pH measurements.

Table 1 Recommended experimental conditions

Flame: acetylene-air (L min^{-1})	
Acetylene flow-rate	120
Air flow-rate	480
Analytical wavelength(nm)	
Cu(II)	349.2
Ni(II)	351.5
Co(II)	346.6
Mn(II)	321.7

Lamp current (mA)	8.0
Measurement mode	Background correction
Detection limits ($\mu g\ mL^{-1}$)	
Cu(II)	2.2
Ni(II)	2.6
Co(II)	3.0
Mn(II)	3.2

Reagents and Solutions

Reagents used were of analytical reagent grade and doubly distilled water is used for the preparations of stock and standard solutions unless specified. All the chemicals were purchased from Merck Chemicals, Mumbai, India. Standard stock solutions (1000 mg L^{-1}) of Cu(II), Ni(II), Co(II) and Mn(II) were prepared by dissolving the proper amounts of analyte in doubly distilled water. Working standards of solutions were prepared by the appropriate dilution of the stock solution daily in doubly-distilled water for reference solutions. Equimolar solutions of NH_4OH and HCl were added appropriately to get a desirable pH of 6.0. The Schiff-base derivative 6-aminopyridin-2-made up to the mark with doubly distilled water in a 100mL standard flask.

Synthesis of the 6-aminopyridin-2-yliminomethylnapthalen-2-ol
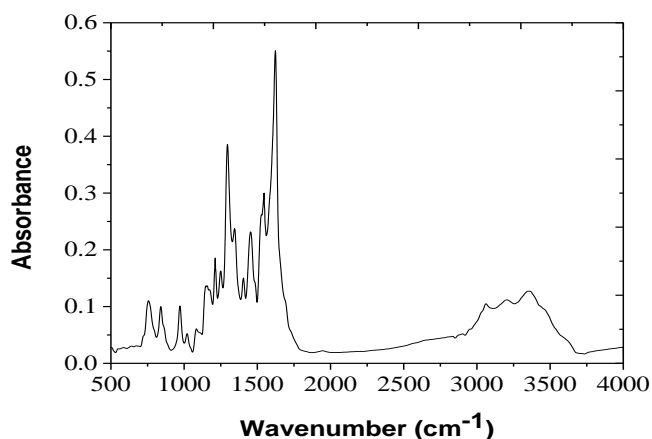

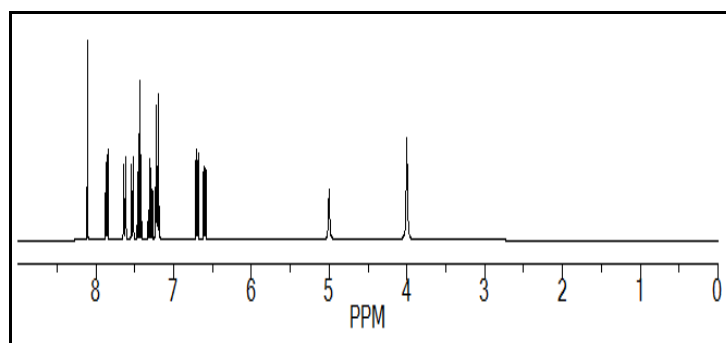**Figure 1a** FTIR spectrum of APIMN

Figure 1b NMR spectra of the APIMN

A mixture of 2-hydroxynapthalene-1-carbaldehyde (3.44 g, 20.0 mmol) and pyridine-2,6-diamine (2.15 g, 20.0 mmol) in a methanol (20 mL) and the solution was reflux at 50 for 4hours. The resulting precipitate was filtered, washed with cold water, and dried under vacuum at 70 $^\circ$C for 5 hours to give 5 g, 91% yield of 6-aminopyridin-2-yliminomethylnapthalen-2-ol as brown solid, IR (KBr) ($\ddot{u}_{max}$, cm^{-1}): 3400 (OH), 3210–3370 (N–H, NH$_2$), 1780, (C=O), 1666 (C=N) as shown in (**Figure 1a**). 1H-NMR (DMSO d6, 500 MHz); $\delta\delta$(ppm): 14.89 (1H, OH), 8.25 (2H, NH$_2$), 4.0 (1H, NH) as shown in (**Figure 1b**).

Functionalization of Amberlite XAD-1180 with APIMN

A 5g sample of Amberlite XAD-1180 was treated with a nitrating mixture, containing l0 mL of concentrated HNO$_3$ and 25 mL of concentrated H$_2$SO$_4$ and stirred for 1 h at 60°C on water bath. The reaction mixture was poured into ice-water and the nitrated resin, then filtered off, and washed with water until the effluents were pH neutral and reduced with a mixture of SnCl$_2$ (40 g) in the presence of concentrated HCl (45 mL), and ethanol (50 mL), and refluxed for 12 h at 90°C. The amino polymer was filtered off and washed with distilled water and 2 M NaOH, so as to get the free amino polymer.
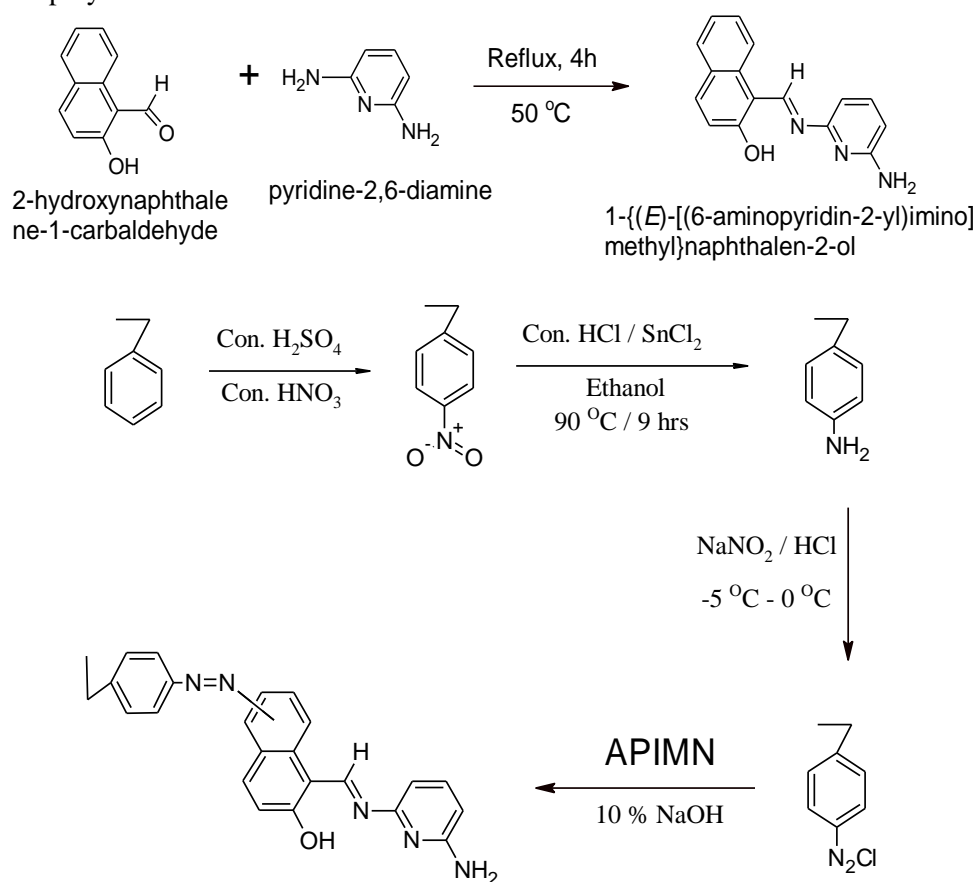
Scheme 1 Scheme of the Amberlite XAD-1180/APIMN chelating resin

The amino polymer was treated with 100 mL of 2 M HCl for 30 min, washed with distilled water to remove excess of HCl, and suspended in 250 mL of ice cold water. It was then diazotized with an equimolar mixture of 1 M HCl and NaNO$_2$ by adding 1 mL each time with constant stirring until the reaction mixture showed a permanent blue color with starch-iodide paper. The diazotized Amberlite XAD-1180 was filtered at -5 to 0°C to avoid its disintegration at higher temperature and treated with APIMN (3 g taken in a mixture of 100 mL water and 25 mL of 4 % sodium hydroxide) at 0-5 ^{0}C for 24 h. The dark brownish crimson colored beads were filtered, washed with 4M

HCl and doubly distilled water successively and finally vacuum-dried. Synthesis and schematic representation of the reaction sequence of Amberlite XAD-1180-APIMN was shown in (**Scheme 1**).

Recommended procedure for preconcentration and separation

A glass column (1.0 cm x 10.0 cm) with a stopcock was taken. 400 mg of Amberlite XAD-1180 functionalized with resin was slurred in doubly distilled water and poured into the column. A small amount of glass wool was placed on the disk to prevent loss of resin beads during sample loading. Then treated with 2.0 M HCl and washed with doubly distilled water until free from acid. An aliquot of the sample solution containing 28, 26, 22 and 20 μg mL^{-1} of Cu(II), Ni(II), Co(II) and Mn(II) was taken and the pH was adjusted to the 6.0, was passed through the column at a flow rate of 5 mL min^{-1}. The bound metal ions were stripped from the resin bed by using 10 mL of 2.0 M HNO$_3$. The concentration of metal ions in elutes were determined by FAAS.

Preparation of water samples

The proposed method was employed for natural water samples (river and sea) (200 mL each) collected from around the Nellore district, A.P., India , using polyethylene containers cleaned with nitric acid (1:1, v/v). The water samples were acidified with conc. HNO$_3$ to pH ~2 just after collecting. Once the water samples had come to the laboratory, they were heated at 80°C for 30 min to digest potential humic and fulvic acid complexes of metals. After cooling the samples to room temperature, they were filtered through cellulose acetate membrane filters (0.45 μm pore size) in order to eliminate any particulate and/or insoluble materials before analysis. NIST® certified drinking-water reference material CRM 1640a and high purity standards certified reference material for drinking water were used for validating the developed method.

Preparation of Biological (Hair) samples

The digestion time was varied from 15 to 60 min, at intervals of 15 min, during the mineralization of 1 g of hair sample heated at 150 ^{0}C with 12 ml of 2:1 HNO$_3$ – H$_2$O$_2$ acid mixture. The hair samples were collected from Ekambarakuppum,Chitoor dist. The results obtained indicate that a minimum of 30 min digestion time is sufficient to complete mineralization Standard reference materials (NIES CRM Human Hair No. 5) were brought into solution following the developed dissolution procedure and analyzed. The results are found to be in good agreement with the certified values.

Results and Discussion

Effect of pH

The pH is one of the important factors which affect the efficiency of the retention/elution of metal ions by solid phase extraction [29]. Probably this is mostly due to the formation of soluble metal complexes and their stabilities in aqueous solutions are strongly related to the pH of the medium. The effect of pH was studied by varying pH in the range of 2–9 (**Figure 2**).

To evaluate the effect of pH on the extraction efficiency, the pH of the 500mL sample solutions containing 50μg of Cu(II), Ni(II), Co(II) and Mn(II) was adjusted 6.0 and the recommended procedure was applied**.** The solutions were passed through the column at a flow-rate of 3 mL min^{-1}. The metal ions were then eluted by an appropriate eluent and determined by FAAS. In all the cases, metal retention by the fictionalized Amberlite XAD-1180-APIMN was increased with increasing pH and reached a maximum (pH 6.0) after which the retention decreased. On the other hand, the progressive decrease in the retention of these metal ions at lower pH is due to the competition of hydrogen ions with the metal ions for the complexation and binding to Schiff base. In contrast, at higher pH (>6.0), the decrease in adsorption is due to the precipitation of metal ions as insoluble M(OH)$_2$ or M(OH)$^+$ in the reaction medium. To achieve the highest efficiency and good selectivity, the optimum pH of 6.0 was selected for the further studies.
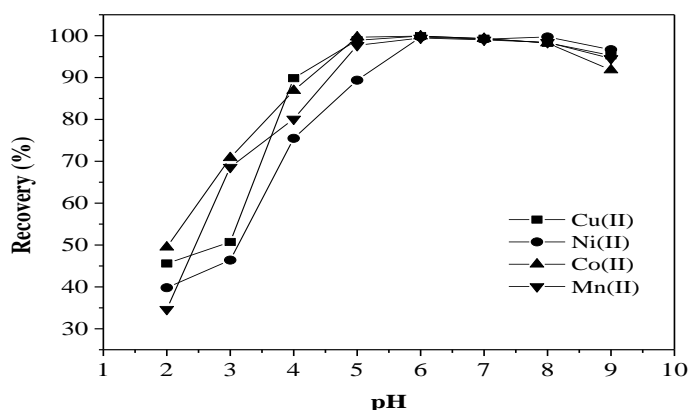
Figure 2 Effect of the pH on the recovery of metal ions

Effect of the amount of resin on preconcentration of metals

The amount of solid phase in the column is a main parameter for the quantitative recovery of the analyte ions. The efficiency of the functionalized Amberlite XAD-1180-APIMN column for the sorption of metals was studied by varying amounts (100-600 mg) of the functionalized resin. It was observed that by increasing the amount of modified solid phase upto 500 mg, the metal ions Cu(II), Ni(II), Co(II) and Mn(II) recovery were increased. Further, increasing the amount of solid phase at a fixed value of eluting solution (10 mL of 2.0 M HNO$_3$), the recoveries are lower due to the insufficiency of eluting solution. Hence, in the proposed procedure 500 mg of Amberlite XAD-1180-APIMN resin was recommended.

Loading capacity

The loading capacity of 6-aminopyridin-2-yliminomethylnapthalen-2-ol on Amberlite XAD-1180 was evaluated from the breakthrough curve plot by a method reported in the literature [33]. The capacities were found as to be 28, 26, 22 and 20 μg mL^{-1} for Cu(II), Ni(II), Co(II) and Mn(II) when using and 18, 16, 14 and 12 μg mL^{-1} without using 6-aminopyridin-2-yliminomethylnapthalen-2-ol.
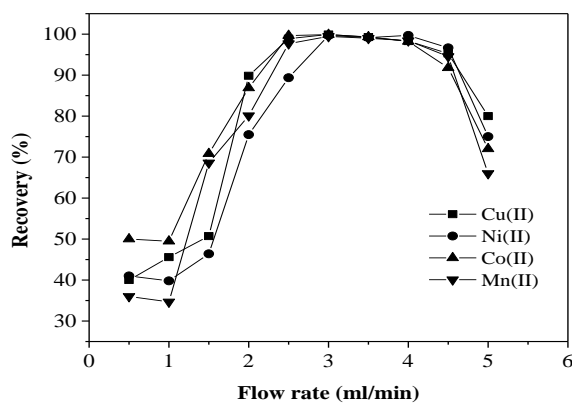
Effect of flow rate

Figure 3 Effect of flow rate sample complete retention of analyte volume

The effect of flow rate of the sample solution on the retention of the metal ions Cu(II), Ni(II), Co(II), and Mn(II) on the Amberlite XAD-1180- APIMN resin was studied in the column packed with 500 mg resin. Sample solutions were passed through the column at various flow rates (1.0 – 5.0 mL min^{-1}) were maintained by peristaltic pump at their optimum pH. The optimum flow rate may be defined as the rate of flow of the solution through the column at which more than 99% retention of metal ions takes place. The studies showed that the optimum flow rate for quantitative sorption of metal ions on the resin is between 1.0 and 3.0 mL min^{-1}.The increased flow rate more than 3.0 mL min^{-1}causes a gradual decrease in sorption due to insufficient contact time between the resin and metal ions, therefore the flow rate was chosen as 3.0 mL min^{-1} as shown in **(Figure 3).**

Selection of the best eluent and its optimization of concentration

For the analytical performance of the solid phase preconcentration system, the type and concentration of eluent is also important. A series of selected eluent solutions such as hydrochloric acid, nitric acid and sulphuric acid were used for desorbing the adsorbed lead, nickel, copper and cadmium ions. For each sample the recovery percents of Cu(II), Ni(II), Co(II) and Mn(II) ions were calculated and the results were shown in **(Table 2)**. As a result of the experiments, 2.0 M HNO$_3$ solution was found to be satisfactory for all of the analytes. Hence 2.0 M HNO$_3$ were selected as the eluent for the analysis of the metals.

Table 2 Recovery of trace metals (Cu(II), Ni(II), Co(II) and Mn(II)) using various eluent

Eluents	Recovery (%)[a]			
	Cu(II)	Ni(II)	Co(II)	Mn(II)
0.5 M HCl	48.6	48.1	53.4	48.6
1.0 M HCl	82.3	78.9	84.5	82.4
2.0 M HCl	97.5	95.9	95.7	95.2
3.0 M HCl	97.7	96.4	97.9	97.3
0.5 M HNO$_3$	51.4	51.2	54.6	51.1
0.1 M HNO$_3$	84.4	84.6	86.1	84.3
1.0 M HNO$_3$	92.3	91.8	89.6	87.2
2.0 M HNO$_3$	100.0	99.3	100.0	99.9
0.5 M H$_2$SO$_4$	46.8	46.6	46.8	45.4
1.0 M H$_2$SO$_4$	79.7	74.9	80.6	73.5
2.0 M H$_2$SO$_4$	96.7	96.9	97.3	97.2
3.0 M H$_2$SO$_4$	97.2	97.61	98.6	95.7

[a] Mean ± standard deviation (n=5)

Effect of the sample volume

The solid-phase extraction technique is a common procedure for the extraction and separation from large volumes to obtain a high enrichment factor. To obtain a high preconcentration factor, the volume of the sample solution is an important parameter [30-31]. The effect of sample volume on the elution of Cu(II), Ni(II), Co(II), and Mn(II) was

studied. Different volumes of the water samples were taken in the range of 100, 250, 500, 750 and 1000 mL and the results were shown in the (**Table 3**). It was observed that the extraction was almost constant up to 500mL of aqueous phase (preconcentration factor ~70) in the case of Cu(II), Ni(II), Co(II), and Mn(II). However, the efficiency of the recovery slightly decreased when sample volume was more than 500 mL. Hence, 500 mL water sample was chosen for the present study. The enrichment factors were found to be 60 for Co(II), 120 for Cu(II) and 300 for Mn(II) and Ni(II) ions when the final measurement volume was taken to be 5 mL.

Table 3 Effect of sample volume on elution of metal ions

Volume of sample(mL)	Recovery (%)[a]			
	Cu(II)	Ni(II)	Co(II)	Mn(II)
100	94.9	95.1	95.5	95.4
200	95.7	95.9	96.4	96.2
300	96.3	96.9	97.4	97.8
400	96.8	97.2	99.2	98.6
500	98.6	98.7	98.9	98.6
600	99.3	99.1	99.6	99.5
700	97.3	98.2	98.7	97.6
800	98.4	98.5	98.6	98.9
900	96.7	98.3	97.2	98.4
1000	97.8	98.3	95.4	98.9

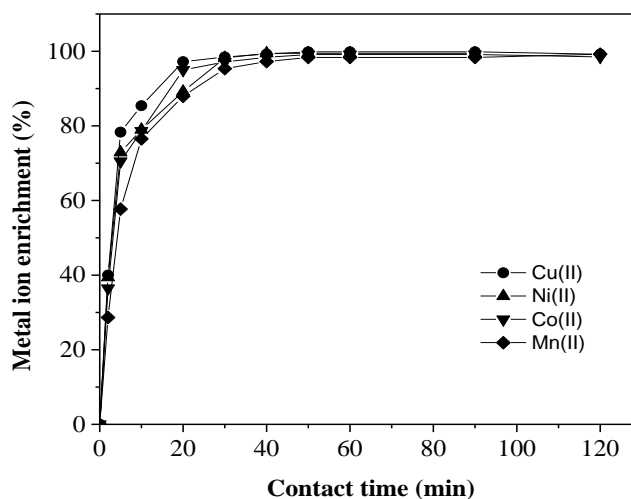[a] Mean ± standard deviation (n=5)

Kinetics of sorption

Figure 4 Kinetics of metal ion sorption on Amberlite XAD-1180-APIMN resin

Sorption kinetics is one of the important parameters that are being studied in solid phase extraction methods because it provides the rate of sorption of metals onto resin loaded with a reagent in the dynamic column mode for routine analysis of water. The rate of uptake of metal ions on Amberlite XAD-1180-APIMN was studied by batch method. Fifty micrograms of individual metal ion solutions were added to 1 g of resin and stirred for 2, 5, 10, 20, 30, 40, 50, 60, 90 and 120 min at room temperature. The metal ions on the resin surface were eluted with 2.0 M HNO_3 and analyzed by FAAS as described in the recommended procedure.

The saturation of resin with time is graphically presented in (**Figure 4**). The loading half-time, $t_{1/2}$, needed to reach 50% sorption of the total loading capacity has been found to be less than 5 min for each metal ion (Cu(II), 4.4; Ni(II), 3.1; Co(II) and Mn(II) 4.3 min, respectively). The kinetics of the resin-metal interaction is sufficiently rapid for all the metal ions at optimum pH. The faster uptake of these metal ions on Amberlite XAD-1180-APIMN reflects a good accessibility of the chelating sites of the resin to metal ions.

Sorption Capacity and detection limits

The sorption capacity of Amberlite XAD-1180-APIMN (maximum amount of metal sorbed per gram) of each metal ion was determined by batch method. The resin (1g) was saturated with Cu(II), Ni(II), Co(II) and Mn(II) ion solutions (concentration, 50 μg mL-1) by equilibrating the solutions on a mechanical shaker under optimum conditions. The solid matrix was filtered and washed with distilled water. The sorbed metal ions on the resin was desorbed with 10 mL of 2.0 mol L-1 HNO3 and determined by FAAS. Afterwards, the maximum sorption capacities of the resin were converted from units of mg g–1 into units of μmol g–1, and the results were found to be 380, 300, 170 and 120 μmol g–1 for Cu(II), Ni(II), Co(II) and Mn(II)respectively.

Effect of non-target species

The interference of co-existing ions on the determination of Cu(II), Ni(II), Co(II) and Mn(II) was investigated. A solution containing 50, 75, 100 and 150 µg mL^{-1} of Cu(II), Ni(II), Co(II) and Mn(II) respectively and various amounts of foreign ion solutions were prepared, applied for the determination of Cu(II), Ni(II), Co(II) and Mn(II) in natural water samples. The deviation of (2.5 % or more of the absorbance value of the standard solution was taken as interference. (**Table 4**), indicates that the results obtained from the present method are highly selectivity.

Table 4 Tolerance limits of matrix Ions for determination of Cu(II), Ni(II), Co(II) and Mn(II) by the proposed method

matrix ion	tolerance limit (mg L^{-1})	matrix ion	tolerance limit (mg L^{-1})
Ca^{2+}	32000	PO_4^-	4000
K^+	30000	SO_4^{2-}	2800
Na^+	26000	Al^{3+}	400
Fe^{3+},Mg^{2+}	23000	Fe^{2+},Cd^{2+}	75
Cl^-	20000	Zn^{2+}	50
HCO_3^-	20000	Cr^{6+}	40
NO_3^-	24000		

Effect of column reuse

In order to examine the long-term stability of the reagent, it was subjected to successive adsorption and desorption cycles (10 runs in a day and the next 10 runs one-day later, and so on, total 20 runs) by passing 500 mL of metal solutions through the column. The stability and potential recyclability of the column-containing reagent were assessed by monitoring the change in the recoveries of the analytes. After 20 runs, the recoveries of all of the analytes slightly decreased to below 95%.

Evaluation of the method performance

In order to check the applicability of the proposed method in the river, sea water and hair samples containing Cu(II), Ni(II), Co(II) and Mn(II) were determined in real water samples. An appropriate volume of sample solutions was adjusted to the optimum pH and subjected to the recommended column procedure for the preconcentration and determination of metal ions. The mean recovery and deviation values for the metal ions were found to be in the range of 94.0 to 99.0 and 0.1 – 0.8%, respectively. The results reported in **(Tables 5)** with a confidence interval for the 98 % confidence level. The proposed method was evaluated in terms of recovery followed by five repeations (n=5).

The analytes were determined with a relative error lower than 10 % in all samples. The accuracy of the proposed method was verified by an analysis of the certified reference material (Analysis of NIST® CRM for drinking water 1640a). The results show that the proposed method was in good agreement with the certified values **(see Table 6)**. The preconcentration method also applied for hair samples. The results are represented in **(Table 7, Table 8)** .It is evident from the data in the proposed method is rapid and more sensitive. The sorption capacities and preconcentration factors of the presented resin were compared with those of other promised chelating resins, as shown in **(Table 9)**. The enrichment factors of the presented method for the investigated metal ions are better than, or comparable to, the other cheating resins.

The analytical features of the proposed method such as precision, linear range of the calibration curve, limit of detection were also examined. The precision of the method was estimated by applying successive retention and elution cycles with 500 mL of a sample solution containing 50 µg of Cu(II), Ni(II), Co(II) and Mn(II) under the optimum conditions, mentioned above. The recoveries of Cu(II), Ni(II), Co(II) and Mn(II) were quantitative (>93%) and the precision of the method was very good (S.D<3%) for functionalized Amberlite XAD-1180-APIMN. The recoveries and the precision found by using Triton X-1180 as adsorbent alone were very low (below 70 %). The linear calibration ranges for measurements under the optimum conditions were 1.0–8.0 µg mL^{-1} for Cu(II), Ni(II), Co(II) and Mn(II) . The detection limits based on three-times the standard deviation of the blank solution were found to be 2.2, 2.6, 3.0 and 3.2 µg mL^{-1} detection limit for Cu(II), Ni(II), Co(II) and Mn(II) respectively.

Table 5 Determination of trace metal ions in various water samples

Elements	Added (µg)	River water[b]		Sea water[c]	
		Found (µg/ml)	Recovery (%)[a]	Found (µg/ml)	Recovery (%)
Cu(II)	0	4.8	--	3.3	--
	5.0	9.4	96.0±0.2	7.9	96.0±0.8
	15.0	19.5	99.4±0.3	12.8	97.0±0.2
Ni(II)	0	0.4	--	0.8	--
	5.0	5.3	98.0±0.6	5.4	92.0±0.3
	15.0	15.0	97.3±0.2	10.7	99.0±0.2

	0	0.5	--	1.2	--
Co(II)	2.5	2.9	96.0±0.4	3.6	96.0±0.2
	5.0	5.2	94.0±0.2	6.1	98.0±0.6
	0	2.2	--	2.8	--
Mn(II)	2.5	4.6	96.0±0.8	5.2	96.0±0.7
	5.0	7.1	98.0±0.2	7.5	94.0±0.4

[a]Mean standard deaviation(n=5), [b]Collected from Penna river (Nellore),
[c]Collected from Bay of Bengal (Nellore, A.P, India)

Table 6 The results for Cu(II), Ni(II), Co(II), and Mn(II) ions in certified samples and the recovery values

Metal ion	Concentration/µg L^{-1}		Relative error (%)
	Certified	**Found[abc]**	
Cu(II)	85.75±0.51	22.16±0.6	1.01
Ni(II)	25.32±0.14	24.48±0.4	1.02
Co(II)	20.24±0.24	6.40±0.12	0.16
Mn(II)	38.97±0.45	37.60±0.2	0.03

[abc]At 95% confidence level, $(x \pm ts/n)$; [b]$n = 5$
[c]Sample volume, 25 mL; final volume, 5 mL

Table 7 Elemental concentrations in standard reference materials

Elemental concentrations in standard reference materials		
Element	**NIES No 5**	**CRM human hair**
	Found	Certified
Cu (II)	16.20 ± 0.70	16.3 ±1.2
Ni (II)	1.72 ± 0.10	1.80 ± 0.1
Co (II)	0.097 ± 0.01	0.1 ± 0.01
Mn (II)	14.29 ± 0.60	14.82 ± 0.3

Table 8 Elemental Concentrations in hair samples (µg g -1) (*n*=3)

S.NO	Cu (II)	Ni (II)	Co(II)	Mn(II)
Sample-1	4.90 ± 0.1	0.62 ± 0.02	0.40 ± 0.01	1.12 ± 0.03
Sample-2	7.86 ± 0.08	1.25 ± 0.03	0.8 ± 0.02	2.73 ± 0.05
Sample 3	10.60 ± 0.1	1.61 ± 0.05	0.12 ± 0.01	1.97 ± 0.04
Sample 4	8.90 ± 0.1	0.72 ± 0.04	0.30 ± 0.01	1.12 ± 0.03

Table 9 Comparison of the sorption capacities (SC, µmol g^{-1}) and enrichment factors (EF) of chelating resins prepared with different ligands and support materials

Support material	Immobilized ligand		Metal ion				Ref.
			Cu(II)	Ni(II)	Co(II)	Mn(II)	
Amberlite XAD-2	Thiosalisicyclic acid	SC	214	310	106	-	34
		EF	200	200	180	-	
	Pyrocatecchol violet	SC	11	-	-	-	35
		EF	-	18	-	-	
	Pyrogallol	SC	71	70	70	82	36
		EF	65	120	65	64	
Amberlite XAD-4	O-aminobenzoic acid	SC	-	115	84	-	37
		EF	-	200	400	-	
Amberlite XAD-16	Gallic acid	SC	344	250	281	180	38
		EF	400	300	286	200	
Silica gel	8-hydroxyqunoline	SC	400	220	178	-	39
		EF	300	200	250	-	
Amberlite XAD-1180	APIMN	SC	380	300	170	120	Present work
		EF	120	250	60	260	

Conclusion

The results presented in this paper demonstrate the usability of functionalized Amberlite XAD-1180-APIMN for the preconcentration of trace metal ions in river and sea water samples. The proposed procedure provides a precise, reliable and accurate technique for the preconcentration and separation of Cu(II), Ni(II), Co(II) and Mn(II). The synthesized chelating resin has several advantages, such as low detection limits (from 0.1 to 3.6 µg L^{-1}), high sorption capacities (3.1 to 5.6 mg g^{-1}), enrichment factors (50 to 200) and high sorption-desorption cycles for all metal ions The chelating resin was quite stable with a recycling period greater than 20 cycles, without any significant loss in its quantitative recovery properties for the metal ions. The results acquired from analyzing the certified reference material (NIST® CRM for drinking water 1640a) confirmed the reliability of the method.The recoveries for these elements were very satisfactory and it is evident for the reliability of the proposed method.

References

[1]   L. Jarup, Hazards of heavy metal contamination, Br Med Bull. (2003) 68 (1): 167-182.
[2]   S. Squadrone, M. Prearo, P. Brizio, S. Gavinelli, M. Pellegrino, T. Scanzio, S.Guarise, A. Benedetto, M.C. Abete, Heavy metals distribution in muscle, liver, kidney and gill of European catfish (Silurus glanis) from Italian Rivers Chemosphere 90 (2013) 358–365.
[3]   X.A. Li, D.M. Zhou, J.J. Xu, H.Y. Chen, In-channel indirect amperometric detection of heavy metal ions for electrophoresis on a poly(dimethylsiloxane) microchip, Talanta 71 (2007) 1130–1135.
[4]   M. Tuzen, E. Sesli, M. Soylak, Trace element levels of mushroom species from East Black Sea region of Turkey, Food Control 18 (2007) 806–810.
[5]   M.D. Pereira, M.A.Z. Arruda, Trends in preconcentration procedures for metal etermination using atomic spectrometry techniques, Microchim. Acta 141 (2003) 115–131.
[6]   M. Ghaedi, M.R. Fathi, A. Shokrollahi, F. Shajarat, Highly selective and sensitive preconcentration of mercury ion by cold vapor atomic absorption spectroscopy, Anal. Lett. 39 (2006) 1171–1185.
[7]   D. Hammer, M. Nicolas, D. Andrey, Improved chromium determination in various food matrices using dynamic reaction cell ICP-MS, At. Spectrosc. 26 (2005) 203–208.

[8]   E.P. Nardi, F.S. Evangelista, L. Tormen, T.D.S. Pierre, A.J. Curtius, S.S. de Souza, F. Barbosa Jr., The use of inductively coupled plasmamass spectrometry (ICP-MS) for the determination of toxic and essential elements in different types of food samples, Food Chem. 112 (2009) 727–732.

[9]   Q. He, X.J. Chang, X.P. Huang, Z. Hu, Determination of trace elements in food samples by ICP-AES after preconcentration with p-toluenesulfonylamide immobilized on silica gel and nanometer SiO2, Microchim. Acta 160 (2008) 147–152.

[10] R. Manjusha, K. Dash, D. Karunasagar, UV-photolysis assisted digestion of food samples for the determination of selenium by electrothermal atomic absorption spectrometry (ETAAS), Food Chem. 105 (2007) 260–265.

[11] M.H. Mashhadizadeh, M. Pesteh, M. Talakesh, I. Sheikhshoaie, M.M. Ardakani, M.A. Karimi, Solid phase extraction of copper (II) by sorption on octadecyl silica membranedisk modified with anewSchiff base and determination with atomic absorption spectrometry, Spectrochim. Acta Part B 63 (2008) 885–888.

[12] V.A. Lemos, D.G. da Silva, A.L. de Carvalho, D.D. Santana, G.D. Novaes, A.S. dos Passos, Synthesis of amberlite XAD-2-PC resin for preconcentration and determination of trace elements in food samples by flame atomic absorption spectrometry, Microchem. J. 84 (2006) 14–21.

[13] J.A. Da-Col, S.M.A. Domene, E.R. Pereira, Fast Determination of Cd, Fe, Pb, and Zn in Food using AAS, Food Anal. Methods 2 (2009) 110–115.

[14] S.H. Refiker, M. Merdivan, R.S. Aygun, Solid-phase extraction of silver in geological samples and its determination by FAAS, Sep. Sci. Technol. 43 (2008) 179–191.

[15] E.M. Gama, A.D. Lima, V.A. Lemos, Preconcentration system for cadmium and lead determination in environmental samples using polyurethane foam/Me-BTANC, J. Hazard. Mater. 136 (2006) 757–762.

[16] S. Meesri, N. Praphairaksit, A. Imyim, Extraction and preconcentration of toxic metal ions from aqueous solution using benzothiazole-based chelating resins, Microchem. J. 87 (2007) 47–55.

[17] P.L. Malvanker, V.M. Shinde, Ion-pair extraction and determination of copper(II) and zinc in environmental and pharmaceutical samples, Analyst 116 (1991) 1081–1084.

[18] J. Dumont, M. Cote, J. Hubert, Preconcentration of trace elements in aluminium alloys using a chelating ion-exchanger and determination by ICP-AES, Appl. Spectrosc. 43 (1989) 1132–1135.

[19] U. Divrikli, L. Elci, Determination of some trace metals in water and sediment samples by flame atomic absorption spectrometry after coprecipitation with cerium(IV) hydroxide, Anal. Chim. Acta 452 (2002) 231–235.

[20] J.A. Baig, T.G. Kazi, A.Q. Shah, M.B. Arain, H.I. Afridi, G.A. Kandhro, S. Khan, Optimization of cloud point extraction and solid phase extraction methods for speciation of arsenic in natural water using multivariate technique, Anal. Chim. Acta 651 (2009) 57–63.

[21] X.D. Wen, P. Wu, L. Chen, X.D. Hou, Determination of cadmium in rice and water by tungsten coil electrothermal vaporization-atomic fluorescence spectrometry and tungsten coil electrothermal atomic absorption spectrometry after cloud point extraction, Anal. Chim. Acta 650 (2009) 33–38.

[22] N. Garcia-Otero, C. Teijeiro-Valino, J. Otero-Romani, E. Peˇna-Vázquez, A. Moreda-Piˇneiro, P. Bermejo-Barrera, On-line ionic imprinted polymer selective solid-phase extraction of nickel and lead from seawater and their determination by inductively coupled plasma-optical emission spectrometry, Anal. Biochem. Chem. 395 (2009) 1107–1115.

[23] C. Puls, A. Limbeck, Determination of trace metal fractionation in aqueous solutions using a solid phase extraction flow injection system on-line coupled to ICP-AES, J. Anal. At. Spectrom. 24 (2009) 1434–1440.

[24] V.S. Camel, Solid phase extraction of trace elements, Spectrochim. Acta Part B 58 (2003) 1177–1233.

[25] Tsogas, G. Z., Giokas, D. L., & Vlessidis, A. G. (2009). Graphite furnace and hydride generation atomic absorption spectrometric determination of cadmium, lead, and tin traces in natural surface waters: Study of preconcentration technique performance. J. Hazard. Mater., 163, 988–994.

[26] Buke, B., Divrikli, U., Soylak, M., & Elçi, L. (2009). Online preconcentration of copper as its pyrocatechol violet complex on Chromosorb 105 for flame atomic absorption spectrometric determinations. J. Hazard. Mater., 163, 1298–1302.

[27] Faraji, M., Yamini, Y., & Shariati, S. (2009). Application of cotton as a solid phase extraction sorbent for on-line preconcentration of copper in water samples prior to inductively coupled plasma optical emission spectrometry determination. J. Hazard. Mater., 166, 1383–1388.

[28] Dadfarnia, S., Shabani, A. M. H., Tamaddon, F., & Rezaei, M. (2005). Immobilized salen (N,N-bis (salicylidene) ethylenediamine) as a complexing agent for on-line sorbent extraction/preconcentration and flow injection–flame atomic absorption spectrometry. Analytica Chimica Acta, 539, 69–75.

[29] G. Gentscheva, P. Tzvetkova, P. Vassileva, L. Lakov, O. Peshev, E. Ivanova, Analytical characterization of a silica gel sorbent with thioetheric sites, Mıcrochım. Acta 156 (2006) 303–306.

[30] M. Tuzen, K.O. Saygi, C. Usta,M. Soylak, Pseudomonas aeruginosa immobilized multiwalled carbon nanotubes as biosorbent for heavy metal ions, Bioresource Technol. 99 (2008) 1563–1570.

[31] M. Ghaedi, A. Shokrollahi, A.H. Kianfar, A.S. Mirsadeghi, A. Pourfarokhi, M. Soylak, The determination of some heavy metals in food samples by flame atomic absorption spectrometry after their separation-preconcentration on bis salicyl aldehyde, 1,3 propandiimine (BSPDI) loaded on activated carbon, J. Hazard. Mater. 154 (2008) 128–134.

[32] R. Jamshidi, Z. Afzali, K. Afzali, Modified natural zeolites as sorbents for separation and preconcentration of traces amount of metal ions, Asian J. Chem. 21 (2009) 3381–3384.

[33] Berrin T; Mustafa M; Solid phase extraction and preconcentration of Cu(II), Pb(II) and Ni(II) in environmental samples on chemically modified Amberlite XAD-4 with a proper Schiff base, Environ Monit Assess, 173, 2011, 709-722.

[34] P. K. Tewari and A. K. Singh, Thiosalicylic acid-immobilized Amberlite XAD-2: metal sorption behaviour and applications in estimation of metal ions by flame atomic absorption spectrometry,Analyst, 2000, 125, 2350-5

[35] R. Saxena and A. K. Singh, Pyrocatechol Violet immobilized Amberlite XAD-2: synthesis and metal-ion uptake properties suitable for analytical applications, Anal. Chim. Acta, 1997, 340,285.

[36] M. Kumar, D. P. S. Rathore, and A. K. Singh, Pyrogallol immobilized Amberlite XAD-2: a newly designed collector for enrichment of metal ions prior to their determination by flame atomic absorption spectrometry, Mikrochim.Acta, 2001, 137, 127-134.

[37] S. Demirci Çekiç, H. Filik, and R. Apak, Use of an O-aminobenzec acid functionalized XAD-4 copolymer resin for the separation and preconcentration of heavy metal(II) ions, Anal. Chim. Acta,2004, 505, 15-24.

[38] R. K. Sharma and P. Pant, Preconcentration and determination of trace metal ions from aqueous samples by newly developed gallic acid modified Amberlite XAD-16 chelating resin, J. Hazard. Mater. 2009, 163,295.

[39] A.Goswami, A. K. Singh, and B. Venkatramani, 8-Hydroxyquinoline anchored to silica gel via new moderate size linker: synthesis and applications as a metal ion collector for their flame atomic absorption spectrometric determination, Talanta, 2003, 60, 1141-1154.