

SIMULTANEOUS SEPARATION AND PRECONCENTRATION OF TRACE AMOUNT OF COPPER, NICKEL, CADMIUM AND ZINC IONS ONTO MODIFIED AMBERLITE XAD-4 LOADED WITH 5-Br-PADAP

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ABSTRACT. In this work, a simple, rapid, selective, sensitive and economical method has been developed for the simultaneous separation and preconcentration of trace amounts of copper, nickel, cadmium, and zinc in aqueous medium using XAD-4 resins that were modified with 2-(5-bromo-2-pyridylazo)-5-diethylaminophenol (5-Br-PADAP) as an analytical reagent. The sorption is quantitative in the pH range 7.0-9.5, whereas quantitative desorption occurs instantaneously with 2 M HCl and selected trace elements have been determined using flame atomic absorption spectrometry. The linearity is maintained between 0.04-4.0 mg L⁻¹ for copper, 0.1-4.0 mg L⁻¹ for nickel, 0.02-1.3 mg L⁻¹ for cadmium and 0.01-1.4 mg L⁻¹ for zinc. The detection limits were 12 µg L⁻¹ for Cu(II), 30 µg L⁻¹ for Ni(II), 6 µg L⁻¹ for Cd(II), and 4 µg L⁻¹ for Zn(II) in the final solution. Various parameters such as the effect of pH, flow rate, breakthrough volume and interference of a large number of anions and cations have been studied and the proposed method was used for determination of these metal ions in water and standard samples. In order to compare the proposed method, the actual water samples were analyzed by direct FAAS (using standard addition method). Determination of these metal ions in standard samples confirmed that the proposed method has good accuracy.

KEY WORDS: Simultaneous separation and preconcentration, Determination of Cu, Ni, Cd, and Zn, Amberlite XAD-4 resins modified with 2-(5-bromo-2-pyridylazo)-5-diethylaminophenol (5-Br-PADAP), Analytical reagent

INTRODUCTION

Due to the industrial facilities, heavy metal contents in environmental samples increase unfavorably. So, it is very important and necessary to develop reliable, fast and sensitive methods for the determination of heavy metals in environmental and biological samples. Several techniques such as neutron activation analysis (NAA) [1], energy dispersive X-ray fluorescence (XRF) spectrometry [2, 3], inductively coupled plasma-atomic emission spectrometry (ICP-AES) [4, 5], atomic absorption spectrometry using either flame (FAAS) [6-8], or electrothermal atomization (ETAAS) [9-11], chromatography [12-16], electroanalytical techniques [17, 18], UV-Vis spectrophotometry [19-22], have been used for the multielement analysis in different matrices. Also, inductively coupled plasma-mass spectrometry (ICP-MS) can be used as a very popular technique for trace element determination. Most of these methods such as NAA, XRF and ICP-AES necessitate to use rather sophisticated and high cost operated instruments. High performance liquid chromatography (HPLC) having different techniques such as ion chromatography [12, 13], chelation ion chromatography [14, 15], and reversed phase liquid chromatography [16], were successfully used for multielement analysis but these techniques are time consuming and expensive. Also, the simultaneous determination of multielements by the use of traditional UV-Vis spectrophotometric techniques is difficult without any separation processes because of overlapping of absorption spectra.

Trace and toxic elements, such as cadmium, copper, nickel, and zinc in various samples have been important and great interest due to several hazardous effects that these elements could provide to humans. On the other hand, the direct determination of the trace metals in

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environmental waters by atomic absorption spectrometry (AAS) is very difficult due to the low levels of metal ions and also interfering influences of main components of the water samples. One way to solve this problem is separation and concentration the ion of interest in order to enhance the detection limit and selectivity and thereby improve the precision and accuracy of analytical results. Solid phase extraction is one of the several procedure techniques used for this purpose. The most common techniques available for this purpose are solvent extraction and solid-phase extraction using various adsorbents such as thiol cotton [23], activated carbon [24], green tea leaves [25], adsorption resins [26], cellulose [27], polythioether [28], microcrystalline naphthalene [29-31], Amberlite XAD-2 resin [32], octadecylsilica membrane disk [33], synthetic Zeolites [34], modified kaolinite [35] and analcime Zeolites [36]. Some of these adsorbents may be fairly effective for preconcentration of metal ions, but their methods of preparation are lengthy and involve rigid control of conditions. The solid-phase extraction process has received more acceptances due to a number of possible advantages including availability and easy recovery of the solid-phase, high preconcentration factors and easiness of separation and enrichment using continuous flow systems.

In this study, a simple, sensitive and rapid method for simultaneous separation and preconcentration of trace amounts of Cu(II), Ni(II), Cd(II), and Zn(II) ions has been proposed without any pretreatment processes.

EXPERIMENTAL

Apparatus and reagents

A Varian model SpectrAA 220 atomic absorption spectrometer was used for measuring Cu(II), Ni(II), Cd(II), and Zn(II) in air-acetylene flame. A Beckman pH meter was employed for pH measurements. A funnel-tipped glass tube (60 x 6 mm) was used as a column for preconcentration. All glassware and columns were washed with a mixture of concentrated hydrochloric acid and concentrated nitric acid (1:1) before use. All reagents were of analytical reagent grade. The stock solutions of Cu(II), Ni(II), and Cd(II) were prepared by dissolving 1.000 g of copper, nickel and cadmium metal strip 99.99% (Merck, Germany) in 20 mL 1:1 nitric acid and diluted to 1 liter. The stock solution of Zn(II) was prepared by dissolving 1.000 g of zinc metal granules 99.99% (Merck, Germany) in 40 mL 1:1 hydrochloric acid and diluted to 1 liter. The stock solutions were standardized by known methods given in the literature [37]. Working solutions were prepared by appropriate dilution of the stock solutions. A 0.5% solution of 2-(5-bromo-2-pyridylazo)-5-diethylaminophenol (5-Br-PADAP) in ethanol was prepared for complex formation with metal ions. Buffer solutions were prepared from 0.5 M acetic acid and 0.5 M sodium acetate for pH 3-6, from 0.1 M potassium dihydrogen phosphate and 0.1 M disodium hydrogen phosphate for pH 6-8 and from 0.5 M ammonia and 0.5 M ammonium acetate for pH 8-11. Solutions of alkali metal salts (1%) and various metal salts (0.1%) were used in order to test the interference of anions and cations, respectively.

Preparation of Amberlite XAD-4 column loaded with 5-Br-PADAP

Amberlite XAD-4 was treated with an ethanol 96%:1 M of hydrochloric acid:deionized water (2:1:1) solution overnight. The resin was rinsed with 10 mL of deionized water. Packing of the column must be done using ethanol as eluent since water makes resin beads float. The resin was saturated with the reagent by passing 5 mL of a 0.5% 5-Br-PADAP solution in ethanol at a flow rate of 1 mL min⁻¹. Afterwards it was washed with 10 mL of deionized water until reagent excess was eliminated from the resin. All experiments were done in a funnel-tipped glass tube (60 x 6 mm) as a column for preconcentration. It was plugged with polypropylene fibers and

then filled with the XAD-4 resin. Before sample loading the column must be preconditioned by passing a buffer solution. Then, the column could be used repeatedly for several times.

General procedure

An aliquot of copper, nickel, cadmium, and zinc (0.4-40.0 μg for copper, 1.0-40.0 μg for nickel, 0.2-13.0 μg for cadmium, and 0.1-14.0 μg for zinc) was taken in a 50 mL beaker and to it was added 3 mL buffer solution with pH 8.5. The total volume of the metal ion solution was made up to 30 mL with deionized water. Then, this solution was passed through the column at the flow rate of 3 mL min^{-1} . At the end, the column was eluted with 10 mL of deionized water. The adsorbed metal ions on the column were eluted with 10.0 mL of 2 M hydrochloric acid solution at a flow rate of 1 mL min^{-1} . The eluent was collected in a 10.0 mL volumetric flask. The final solution was aspirated directly into the flame of AAS against the blank prepared in the same manner without the addition of metal ions.

RESULTS AND DISCUSSION

Reaction conditions

The reaction conditions were investigated with 10 μg of Cu(II), 15 μg of Ni(II), 4 μg of Cd(II), and Zn(II), individually. Adsorption studies were carried out at different pH, keeping the other variables constant. It was found that the zinc, nickel and cadmium were quantitatively adsorbed on modified resin in the pH range 7.0-9.5 and the copper complex was quantitatively adsorbed on resin in the pH range 4.0-9.5. The pH curves for all the metal ions are shown in Figure 1. In subsequent studies, the pH was maintained at approximately 8.5. Addition of 1-6 mL of buffer did not have any effect on the adsorption. Therefore, 3 mL of the ammonia-ammonium acetate buffer pH ~8.5 was used in all subsequent experiments.

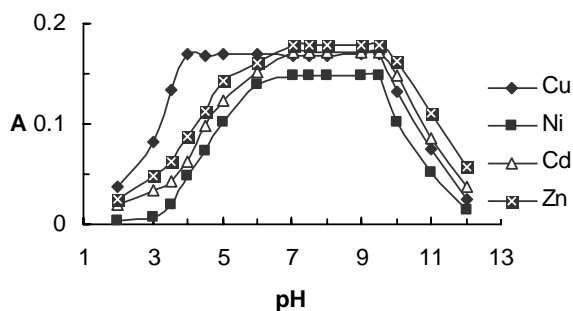


Figure 1. Effect of pH on adsorption of metal ions. (Conditions: Cu(II), 10.0 μg ; Ni(II), 15 μg ; Cd(II) and Zn(II) 4 μg in final solution; buffer, 3 mL; flow rate of sample, 3 mL min^{-1} ; final solution, 10.0 mL of 2 M HCl solution; flow rate of eluent, 1 mL min^{-1} ; reference, reagent blank).

In order to test of sample volume on the recovery, different volumes (20 to 1700 mL) of test solutions containing a fixed amount of the analyte (Cu(II), 10.0 μg ; Ni(II), 15.0 μg ; Cd(II) and Zn(II) 4.0 μg) were enriched on the column. It was observed that absorbances were almost constant up to 1500, 1000, 1100, and 1200 mL of the aqueous phase in the case of copper, nickel, cadmium, and zinc, respectively (preconcentration factor 150, 100, 110, and 120,

respectively). However, for convenience, all the experiments were carried out with 30 mL of the aqueous phase.

A number of eluents were tested to desorb metal ions from the column. Organic solvents can be used as eluents, but they removed only 5-Br-PADAP reagent from the column. If acid solutions as eluent were used, the reagent was retained on the column and therefore, allowed using the column several times. Preliminary observations indicated that 2 M HCl desorbed these metal ions better than 2 M HNO₃ and H₂SO₄. Hence, 10.0 mL of 2 M hydrochloric acid was used in the present work.

The flow rate of the sample was varied from 0.5-10 mL min⁻¹. It was found that a flow rate of 0.5-6 mL min⁻¹ for Cu(II), 0.5-4.5 mL min⁻¹ for Ni(II), 0.5-3.5 mL min⁻¹ for Cd(II) and Zn(II) did not affect their retention. Therefore, a flow rate of 3 mL min⁻¹ was recommended in all experiments. The flow rate of eluent was varied from 0.2-2 mL min⁻¹. It was found that a flow rate of 0.2-1 mL min⁻¹ for Cu(II), 0.2-1.2 mL min⁻¹ for Ni(II), Cd(II), and Zn(II) did not affect their desorption. Therefore, a flow rate of 1 mL min⁻¹ was used in all experiments.

Calibration and sensitivity

Under the optimized conditions, calibration curves were constructed for the determination of copper, nickel, cadmium, and zinc according to the general procedure. Linearity in final solution was maintained between 0.04-4.0 mg L⁻¹ for copper, 0.1-4.0 mg L⁻¹ for nickel, 0.02-1.3 mg L⁻¹ for cadmium, and 0.01-1.4 mg L⁻¹ for zinc with correlation factors 0.9996, 0.9997, 0.9995, and 0.9994, respectively. Seven replicate determinations of mixture of 1.0 mg L⁻¹ copper, 1.5 mg L⁻¹ nickel, 0.4 mg L⁻¹ cadmium and zinc in final solution give a mean absorbance of 0.1687, 0.1483, 0.1721, and 0.1788 with relative standard deviation ±1.2%, ±1.1%, ±1.3%, and ±1.4%, respectively. The detection limits were 12 µg L⁻¹ for Cu(II), 30 µg L⁻¹ for Ni(II), 6 µg L⁻¹ for Cd(II), and 4 µg L⁻¹ for Zn(II) in the final solution. Sensitivities for 1% absorbance for Cu(II), Ni(II), Cd(II), and Zn(II) were 44.5, 92.3, 8.2, and 3.8 µg L⁻¹, respectively.

Sorption capacity of resin for metal ions

The sorption capacity of Amberlite XAD-4 with 5-Br-PADAP for metal ions was also evaluated. In this case the column containing 1 g of modified Amberlite XAD-4 was used and different volumes of 100 mg L⁻¹ from copper, nickel, cadmium, and zinc solutions were passed through the column. Each time, effluent of the column was determined by using of flame atomic absorption spectroscopy until the effluent showed the presence of ions. The Amberlite XAD-4 has a sorption capacity of 0.166, 0.088, 0.154, and 0.170 mg per gram of XAD-4 resin for copper, nickel, cadmium, and zinc, respectively.

Effect of different ions

Various salts and metal ions were added individually to a solution containing 10 µg of Cu(II), 15 µg of Ni(II), 4 µg of Cd(II) and Zn(II) ions, individually and the general procedure was applied. The tolerance limit was set as the concentration of the different ion required to cause 3% error. The results obtained are given in Table 1. Among the cations and anions examined most could be tolerated up to milligram levels except EDTA which interfered seriously because of the higher stability constants of the metal-EDTA complexes than of the 5-Br-PADAP-metal complexes. Thus, the proposed method is selective and can be used for determination of these metals in environmental samples without any prior separation.

Table 1. Effect of different salts and metal ions.

Salt or metal ion	Tolerance limit (mg)			
	Cu	Ni	Cd	Zn
NH ₄ Cl	100	120	120	200
KNO ₃ , sodium acetate	800	800	900	700
KI	85	100	120	100
K ₂ SO ₄	100	40	80	100
KSCN	15	15	10	10
Na ₃ PO ₄ .10H ₂ O	100	120	100	120
Sodium potassium tartrate	18	20	15	50
NaF	100	200	150	100
Na ₂ S ₂ O ₃	10	15	10	5
Sodium oxalate	30	20	15	12
Na ₂ EDTA	0.2	0.05	0.06	0.06
Mn(II) from Mn(NO ₃) ₂ .4H ₂ O	3	2	0.5	0.5
Ca(II) from Ca(NO ₃) ₂ .3H ₂ O	50	50	40	40
Mg(II) from Mg(NO ₃) ₂ .6H ₂ O	100	80	40	20
Co(II) from Co(NO ₃) ₂ .3H ₂ O	3	1.5	1	1
Mo(VI) from MoO ₂ F ₂	3	2.5	1.5	1
Bi(III) from Bi(NO ₃) ₃ .5H ₂ O	5	3	1	2
Pb(II) from Pb(NO ₃) ₂	2	1.5	2	0.5
Fe(III) from Fe(NO ₃) ₃ .6H ₂ O	4	4	3	3
Al(III) from Al(NO ₃) ₃ .9H ₂ O	5	5	4	4
Cr(III) from Cr ₂ (SO ₄) ₃	4	3	3	2
Hg(II) from HgCl ₂	2	1	0.5	0.5
Sb(III) from SbF ₃	5	5	3	2
Cu(II) from Cu(NO ₃) ₂ .6H ₂ O	-	0.2	0.2	0.3
Ni(II) from Ni(NO ₃) ₂ .6H ₂ O	0.2	-	0.4	0.6
Cd(II) from Cd(NO ₃) ₂	0.2	0.3	-	0.2
Zn(II) from Zn(NO ₃) ₂ .3H ₂ O	0.2	0.2	0.3	-

Conditions: Cu(II), 10.0 µg; Ni(II), 15.0 µg; Cd(II) and Zn(II) 4.0 µg, individually in final solution; buffer, 3 mL; flow rate of sample, 3 mL min⁻¹; final solution, 10.0 mL of 2 M HCl solution; flow rate of eluent, 1 mL min⁻¹; reference, reagent blank.

Determination of metal ions in pepperbush and pond sediment

The accuracy and applicability of the proposed method has been applied to the determination of these metal ions in National Institute for Environment Studies (NIES) No. 1 pepperbush and NIES No. 2 pond sediment. A 0.5 g sample was taken in a beaker and dissolved in concentrated nitric acid (~5 mL) with heating. The solution was cooled, diluted and filtered. The filtrate was made to 100 mL with distilled water in a calibrated flask. An aliquot of the sample solution was taken individually and these metal ions were determined by the general procedure. The results are given in Table 2 and are in good agreement with the certified values.

Determination of Cu(II), Ni(II), Cd(II), and Zn(II) ions in water samples

The method has been employed for determination of these metal ions in spring and river water samples. A 200 mL water sample was adjusted to pH 1.5 with nitric acid, filtered to remove suspended material and general procedure was applied. In order to compare the proposed method, the actual water samples were analyzed by direct FAAS (using standard addition method). The results were given in Table 3.

Table 2. Determination of Cu, Ni, Cd, and Zn ions in certified reference materials.

Sample	Composition	Found ^a ($\mu\text{g g}^{-1}$)	Recovery (%)
NIES, No. 1 Pepperbush	K, 1.51±0.06; Mn, 0.203±0.17; Ca, 1.38±0.07; Mg, 0.408±0.020%; Cd, 6.7±0.5; Ni, 8.7±0.6; Cu, 12±1; Cs, 1.2; Tl, 0.13; Fe, 205±17; Co, 23.0±3; Pb, 5.5±0.8; P, 1100; Cr, 1.3; Zn, 340±20; Ba, 165±10; Sr, 36±4; As, 2.3±0.3; Rb, 75±4; Na, 106±13; Hg, 0.05 $\mu\text{g g}^{-1}$	Cu: 12.40±0.13 Ni: 8.50±0.08 Cd: 6.70±0.06 Zn: 340.0±2.8	103.3 97.7 100.0 100.0
NIES, No. 2 Pond sediment	Al, 10.6±0.5; Fe, 6.53±0.35; Ca, 0.81%; Zn, 343; Cu, 210; Pb, 105; Cd, 0.82; Ni, 40; Cr, 75; Co, 27 $\mu\text{g g}^{-1}$	Cu: 210.0±1.1 Ni: 40.20±0.12 Cd: < D.L. ^b Zn: 343.0±2.4	100.0 100.0 - 100.0

^aAverage of five determinations, \pm standard deviation. ^bLess than detection limit. NIES: National Institute of Environmental Studies reference materials. Conditions: Buffer, 3 mL; flow rate of sample, 3 mL min⁻¹; final solution, 10.0 mL of 2 M HCl solution; flow rate of eluent, 1 mL min⁻¹; reference, reagent blank.

Table 3. Determination of Cu, Ni, Cd, and Zn ions in water samples.

Sample	Element determined	Recommended procedure ^a ($\mu\text{g L}^{-1}$)	FAAS ^b ($\mu\text{g L}^{-1}$)	Recovery (%)
Spring water	Cu	13.65±0.06	13.58±0.05	100.5
	Ni	18.08±0.04	18.13±0.05	99.7
	Cd	2.50±0.04	2.53±0.03	98.8
	Zn	56.60±0.46	57.05±0.32	99.2
River water of Rayen in Kerman	Cu	27.20±0.12	27.36±0.11	99.6
	Ni	20.30±0.07	20.26±0.05	100.2
	Cd	4.47±0.06	4.46±0.05	100.2
	Zn	65.72±0.38	66.19±0.44	99.3
River water of Kohpayeh in Kerman	Cu	30.64±0.14	30.61±0.14	100.1
	Ni	15.08±0.05	15.12±0.04	99.7
	Cd	3.41±0.03	3.40±0.04	100.3
	Zn	50.06±0.41	50.10±0.32	99.9

^aAverage of five determinations, \pm standard deviation. ^bLess than detection limit. NIES: National Institute of Environmental Studies reference materials. Conditions: Buffer, 3 mL; flow rate of sample, 3 mL min⁻¹; final solution, 10.0 mL of 2 M HCl solution; flow rate of eluent, 1 mL min⁻¹; reference, reagent blank.

CONCLUSION

The aim of this study was to develop a suitable method for simultaneous separation and preconcentration of trace amounts of Cu(II), Ni(II), Cd(II), and Zn(II) ions in various samples with a recovery rate better than 97% of the expected concentration. The results of our study indicate that the procedure proposed, consisting of preconcentration of Cu(II), Ni(II), Cd(II), and Zn(II) followed by FAAS measurement in the aqueous phase, can accurately determine these metal ions in various aqueous samples. The main advantages of this procedure are: (i) the proposed method is sensitive and selective, (ii) it offers advantages like reliability and reproducibility in addition to its simplicity and suffers from less interference, (iii) the preparation of the extractor system is simple and fast, (iv) during desorption, the 5-Br-PADAP reagent remains in the column, which allows to use the column several times, and (v) good enrichment factors (100-150) can be achieved.

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