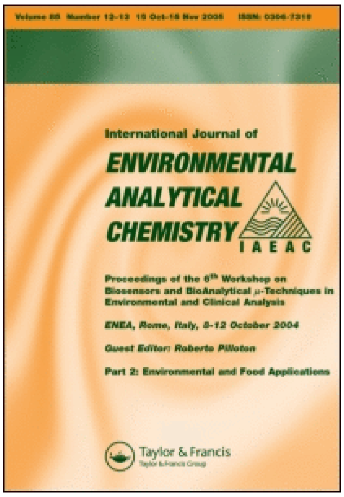

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DETERMINATION OF TRACE METAL IONS IN SEAWATER BY ATOMIC ABSORPTION SPECTROMETRY AFTER SEPARATION/PRECONCENTRATION WITH CALMAGITE ON AMBERLITE XAD-1180

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A preconcentration/separation method for the atomic absorption spectrometric determinations of Cu(II), Ni(II) and Pb(II) ions in seawater have been established by using a chromatographic column filled Amberlite XAD-1180. The recoveries of Cu(II), Ni(II) and Pb(II) ions were quantitative (> 95%) at pH 8–9. The influences of the various analytical parameters including the amount of calmagite, amount of Amberlite XAD-1180, eluent type, etc. were investigated. The influence of the seawater matrix was also examined. Simultaneous enrichment and determination of copper, nickel and lead ions in seawater are possible with satisfactory results (recoveries > 95%, RSD < 9%).

Keywords: Amberlite XAD-1180; Column; Preconcentration; Separation; Cu(II); Ni(II); Pb(II); Seawater

INTRODUCTION

Heavy metal ions such as copper, chromium, lead and cadmium are important indicators for monitoring environmental pollution. Numerous studies have been performed for the investigation of these trace metals in various environmental samples like sediments, soils, geological samples, natural water samples, etc. [1–4]. However, the determination of metal ions by various modern instrumental techniques such as AAS, ICP-AES, ICP-MS, etc. is affected by the matrix of the substrate particularly in seawater [5,6]. Preconcentration and separation methods such as ion-exchange, solid phase extraction, coprecipitation, electroanalytical techniques, membrane

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filtration, liquid–liquid extraction etc. [7–10]. have been routinely used to eliminate matrix effects and cope with low metal levels.

The solid phase extraction approach has gained rapid acceptance because of its amenability to automation and the availability of a wide variety of sorbent phases [5,6,11]. Various sorbents including activated carbon, silica gel and naphthalene have been used for this purpose [12–16]. Amberlite XAD resins meet many of these requirements and because they have good physical properties such as porosity, uniform pore size distribution, high surface area as chemical homogeneous non-ionic structure, and good adsorbent properties for great amounts of uncharged compounds, they have been used as supports for preconcentration of metal complexes [17–22]. Amberlite XAD-1180 is a polystyrene-divinyl benzene copolymer and has been used for separation and preconcentration of traces metal ions in various media including natural waters [23,24].

Calmagite (3-hydroxy-4-((6-hydroxy-m-tolyl)azo)-naphthalenesulfonic acid) is a widely used organic chelating agent [25]. Calmagite is also used in chemical enrichment and separation of trace heavy metal ions by various preconcentration techniques prior to their determination [26–28]. In the present study, a simple, rapid and economic preconcentration/separation method for the determination of traces amounts of Cu(II), Ni(II) and Pb(II) in the natural water samples has been established.

EXPERIMENTAL

Reagents and Solutions

Analytical reagent-grade chemicals were employed for the preparation of all solutions. Freshly prepared doubled distilled water, from a quartz still, was used in all experiments. A 0.05% (w/v) solution of calmagite was prepared by dissolving the required amount of calmagite in water.

In order to remove organic and inorganic contaminants, Amberlite XAD-1180 Resin (Sigma Chem. Co., St. Louis) was washed successively with methanol, water, 1 M HNO_3 in acetone, water, 1 M NaOH and water, respectively. A 20–50 mesh resin was selected for the preconcentration procedure in XAD-1180 column. Smaller resin particles could have improved retention capacity, but the flow rates of sample solution and eluent solution ought to have been reduced, with subsequent increase in preconcentration time [21,29].

The glass column, having a stopcock and a porous disk, was 10 cm long, and 1.0 cm in diameter. The column contains about 500 mg resin (*ca.* 20 mm bed). The column was prepared by aspirating a water slurry of XAD-1180 into the glass column. It was conditioned with 10–15 ml of pH 8 buffer.

Instrument

Metal determinations were performed using a Perkin-Elmer Model 3110 flame absorption spectrometer. All flame measurements were carried out in air–acetylene flame. The operating parameters for elements were set as recommended by the manufacturer.

A pH meter with a glass and calomel electrode pair, Nel pH 900, was employed for measuring pH values.

Sampling

The surface seawater samples were collected in pre-washed (with detergent, doubly de-ionised distilled water, dilute HNO_3 and doubly de-ionised distilled water, respectively) polyethylene bottles from three stations in Mersin Bay (Mediterranean Sea) Turkey. The samples were filtered through a Millipore cellulose nitrate membrane of pore size 0.45 µm. The samples were stored in 1 litre polyethylene bottles and acidified to 1% with nitric acid and were subsequently stored at 4°C in a refrigerator.

Preconcentration Procedure

50 to 60 ml of a solution containing 5–10 µg of each metal ions was added to 1 ml of a 0.05% (w/V) solution of calmagite and brought to desired pH between 2 and 10. The column was preconditioned with 10–15 ml of the water brought to the same working pH. The metal solution was passed through the column at a 2 ml/min flow rate. The column was then washed with calmagite solution adjusted to the working pH. The retained metal-chelates were eluted with 10.0 ml of 0.5 M HNO_3. The metal concentrations in the solution were determined by flame AAS.

Determination of Metal Contents of Seawater Samples

The pH of 250 ml of the sample was adjusted to 8 with NH_3/NH_4CI buffer. Then, 1 ml of the ligand solution was added. After 10 min, the sample was passed through the column at a 2 ml/min flow rate. The metal chelates adsorbed on the XAD-1180 column were eluted with 2–5 ml 0.5 M HNO_3. The concentrations of metal ions in the eluent were determined by FAAS.

RESULT AND DISCUSSIONS

Optimisation of the Extraction Method

The method was optimised for various analytical parameters such as pH, sample volume, amounts of calmagite and type of eluent, in order to obtain quantitative recovery of metal ions on Amberlite XAD-1180 column. The percentage of metals adsorbed on the column was calculated from the amounts of metal in the starting sample and those eluted from the column.

Effects of pH on the Recoveries

The influence of the pH on the retention of analyte ions was investigated in the pH range of 2–10 by keeping the other parameters constant. The pH of the model solutions at the range of 2–10 was adjusted with buffer solutions. For pH 2 phosphate buffer, for pH 4–6 acetate buffers for pH 7 borate buffer and for pH 8–10 ammonium buffers were used. The results were given in Table I. Cu(II), Pb(II) and Ni(II) were quantitatively ($> 95\%$) recovered at pH 8–9. The recoveries of manganese and cobalt ions were not quantitative (below 95%) at all the working pH. The volume of

TABLE I Effect of pH on the recoveries of trace metal ions (Eluent: 0.5 M HNO_3, $N=3$)

	Recovery, %				
pH	*Cu*	*Pb*	*Ni*	*Mn*	*Co*
2	34 ± 2	12 ± 3	13 ± 2	10 ± 1	10 ± 1
4	78 ± 3	13 ± 2	20 ± 3	10 ± 1	58 ± 2
5	81 ± 2	12 ± 3	33 ± 3	12 ± 1	60 ± 2
6	81 ± 1	13 ± 2	97 ± 3	13 ± 2	60 ± 2
8	96 ± 2	100 ± 2	100 ± 3	68 ± 2	64 ± 3
9	96 ± 1	98 ± 2	96 ± 2	75 ± 3	68 ± 3
10	10 ± 1	13 ± 2	11 ± 2	10 ± 1	11 ± 1

buffer added (10 ml) had no effect on the recoveries. All subsequent work was performed at pH 8.

The studies were also performed at a pH range of 8–10 without calmagite. The recoveries of Cu(II), Pb(II) and Ni(II) were below 20%. This situation concluded that calmagite as complexing agent is necessary for preconcentration on Amberlite XAD-1180 resin column.

Influence of the Amount of Calmagite

The influence of the amount of calmagite on the quantitative recoveries of the analyte ions was also examined. 0.1–8.0 ml portion of a 0.05% (w/v) calmagite solution was added to a model solution containing 5–10 μg of each analyte ions. The amounts of investigated ions adsorbed on the XAD-1180 resin were determined. Over 0.1 ml of 0.05% (w/v) calmagite solution, copper, nickel and lead were quantitatively adsorbed. Thus, all further studies were performed by using 1.0 ml of 0.05% calmagite.

Effects of Sample Volume

In order to explore the possibility of enriching low concentrations of the analyte ions from large sample volumes, the effect of the sample solution volume on the metal sorption was also studied at pH 8 by passing 25–1000 ml through the XAD-1180 column at a 2 ml/min flow rate. In these studies 1.0 ml of 0.05% (w/v) calmagite was used. The adsorption of the metal ions with 500 mg of XAD-1180 was not affected by the sample volume below 750 ml. Above 750 ml the sorption decreased for the analytes (Fig. 1). The recoveries of analyte ions decrease probably due to the excess analytes loaded over the column capacity with increasing sample volume above 750 ml. The highest preconcentration factor was 375.

Effects of Eluent Type

The effect of the various eluents on the recoveries of Cu(II), Pb(II) and Ni(II) ions from the Amberlite XAD-1180 resin column was investigated by using 10 ml of each eluent solution. The results are given in Table II. Except acetone, quantitative recoveries for each analyte ions were obtained with all solutions given in Table II. In the light of the results found in the present and our previous studies [4,11,30,31], in all subsequent studies 10 ml of 0.5 M HNO_3 were used as eluent.

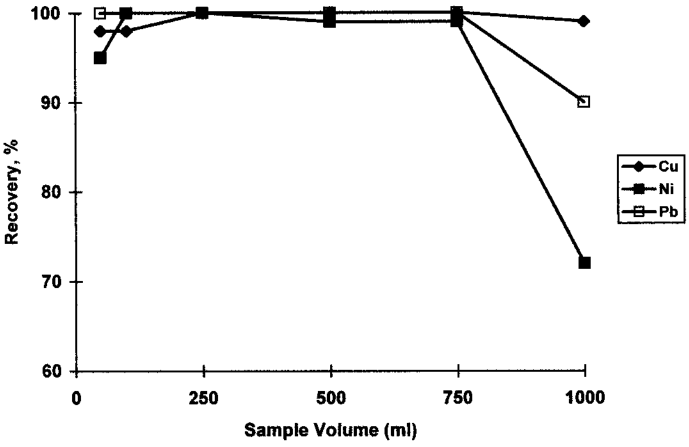

FIGURE 1 The effect of sample volume on the recoveries of trace metal ions (Eluent: 0.5 M HNO_3, $N = 3$).

TABLE II Effect of the eluent type on the recoveries ($N = 4$)

Eluent Type	%*R*		
	Cu	*Ni*	*Pb*
Acetone	100 ± 2	88 ± 3	20 ± 1
0.5 M HNO_3	100 ± 1	100 ± 2	100 ± 2
1 M HNO_3	95 ± 3	100 ± 2	100 ± 2
1 M HNO_3 in acetone	100 ± 2	100 ± 1	100 ± 2
0.5 M HCl	95 ± 2	100 ± 2	100 ± 3
1 M HCl	100 ± 1	95 ± 2	100 ± 1

The flow rates of sample volume and eluent solution were studied in the range of 0.5–10 ml/min under optimal conditions. The best results were obtained at 2.0 ml/min for retention and elution.

Effects of Foreign Ions

The effect of foreign ions coexisting in natural water samples on the determination of the analyte ions was investigated. A 50 ml portion of sample solution containing analytes and a given amount of foreign ions was concentrated. The experimental results are shown in Table III. The tolerance limit is defined as the ion concentration causing a relative error smaller than ± 5% related to the preconcentration and determination of analytes. Na^+, K^+, Ca^{2+}, Mg^{2+}, SO_4^{2-}, and Cl^- at high concentrations did not interfere with the determination. The small amounts retained of the matrix ions were removed by washing with 10 ml of the accompanying buffer solution.

Analytical Performance of the Method

The accuracy of results was verified by analyzing the concentration after addition of known amounts of analytes into a seawater sample. Good agreement was obtained

TABLE III Effect of the matrix ions for recoveries of the metal ions ($N = 4$)

Ion	*Concentration in effluent,* mg/l	*Tolerance Limits,* mg/l
Na^+	8.3	50,000
K^+	2.0	2500
Mg^{2+}	6.1	5000
Ca^{2+}	18.7	2500
Cl^-	–	75,000
SO_4^{2-}	–	2500

TABLE IV Recovery of Cu, Pb and Ni in seawater sample ($N = 4$, volume: 50 ml)

Element	*Added,* μg	*Found,* μg	%*R*
Cu	0	N.D.	–
	2.5	2.5 ± 0.1	100 ± 4
	5	4.8 ± 0.1	96 ± 2
	10	9.3 ± 0.2	93 ± 2
Ni	0	N.D.	–
	2.5	2.5 ± 0.1	100 ± 4
	5	5.0 ± 0.2	100 ± 4
	10	9.2 ± 0.3	92 ± 3
Pb	0	N.D.	–
	5	5.0 ± 0.2	100 ± 4
	10	10 ± 0.1	100 ± 1
	20	20 ± 0.2	100 ± 1

N.D.: Not Detected.

between the added and analyte recovered content using the experimental procedure (Table IV). The recovery values calculated for the standard additions were always higher than 95%, thus confirming the accuracy of the procedure and the absence of matrix effects.

The precision of the column method, evaluated as the relative standard deviation (R.S.D). obtained after analyzing a series of ten replicates for 5 μg Cu(II), 10 μg Pb(II) and 5 μg Ni(II) in 50 ml of model solutions were 3.3%, 2.5% and 3.6%, respectively.

The limits of detection (LOD) of the proposed method for the determination of the investigated elements were studied under the optimal experimental conditions. The detection limits based on three times the standard deviations of the blank ($N = 20$, $X_L = X_b + 3s$, X_L: Limit of Detection, X_b: Blank Value) for copper, nickel and lead were found to be 1.98 μg/l, 8.97 μg/l and 4.20 μg/l, respectively.

Application to Seawater Samples

The method has been employed for the determination of Cu(II), Ni(II) and Pb(II) ions in three surface seawater samples collected from the Mediterranean Sea. The results, which are shown in Table V, have been calculated by assuming 100% recovery of the working elements. The RSDs ($N = 4$) with related to the determinations were found to be lower than 9%.

TABLE V The concentration of Cu(II), Ni(II) and Pb(II) in seawater samples

Sample	*Concentration*, μg/l[a]		
	Cu	*Ni*	*Pb*
1028	10.5 ± 3.4	27.3 ± 9.3	6.4 ± 0.1
2029	8.7 ± 1.1	59.1 ± 5.6	6.4 ± 0.1
3030	11.6 ± 2.6	70.1 ± 10.8	18.1 ± 2.3

[a] $\pm t.s/\sqrt{N}$, *n*: 5, *P*: 0.95.

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