Determination of Some Trace Elements in Natural Waters by Atomic Absorption Spectroscopy After Preconcentration by XAD-4/GBHA System

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This work was investigated the preconcentration of Pb, Cu and Cd ions by atomic absorption spectroscopy (AAS) using solid phase extraction. The procedure is based on the retention of analytes in the form of glyoxal-*bis*-(2-hydroxyanil) (GBHA) complexes on a mini column of XAD-4 resin and subsequent elution with nitric acid. The influence of various analytical parameters including the pH, resin amount, elution factors (concentration and volume of eluting solution), volume of sample solution and amount of ligand on the extraction efficiency of analytes was investigated. The average relative standard deviations of the determinations were below 7 %. The limits of detection for analytes were found in the range of 0.06-0.50 μg L^{-1}. The method was applied to the analysis of trace elements in some natural waters from Hamedan city of Iran.

Key Words: Solid phase extraction, Water analysis, Atomic absorption spectroscopy.

INTRODUCTION

Determination of trace metal ions in natural waters is becoming increasingly important because of the increase interest in monitoring environmental pollution[1,2]. For preconcentration, different procedures such as liquid-liquid extraction, co-precipitation, electro-deposition, solid phase extraction, mainly using ionic exchange resins, solid phase micro extraction, stir bar supportive extraction have been developed[3-10]. Among all these procedure solid phase extraction techniques are quite popular since they offer a number of important advantages over other new micro preconcentration methods. One of these benefits is that sorbent material which packed into mini-columns or cartridges provide sufficient adsorption capacity for many applications and wide variety of sample. In solid phase extraction, various sorbents such as activated carbon, octadecyl bonded silica membrane disk, silica-gel, polyurethane foam, chelex 100 were used. Amberlite XAD resin family has also been used for the peconcentration of trace metal ions from various media such as natural water samples, urine and geological samples. Amberlite XAD-4 is a polymeric adsorbent with excellent physical, chemical and thermal stability and it is also stable at all pH range in aqueous solutions[11-15].

In this work, a simple and sensitive separation/preconcentration method have been established prior to AAS determination of some trace metal ions in natural water samples. It involves complexation of the metal ions with one of the 8-hydroxy quinoline derivatives as glyoxal-*bis*-(2-hydroxyanil) (GBHA) followed by adsorption on Amberlite XAD-4 resin.

EXPERIMENTAL

A 6300-flame atomic Absorption spectroscopy (Shimadzu, USA) was used for metal determination. The operation conditions and the analytical wavelengths are summarized in Table-1. Sample solution was driven through the columns with a multi-channel Heidolph PD 5001 peristaltic pump. The pH values were controlled with a Mettler Toledo MA235 pH meter (Mettler Toledo Instruments Co. Ltd., Shanghai, China) supplied with a combined electrode. A self-made polytetrafluoroethylene (PTFE) mini-column (50 mm × 5 mm i.d.), packed with XAD-4, was used for separation/preconcentration.

TABLE-1
INSTRUMENTAL AND OPERATING
CONDITIONS FOR AAS MEASUREMENTS

Parameters	
Lamp current low (mA)	8
Lamp current high (mA)	300
Flame type	Air-acetylene
Fuel gas flow rate (L min^{-1})	2
Support flow Rate (ml min^{-1})	15
Slit width (nm)	0.7
Wavelength (nm)	Pb = 283.3, Cu = 397.393, Cd = 226.502

All chemicals used were of analytical-reagent grade. Deionized water was used throughout. Multi-element standard (various concentrations) and model solution were prepared by dilution of single element 1000 mg L^{-1} stock solutions. Nitric acid, hydrochloric acid, methanol and ammonia solutions were purchased from Merck. Amberlite XAD-4 (surface area, 750 m^2 g^{-1} and bead size, 0.2-0.3 nm) were obtained from Serva. Column experiments were performed with micro-particles prepared by crushing XAD-4 resins in a mortar, subsequently sieving into fractions. Fractions were cleaned thoroughly washed in the sequence of 1.0 mol L^{-1} NaOH, deionized water, 2 mol L^{-1} HNO$_3$ and deionized water. It was finally washed with methanol and dried in the air. Glyoxal-*bis*-(2-hydroxyanil) (GBHA) (from Merck) solution, (0.1 mol L^{-1}) was prepared in methanol.

XAD-4 column preparation: A 400 mg of XAD-4 resin (100-150 mesh) was introduced into a mini-column (50 mm × 5 mm i.d.) plugged with a small portion of glass wool at both ends. The column was preconditioned by passing a blank solution prior to use. After each use, the resin in the column was washed with a large volume of water and stored in water for the next experiment.

General procedure: The performance of proposed column was tested with model solution prior to its application to real water samples. A 100 mL of the model solution containing 2 µg each of Pb, Cu and Cd prepared and 100 µL of GBHA solution was added to form the metal-complexes. The pH was adjusted to desired value with addition of appropriate buffer solution. The sample solution was passed through a cleaned and conditioned column at a flow rate of 5 mL min^{-1} by using a peristaltic pump. After loading further washing with buffer solution served to remove any sample still present in the column. Finally, the metal-complexes retained on the mini-column were eluted with methanol. The eluted trace elements were measured by AAS. The column could be used repeatedly after regeneration with 2 mol L^{-1} nitric acid solution, deionized water, methanol and deionized water, respectively.

Sample collection: Samples used for the developing of the analytical procedure were collected from agriculture water in the city of Hamedan, Iran.

All samples were collected in pre-cleaned high density polyethylene bottles. Collected samples acidified at pH lower than 2 by adding concentrated nitric acid in order to avoid metal adsorption on to the inner bottles walls then samples were filtered through a 0.45 µm polycarbonate membranes nucleopore filter.

RESULTS AND DISCUSSION

Effect of pH on the metal complexes formation: The pH value plays an important role in the complexation of GBHA with metals which form chelate complexes. The influence of pH on the solid phase extraction of trace metal ions was studied in the range of 2-12 using acetic acid (2M)/ sodium acetate (2M) and ammonia (1M)/nitric acid (1M) for pH adjustment, respectively. Each pH value was tested more than three times. Quantitative recoveries were obtained in the pH of 8 for Pb, 6 for Cu and 12 for Cd. The data corresponding to each element is shown in the Fig. 1.
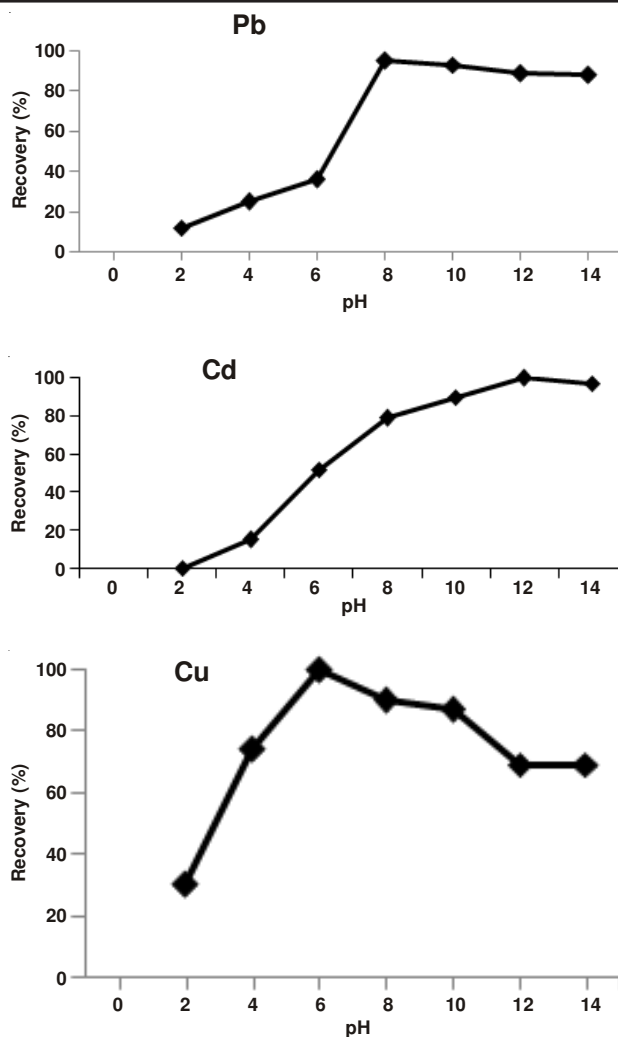

Fig. 1. Effect of pH on the recovery of Pb, Cu and Cd

Effect of volume and concentration of nitric acid for elution: The eluent volume and concentration are other important factors which are studied in this paper. For these, different nitric acid solutions were tested in order to obtain optimum volume and concentration of eluent. Two nitric acid solutions, 2 and 4 mol L^{-1}, were simultaneously studied for eluting volumes between 2.5-10 mL. Result has shown those efficient metals elutions are reached under 5-10 mL nitric acid volume when using 2 mol L^{-1} nitric acid as eluting solution. Similar results have been obtained by using 4 mol L^{-1} nitric acid. Therefore, the lowest nitric acid concentration (2 mol L^{-1}) and the lowest nitric acid volume (5 mL) were chosen for most of the studied elements.

Effect of resin amount: The quantitative retention is not obtained by the smaller amount of resin than the optimum amount and the excess amount of resin also prevents the elution of the quantitative retained chelates by a small volume of eluent. To test the resin amount for quantitative retention of analytes, the column was filled with different amounts of Amberlite XAD-4 (200-700 mg). The procedure was applied to the model solutions given above by use of these columns. The quantitative recoveries for all the examined analytes were obtained in range of 300-600 mg resin. As a result in all experiments 400 mg of XAD-4 was used.

Effect of sample volume: In order to explore the possibility of enriching low concentration of the metal ions from large volumes, the influences of the sample volume on the recoveries of the investigated metal ions were examined and maximum applicable sample volume was determined. The recoveries of the metal ions from different volumes of aqueous model solution containing the same amounts of the metal ions were tested in the range of 50-800 mL. The results were given in Table-2. The recoveries were found to be stable up to 500 mL of sample volume for Pb, 800 mL of sample volume for Cu and Cd.

TABLE-2
EFFECT OF THE SAMPLE VOLUME ON RECOVERIES (%) OF THE INVESTIGATED METAL IONS (n = 5)

Volume of sample (mL)	Pb	Cu	Cd
50	86.5	93.6	77.4
100	87.5	101.53	89.0
200	73.0	97.8	95.0
400	69.8	97.2	93.2
600	65.0	98.9	96.4
800	63.7	90.3	89.5

Effect of ligand concentration: The concentration of GBHA as a chelating agent was also studied. The influence of the GBHA concentration on the recovery of the metals was investigated in the range of 20-500 μL, 0.1 mol L^{-1} GBHA solution using the aforementioned model solution. These results indicate that recoveries of the metal ions increased with increasing concentration of added GBHA. The quantitative values were obtained when using at least 60 μL 0.1 mol L^{-1} GBHA. We chose 100 μL, 0.1 mol L^{-1} GBHA for all experiment.

Effect of matrix ions: One of the challenging principles in preconcentration method is the elimination of interfering ions. The matrix related problems in river water analysis are alkali and alkaline earth metals (in the chloride form). Fortunately, the method used here rejects more than 99 % of the interfering ions. The recoveries of interfering ions (Na, K and Mg) were less than 1 % in the preconcentration solution. The interferences effects resulting from the presence of major elements are very limited in our method which makes it suitable for the determination of metals in a complex matrix such as sea water.

Analytical performance of the method: The analytical performance of the method can be shown for the results obtained from AAS measurements. The accuracy of the procedure was confirmed by the recoveries of spiked two water samples (100 mL of river water) with analyte quantities of 2, 4, 6 μg for Pb, Cu and Cd. As can be seen in Table-3, good recoveries were reached for all elements which confirmed the accuracy of the procedure. The limit of detection given by LOD = 3 (SD) were calculated, where SD is the standard deviation of (n = 10) measurements of blank. After preconcentration LODs for Pb, Cu and Cd were 0.5, 0.32 and 0.06 μg L^{-1}, respectively.

The repeatability of over-all procedure (solid phase extraction and AAS) was assessed by analyzing a same river water sample three times. The average relative standard deviation (RSD) was lower than 7 %, respectively.

TABLE-3
AVERAGE RECOVERY AS PERCENTAGE FOR ADDED ANALYTES TO RIVER WATER SAMPLES (n = 5)

	Added (μg)	Found (μg)	R (%)
Pb	0	0.445 ± 0.12	–
	2	2.60 ± 0.19	106.3
	4	5.07 ± 0.80	102.5
	6	7.15 ± 1.23	103.6
Cu	0	0.19 ± 0.62	–
	2	2.16 ± 0.74	98.6
	4	4.02 ± 1.3	96.0
	6	5.97 ± 0.55	96.4
Cd	0	N.D.	–
	2	1.86 ± 0.14	93.0
	6	5.7 ± 0.61	95.0
	10	8.95 ± 0.19	89.5

Conclusion

In this study we used XAD-4 resin as a sorbent material for separation and preconcentration of Pb, Cu and Cd (GBHA complexes) from aqueous solution. The procedure is simple but requires very clean instrument and high purity reagents. For this purpose a previous washing step with 2 mol L^{-1} HNO_3, is required to avoid contamination from the XAD-4 adsorbent packing material. Preconcentration of trace metals and elimination of matrix effects were successfully achieved which is one of the advantages of the method. So the proposed procedure can be extended to the determination of the investigated metal ions in the various samples having high salt contents as sea waters, urine and dialysis solutions. In addition, the sample volume required for this method is low when comparing to other methods and XAD-4 columns can be reused for several times without losing of analytical performances.

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