

DEVELOPMENT OF A NEW ENRICHMENT METHOD FOR SIMULTANEOUS DETERMINATION OF COPPER AND ZINC IN WATER SAMPLES

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Abstract—In the present study, an enrichment and separation method for the simultaneous determination of trace amounts of Cu and Zn in water samples was developed. Copper and Zn ions found in water matrix in trace amounts were preconcentrated on Duolite XAD 761 resin without using any chelating agent and determined by flame atomic absorption spectrometer (FAAS). Experimental parameters such as pH, concentration of metal ions, amount of resin, and sample volume for quantitative determination of Cu and Zn ions were optimized. The elution process was performed by using 5 ml of 2 mol/L HCl solution. The preconcentration factors for Cu and Zn were found to be 160 and 200, respectively. Under optimized conditions, limit of detection for Cu and Zn were 2.46 and 3.54 µg/L, respectively. The Langmuir adsorption model was applied to describe the equilibrium isotherm. The Langmuir monolayer adsorption capacity of resin was estimated as 31.2 and 17.7 mg/g for Cu and Zn, respectively. The proposed method was successfully applied to determine the Cu and Zn content of various water samples. Environ. Toxicol. Chem. 2011;30:616–621. © 2010 SETAC

Keywords—Solid phase extraction Duolite XAD 761 Copper Zinc Preconcentration

INTRODUCTION

Zinc and Cu species are commonly used in various industrial processes such as production of corrosion-resistant alloys and brass for galvanizing steel, iron products, and dye pigments [1,2]. Copper and Zn are inorganic substances that are involved in catalytic, enzymatic, and structural activities in the organism and have to be taken from outside the organism with food and water.

Trace elements such as Cu and Zn, when taken into the organism, bind to various blood proteins and are transported to all tissues. Copper and Zn accumulation in tissues can cause progressively various toxic effects, including rheumatoid arthritis, abnormal pregnancies, malignancies, hypocalcemia, and bone resorption [3–6].

The levels of metal ions in natural samples are usually lower than the detection limit of most instruments and of metals that usually exist in very complex matrix environments. Direct analysis of metals without using a sample preparation technique is impossible because of interference [7,8]. Therefore, a separation and preconcentration step is usually required for determination of metal ions with concentrations lower than the detection limit of the technique. Many methods of preconcentration are known, such as liquid–liquid extraction, ion exchange, solid-phase extraction (SPE), ultrafiltration, electro-deposition, cloud point extraction, coprecipitation, and enrichment by vaporization [9–15]. Solid-phase extraction has become a preferred method for concentrating the analyte prior to its analysis by instrumental techniques. In SPE, many different materials are used as solid phase, such as polymeric resins, modified resins (by microorganisms or complexing agent), silica, various biomasses, carbon nano tubes, and metal oxides with nanometer sizes [16–20].

Duolite XAD 761 is one of the macroporous organic ester acrylic polymers with a large surface area. It also has good mechanical stability, is chemically homogenous, and has a nonionic structure. It is easily regenerated for multiple adsorption–desorption cycles with good reproducibility in the sorption characteristics, giving advantages when used [21]. In the present study, a new method for determination of trace amounts of Cu and Zn by using FAAS in water samples without any chelating agent and immobilized material was developed.

MATERIALS AND METHODS

Apparatus

A Varian 240FS flame atomic absorption spectrometer equipped with hollow cathode lamp of elements under investigation and air–acetylene burner was used. The instrumental parameters were performed according to the manufacturer's guidelines. These parameters were as follows: wavelength 324.8 and 213.9 nm, lamp current 4.0 and 5.0 mA, and bandpass 0.5 and 1.0 nm for Cu and Zn, respectively.

Reagents and solutions

All reagents were of analytical grade, and all solutions were prepared using deionized water. Duolite XAD 761, having the particle size of 20 to 60 mesh, was purchased from Sigma Aldrich. Metal solutions were prepared by diluting the atomic absorption standard solutions (Merck; 1,000 ± 2 mg/L).

An adsorption column with 12 cm length and 1.0 cm internal diameter was prepared as follows. A small piece of glass wool was placed at the bottom of the column; 0.5 g of dried resin was placed, and another small glass wool plug was inserted onto the tap of the resin. It was washed successively with ethanol and 2 mol/L HCl, HNO₃ solutions, and deionized water.

Preconcentration procedure

The proposed preconcentration procedure was tested with model solutions. These solutions were prepared as follows:

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2.5 ml of 1.0 mg/L standard solutions of metal ions and 3 ml buffer solutions (0.1 mol/L acetic acid–sodium acetate, pH 4.5) was mixed in a 50-ml volumetric flask. After mixing, deionized water was added to the solution to fill the 50-ml flask to capacity. This solution was permitted to flow through the column under gravity at a flow rate of 4 ml/min. The adsorbed metal species on the column were eluted with 5 ml of 2 mol/L HCl solution at a flow rate of 5 ml/min. Copper and zinc were analyzed with via the direct calibration curve method by FAAS. Blank solution was also run under the same conditions. For each experiment, the mean of three reproducible measurements was used.

Analysis of water samples

Water samples from city line and commercial drinking water were collected from Kırşehir, Turkey. Five hundred milliliters of water samples was filtered using a filter paper (Whatman No. 40) and transferred to a beaker. Next, the pH of this solution was adjusted to 4.5 by using 0.1 mol/L acetate buffer, and then the solution was passed through the Duolite XAD 761 resin. Before use, the column was preconditioned by blank solution for each working pH. After the elution process, analyses of samples were performed according to the recommended preconcentration procedure.

RESULTS AND DISCUSSION

Effect of pH of the test solution

The pH dependence of adsorption of Cu and Zn ions on Duolite XAD 761 resin was studied at various pH values. The effect of pH on recovery values is summarized in Figure 1. As shown in Figure 1, optimum recoveries were achieved when pH was between 3.5 and 6.5 for Cu and between 4.0 and 7.0 for Zn. Therefore, the optimal pH value was chosen as 4.5 in sodium acetate–acetic acid buffer for simultaneous determination of Cu and Zn in further studies.

Effect of sample volume

To determine the influence of the sample volume on the performance of the proposed method, recovery values were examined on an XAD 761 column at a 4.0 ml/min flow rate. For this purpose, 50, 200, 400, 600, 800, and 1,000 ml of test solutions, each containing 2.5 µg of Cu and 2.5 µg of Zn ions, were passed through the column under the optimal conditions. Results are given in Figure 2. Recovery values were found to be quantitative (>95%) when sample volume was in the range of 50 to 800 ml for Cu and 50 to 1,000 ml for Zn. By analyzing 5 ml of the final solution of metal ions after preconcentration of

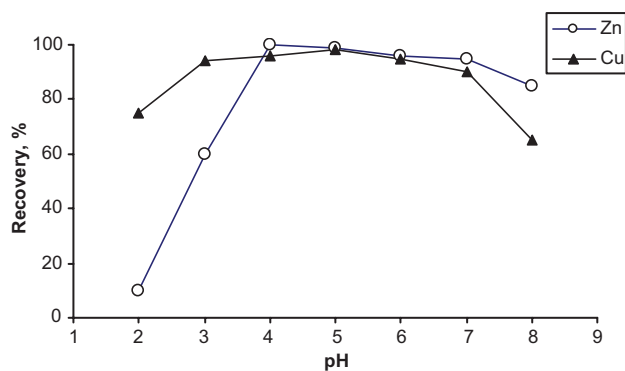


Fig. 1. Effect of pH on the recovery of Cu and Zn.

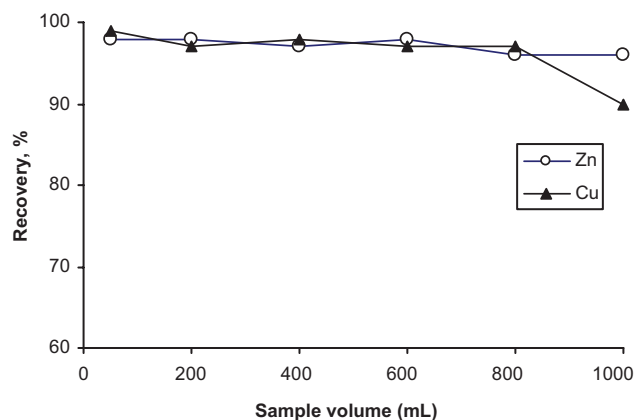


Fig. 2. Effect of sample volume on the recovery of Cu and Zn.

sample solutions (800 ml for Cu and 1,000 ml for Zn), enrichment factors were found to be 160 and 200 for Cu and Zn, respectively.

Effect of flow rate

After the optimization of sample volume, the effects of flow rate on the adsorption of metals were investigated. Metal ions were desorbed from the resin by using 5 ml of 2 mol/L HCl solutions. As shown in Figure 3, it was found that the optimal flow rate of the solutions was up to 4 ml/min for Cu and up to 7 ml/min for Zn. In optimum conditions for other variables, the flow rate was chosen as 4 ml/min to decrease the time of analysis for simultaneous determinations of Cu and Zn.

Choice of eluent agents

To obtain maximal recoveries, various eluents and volumes of reagent were studied. Solutions of nitric acid and hydrochloric acid were tested for eluent of Cu and Zn from XAD 761 resin. The results demonstrated that 5.0 ml of solution of 2 mol/L HCl can be used for maximal recovery of both ions. Recovery values are given in Table 1.

Effect of resin amount

The influence of XAD 761 resin amount on recovery values was studied for different amounts of sorbent. For this reason, different amounts of sorbent in the range of 200 to 600 mg were added into the adsorption column. Test solutions having 50 ml volume and including 2.5 µg Cu and 2.5 µg Zn were passed through the column under optimal conditions. Experimental results showed that the optimal value for an amount of resin was in the range of 450 to 600 mg XAD 761 (Fig. 4). From these

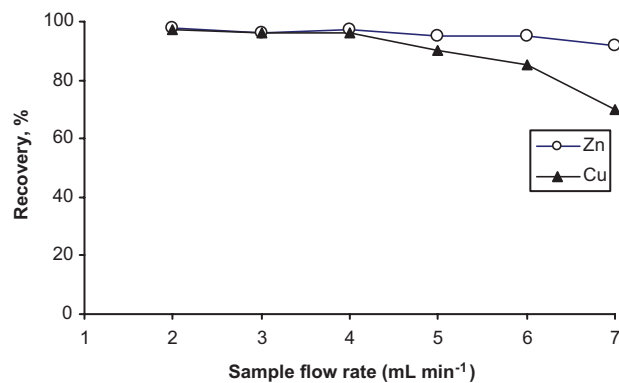


Fig. 3. Effect of solution flow rate on the recovery of Cu and Zn.

Table 1. Effect of type and concentration of eluting agent on copper and zinc ions recovery

Eluent	Recovery (%) ^a	
	Cu	Zn
2 mol/L HCl, 5 ml	99 ± 1	97 ± 2
2 mol/L HCl, 7 ml	99 ± 2	98 ± 2
3 mol/L HCl, 5 ml	97 ± 2	97 ± 1
2 mol/L HNO ₃ , 5 ml	91 ± 2	88 ± 2
3 mol/L HNO ₃ , 5 ml	93 ± 2	90 ± 3
2 mol/L HCl, 5 ml (in ethanol)	94 ± 2	92 ± 1

^a Mean ± standard deviation for three repeated measures

results, 500 mg of resin was used in all further experiments as an optimal amount.

Influence of interfering species

The interference studies were performed using various possible interfering ions on the retentions of the investigated analyte ions. For this purpose, the influences of some cationic and anionic species were tested. In interference studies, 50 ml of solutions containing 2.5 µg of Cu and 2.5 µg Zn ions and various amounts of possible interfering ions were treated according to the preconcentration procedure.

The recovery values should be 100% ideally. However, in analysis of samples, there is always a bias at the recovery for various reasons, such as interference of constituents. This bias may have an effect on results to lower or to higher the recovery. Generally, tolerance levels to bias of the method depend on the intended aim of method under investigation. In trace analysis of metal ions, the relative error of 5% (which corresponds to 95–105% recovery) is acceptable for analytical purposes. Results are given in Table 2.

Capacity of the resin

The adsorption capacity of the XAD 761 resin for Cu and Zn ions was determined by the batch method [22]. The adsorption behavior of resin was determined by studying the amount of adsorbed metal as a function of metal concentration. Fifty milliliters of sample solutions having Zn and Cu ion concentrations in the range of 20 to 100 mg/L at pH 4.5 were shaken for 60 min with a constant mass (100 mg) of the resin. The profile of the adsorption isotherm of the resin for metals is shown in Figure 5, representing the amounts of adsorbed Cu and Zn versus the metal concentration of the supernatant under equilibrium conditions. The data of the isotherm reveals that the

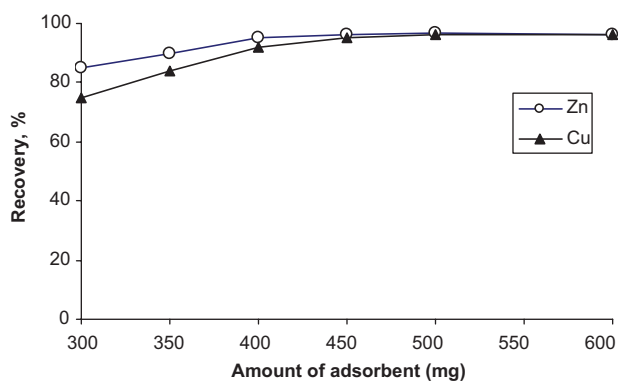


Fig. 4. Effect of Duolite XAD 761 (Sigma Aldrich) amount on the recovery of Cu and Zn.

Table 2. Effects of the matrix ions on the recoveries of copper and zinc ions

Interfering ions	Concentration (mg/L)	Recovery ^a (%)	
		Cu	Zn
K ⁺	500	96 ± 3	101 ± 2
Na ⁺	250	98 ± 3	96 ± 2
	500	94 ± 2	92 ± 2
Mg ²⁺	100	98 ± 2	102 ± 2
Ca ²⁺	250	98 ± 2	95 ± 1
Ni ²⁺	10	101 ± 2	96 ± 2
Al ³⁺	10	97 ± 4	98 ± 3
Fe ³⁺	10	99 ± 2	96 ± 1
Cr ³⁺	10	96 ± 2	98 ± 3
Cd ²⁺	10	94 ± 1	98 ± 1
Cl ⁻	250	97 ± 3	96 ± 3
Cl ⁻	500	94 ± 1	82 ± 1

^a Mean ± standard deviation for three repeated measures.

adsorption process conforms to the Langmuir model. In Figure 6, the graph shows an excellent fit to the data in the studied concentration interval in all cases for the Langmuir model.

A modified Langmuir equation conforming to this kind of adsorption isotherm is represented below:

$$\frac{C_E}{Q_E} = \frac{C_E}{Q_0} + \frac{1}{Q_0 b} \quad (1)$$

where, C_E is the equilibrium concentration of metal ions (mg/L) and Q_E is the amount of the metal ions adsorbed (mg) by unit mass of Duolite XAD 761 (g). Q_0 and b are the Langmuir constants related to the adsorption capacity (mg/g) and the equilibrium constant (L/mg), respectively.

Based on the linearized form of the adsorption isotherm derived from plots of C_E/Q_E versus C_E , the constant Q_0 values were calculated from the slope of the graph according to Kenduzler and Turker [23]. Results are presented in Figure 6. The values of Q_0 were found to be 31.2 and 17.7 mg/g for Cu and Zn, respectively. The adsorption capacities were much higher than the adsorbents already reported in the literature [24–26]. The Langmuir constants for Cu and Zn were 0.03 and 0.08 L/mg, respectively. The correlation coefficient values (r^2) for Cu and Zn were determined to be 0.9876 and 0.9847, respectively.

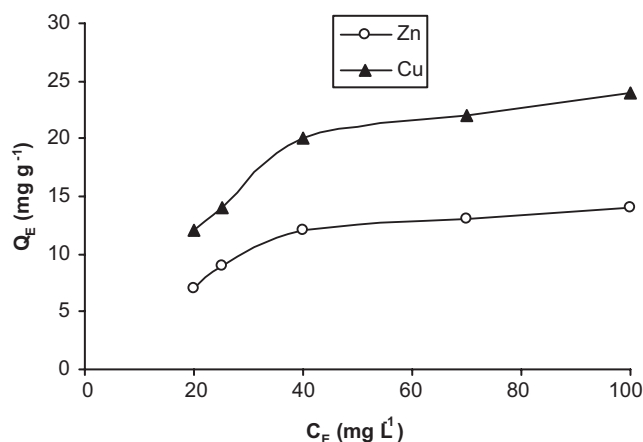


Fig. 5. Adsorption isotherm of Duolite XAD 761 (Sigma Aldrich) for Cu and Zn. C_E is equilibrium concentration of metal ions (mg/L); Q_E is the amount of the metal ions adsorbed (mg) by unit mass of Duolite-XAD 761 (g).

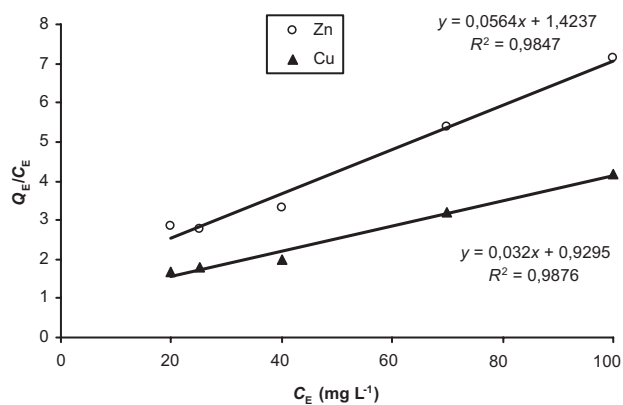


Fig. 6. Linearized Langmuir isotherm obtained from Cu and Zn adsorption on Duolite XAD 761 (Sigma Aldrich). C_E is equilibrium concentration of metal ions (mg/L); Q_E is the amount of the metal ions adsorbed (mg) by unit mass of Duolite-XAD 761 (g).

These r^2 values were in agreement with the Langmuir model for formation of monolayer sorption.

Analytical performance

Under optimized experimental conditions, the analytical features of the proposed method, such as linear range of calibration curve and limit of detection (LOD), were also examined. Limits of detection for Cu and Zn were 2.46 and 3.54 $\mu\text{g/L}$, respectively. Calculation of the LOD values was based on three times the standard deviation of the blank signals ($n = 10$). The response of analytical method changes linearly with concentration of metals in the concentration range of 0.2 to 1.5 mg/L for Cu and Zn with the analytical equation given as follows; $A = 0.14420C + 0.00690$, $r^2 = 0.9986$ for Cu and $A = 0.49281C + 0.05521$, $r^2 = 0.9912$ for Zn. In these equations, A is the absorbance corresponding to concentration C (mg/L) of metal ions. The precision was tested from seven series of measurements of 50 ml of 0.1 mg/L of Cu and Zn ions. The precision of the proposed method is calculated as relative standard deviation (RSD) values of 2.3 and 3.2% for Cu and Zn, respectively, and mean recovery was found be 98.2 and 97.6% for Cu and Zn, respectively. These values show that the method developed is suitable for simultaneous determination of Cu and Zn.

Results of the proposed method were compared with those given in the literature. As shown in Tables 3 and 4, no significant difference exists between the precision of the proposed method and that of the method reported in the literature at the 95% confidence level according to the results of the F test.

Determination of Cu and Zn in water samples

The validity of the proposed method was further proved by analysis of spiked Cu and Zn samples. With this objective, solutions of standard metal ions were spiked into the medium in order to have metal concentration between 5.0 and 20.0 $\mu\text{g/L}$. After homogenizing, the proposed procedure was applied, and then recoveries of Cu and Zn ions were determined. Table 5 shows the experimental results corresponding to spiked metals in samples. The satisfactory recoveries and low relative standard deviations reflect the high accuracy and precision of the proposed solid-phase extraction method.

Table 3. Comparison of some analytical parameters for copper and zinc

Solid phase	Chelating agent	LOD($\mu\text{g/L}$) ^a		Adsorption capacity (mg/g)		Enrichment factor		RSD% ^b		References
		Cu	Zn	Cu	Zn	Cu	Zn	Cu	Zn	
Silica gel	<i>p</i> -Dimethylaminobenzaldehyde	0.69	6.50	25.6	74.7	125	125	—	—	[24]
Sodium dodecyl sulfate coated alumina	<i>N,N</i> -diacetyl-4-bromo-2,6-di(aminomethyl)anisole	1.2	1.1	11.7	13.6	—	—	2.7	2.6	[25]
Activated carbon	4,6-Dihydroxy-2-mercaptopyrimidine	2.9	2.9	0.63	—	260	260	1.2	—	[26]
Activated carbon	5 - ((4-Heptyloxyphenyl)azo)- <i>N</i> -(4-butylloxyphenyl)-salicylaldimine	2.26	—	—	—	25	—	1.4	—	[27]
Amberlite XAD-16	2,6-dichlorophenyl-3,3-bis(indolyl) methane	1.9	1.5	—	—	225	225	2.1	2.3	[28]
Chloromethyl polystyrene polymer	2-Carboxy-2-hydroxy-5-sulfoformazyl benzene	4.0	5.0	80.6	67.6	250	200	1.25	2.25	[29]
Duolite-XAD761	Not used	2.46	3.54	31.2	17.2	200	200	2.3	3.2	Present paper

^aLimits of detection.

^bRelative standard deviation.

—=in related work not specified.

Table 4. Statistical evaluations in between the proposed method and those in the literature

Method	Mean recoveries (%)		RSD (%) ^a		F-test significance		F (tabulated) ^b	
	Cu	Zn	Cu	Zn	Cu	Zn	Cu	Zn
Ghaedi et al. (2009) [25] (n = 8)	96.7	98.3	2.7	2.6	1.17	1.23	4.08	3.85
Ghaedi et al. (2007) [26] (n = 7)	99.2	—	2.9	—	1.26	—	4.16	—
Proposed (n = 7)	98.2	97.6	2.3	3.2				

^aRelative standard deviation.^bValues for the proposed method and from the literature.

—=in related work not specified.

Table 5. Level of copper and zinc in water samples

Sample	Cu			Zn		
	Added (μg/L)	Found (μg/L) ^a	Recovery (%)	Added (μg/L)	Found (μg/L) ^a	Recovery (%)
City line	0	2.6 ± 0.4		0	12.6 ± 0.8	
	5.0	7.8 ± 0.8	102.6	20.0	31.8 ± 2.4	97.5
Commercial drink water A	0	ND ^b		0	ND ^b	
	5.0	4.9 ± 0.5	98	5.0	5.2 ± 0.5	104
Commercial drink water B	0	ND ^b		0	3.8 ± 0.2	
	5.0	5.1 ± 0.7	102	5.0	9.1 ± 0.6	103.4

^aMean ± ts/vN with 95% confidence level.^bNot determined.

CONCLUSIONS

A simple, fast, effective, and economical solid-phase extraction method, using Duolite XAD 761 resin as the preconcentration agent for determination of Cu and Zn species, was developed. The method was applied to several water samples, and results were found to be satisfactory regarding recovery values and low relative standard deviations of series of measurements. The present method is highly useful for the separation, removal, preconcentration, and determination of Cu and Zn ions in water samples.

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