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Preconcentration with 1-Nitroso-2-naphthol Complexes on Dowex MWC-1 Resin: Determination of Cu and Zn at Trace Level in Drinking Water Samples by ICP-AES

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Abstract: In this study, copper(II) and zinc(II) were quantitatively determined in drinking water using ICP-AES after preconcentration. For this purpose, the water samples were treated with 1-nitroso-2-naphthol to form metal complexes on Dowex MWC-1 resin. Prior to the sorption process, the column was treated with a chelating resin Dowex MWC-1 and the column was prepared by passing buffer solution at different pH values. These columns were used for the transportation of water samples through the resin at the flow rate of 2.00 mL min⁻¹. The effluents were then analyzed by ICP-AES using standard addition method. The effect of pH, amount of resin, ligand concentration and eluent type were investigated. The detection limit for Cu(II) and Zn(II) were found to be 2.78 µg L⁻¹ and 6.34 µg L⁻¹ respectively (RSD.% < 5). It would be concluded that the determination of copper(II) and zinc(II) in drinking water was simple, fast and reliable using this technique.

Keywords: 1-Nitroso-2-naphthol, Preconcentration, Resin, Dowex MWC-1 resin.

Introduction

Heavy metal ions such as copper, chromium, lead and cadmium are important indicators for monitoring environmental pollution. Many studies have been conducted for the investigation of these trace metals in various environmental samples like sediments, soils, geological samples, natural water samples, *etc.*¹. Among these samples water is essential to all known forms of life. Although living organisms require trace amounts of some heavy metals known as trace metals, including copper, zinc *etc.*, it should not be forgotten that due to negative effects of heavy metal ions for human health, heavy metal pollution in environment is one of

the important problems for human²⁻³. Because of the importance of the level of these trace metals and the increased interest in the environmental samples including water, soil and plant, the determination methods of them are becoming increasingly important⁴.

In the determination of amounts of heavy metals, several studies were occurred and by the way lots of methods were developed for the low concentrations of them such as flame atomic absorption spectrometry (FAAS)⁵, electrothermal atomization atomic absorption spectrometry (ETAAS)⁶, inductively coupled plasma mass spectrometry (ICP-MS)⁷, inductively coupled plasma atomic emission spectrometry (ICP-AES)⁸, graphite furnace atomic absorption spectrometry (GFAAS)⁹. Among these quantitative determination techniques ICP-AES devices were preferred in the suitable preparation conditions. The inductively coupled plasma-atomic emission spectrometry (ICP-AES) technique, which offers fast multielemental analysis, suffers from a poor sensitivity in the determination of heavy elements in environmental samples like natural water and other real samples. This drawback can be overcome by a combination of a suitable preconcentration technique with subsequent ICP-AES determination. Preconcentration methods that can be used for water samples are solvent extraction, coprecipitation, resin chelation, and various chromatographic techniques. These preconcentration methods provide low detection limit and also help to avoid matrix interferences in the analysis of real samples. Therefore, several workers tried a column solid-phase extraction method for the determination of metals by ICP-AES¹⁰.

For the preconcentration of trace metals, different sorbents has been used such as Amberlite XAD resin¹¹, Dowex resin¹², silica gel¹³, activated carbon¹⁴, polyurethane foam¹⁵. Dowex-type ion exchangers are durable, insoluble and compatible. The structural polymeric backbone of the resin is styrene cross-linked with divinyl benzene functionalized with a sulfonic acid functional group as the ion exchange site. They were supplied in the sodium form. This form is very stable and has an excellent shelf life. This resin traps metals from aqueous solution in an efficient way. In the view of this fact, column chromatography was chosen with the Dowex MWC-1 resin as a preconcentration method before the analysis of metal ions by the ICP-AES.

In the present work, a simple and sensitive preconcentration method using a Dowex MWC-1 resin column has been established for the inductively coupled plasma atomic emission spectrophotometric determination of trace amount of copper and zinc in drinking water from Konya in Turkey.

Experimental

Throughout this research, Magnetic Mixer (Heidolph Instrument Unimax 2010) and pH meter (Denver Instrument) were used for mixing the solutions and for pH adjustments, respectively. Quantitative analyses of metal ions were performed using a Varian/Vista-AX ICP-AES.

Dowex MWC-1 (Fluka) was used as a cation exchange resin having 20-50 mesh grain size. 1000 $\mu\text{g mL}^{-1}$ Cu and Zn standard solutions were purchased from Fluka and their metal solutions were prepared. 1-nitroso-2-naphthol known as also α -nitroso- β -naphthol or only gambin has been used in our study as chelating agent. It reacts with copper(II) and zinc(II) cations, forming stable complexes of composition 1:2 copper(II)-gambin, and so as for zinc(II). These complexes are insoluble in water. The metal-1-nitroso-2-naphthol complexes have also been used in the solvent extraction procedure for the preconcentration of metal ions¹⁶. 1-nitroso-2-naphthol solution (25% ethanol / 75% water) was prepared at different concentrations. Phosphate buffer was prepared at pH 7.00 from KH_2PO_4 and Na_2HPO_4 reagents¹⁷.

A 100 mL solution of $10 \mu\text{g mL}^{-1}$ of Cu(II) and Zn(II) ions and 10 mL 5.0×10^{-3} M chelating agent solution were mixed and then 10 mL buffer solution was added to this mixture. 500 mg Dowex MWC-1 resin was treated with double distilled water over the night prior to precondition with 10 mL buffer solution at optimum pH. The prepared solution was passed through the column at 2 mL min^{-1} flow rate. After this, the column was washed with 10 mL double distilled water twice and the adsorbed metal ions were eluted from the column using 10 mL 3 M HNO_3 /methanol. The eluate was heated to dryness. The residue was dissolved in 10 mL 1 M HNO_3 . The final solution was analyzed for its metal contents by ICP-AES.

In this study, the various analytical parameters such as pH, matrix ions effect, eluent type, chelating agent concentration and resin amount were examined for the optimization of the method.

The buffer solutions were prepared in the pH range of 2.00-11.00. The pH effect on the % recovery is shown in Figure 1. As it is seen from the plot, the maximum % recovery was obtained when $\text{H}_2\text{PO}_4^-/\text{HPO}_4^{2-}$ buffer solution was used at pH 7.00.

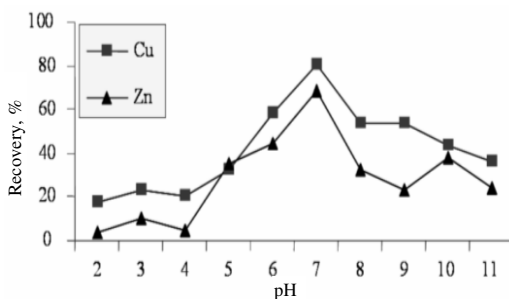


Figure 1. The effect of pH on the recovery of metal ions.

In order to determine the percent recoveries of metal ions, four different resin amounts (250, 500, 750, 1000 mg) were used at optimum pH value. The obtained signals ($\mu\text{g mL}^{-1}$) are plotted against the amount of resin in Figure 2. The optimum resin amount was found to be 500 mg from the plot.

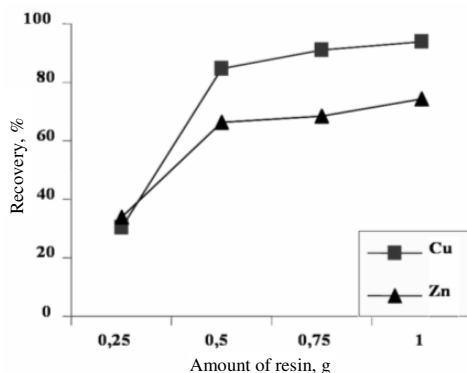


Figure 2. The effect of resin amount on the % recovery of metal ions

The effect of amount of chelating agent on the adsorption of metals in the column, 1-nitroso-2-naphthol solutions having different concentrations were prepared in the recovery of metals. For this purpose, a series of 1-nitroso-2-naphthol solution having (5.0×10^{-4} M, 7.5×10^{-4} M, 1.0×10^{-3} M, 5.0×10^{-3} M and 7.5×10^{-3} M) was prepared. The results are given in Figure 3. As it is seen from this Figure the quantitative % recovery was obtained when chelating agent concentration was 5.0×10^{-3} M. For all studies, 5.0×10^{-3} M 1-nitroso-2-naphthol concentration was used.

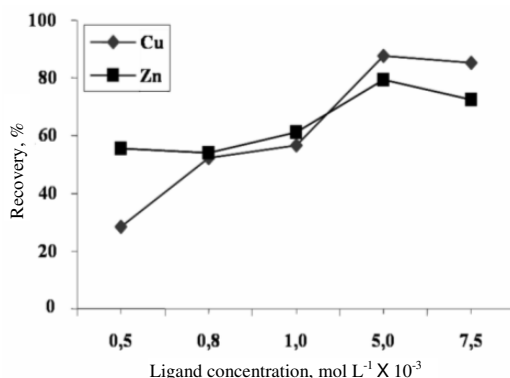


Figure 3. The effect of the chelating agent concentration on the recovery of the metal ions.

The effect of eluent type on the recovery of metals ions was studied. The experiments were performed using $\text{H}_2\text{PO}_4^-/\text{HPO}_4^{2-}$ buffer solution at pH 7.00 and 5.0×10^{-3} M 1-nitroso-2-naphthol solutions. 1 M HNO_3 , 1 M HNO_3 /acetone, pure acetone, 1 M HNO_3 /methanol and 3 M HNO_3 /methanol were used as an eluent to determine their effects and the percent recoveries for each metal are given in Table 1. The best recovery values for both metals were obtained with the 3 M HNO_3 /methanol.

In order to investigate the effect of the volume of eluent, different volumes of 3 M HNO_3 /methanol were prepared in the recovery of metals¹⁶.

Table 1. The effect of the eluent type on recovery of metal ions

Eluent type	Recovery, %	
	Cu	Zn
Concentrated HNO_3	<5	<5
Pure acetone	63	60
1 M HNO_3 / Acetone	56	55
1 M HNO_3 / Methanol	<5	<5
3 M HNO_3 / Methanol	90	80

The sample volume on the metal sorption was studied at pH 7.00 by passing 50-750 mL through the column. 500 mL of sample volume was found to be the optimum value.

The effects of matrix ions such as Ca, Mg, Ni, Fe, Cd and Pb were also examined on the % recovery of Cu(II) and Zn(II). The tolerance limit is defined as the ion concentration causing a relative error smaller than ± 5 % related to the preconcentration and determination of analytes¹⁷. No change was observed on the % recovery of Cu(II) and Zn(II) containing 250, 500 and 1000 $\mu\text{g mL}^{-1}$ Ca, Mg, Ni, Fe, Cd and Pb.

Various amounts of Cu(II) and Zn(II) ions (3, 5, 7, 9 $\mu\text{g mL}^{-1}$) were spiked to drinking water from Konya. The % recoveries of spiked natural drinking water samples were quite satisfactory. As can be concluded from the Table 2 the suggested method can be used for the determination of copper and zinc in drinking water samples.

The statistical calculations were performed at 95 % confidence level. From these calculations, the limit of detection for Cu(II) and Zn(II) were calculated as 2,78 $\mu\text{g L}^{-1}$ and 6,34 $\mu\text{g L}^{-1}$ respectively.

Table 2. Recovery of Cu and Zn in drinking water sample (N=5, volume: 500 mL)

Element	Added, µg	Found*, µg
Cu	0	0.24
	3	3.22
	5	5.21
	7	7.23
	9	9.23
Zn	0	0.32
	3	3.31
	5	5.30
	7	7.34
	9	9.35

*Mean of five results

Conclusion

Due to some difficulties in the quantitative determination of trace heavy metals, a safe and simple method is essential and important. For this reason, a suitable chelating agent 1-nitroso-2-naphthol Dowex MWC-1 was used to improve optimum determination conditions for preconcentration of heavy metals.

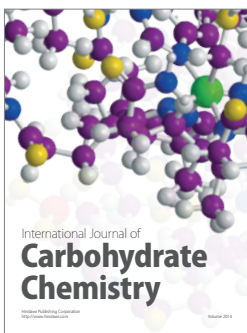
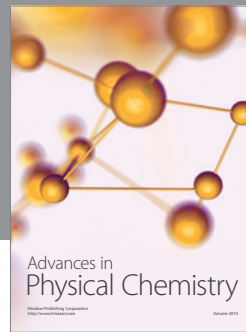
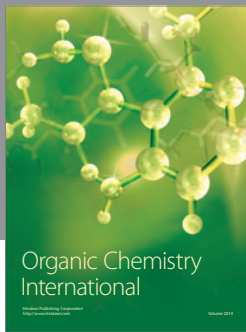
The suggested method is convenient due to its simple application, safety and low detection limit with ICP-AES. This suggested column chromatographic technique can be applied to samples having trace amounts of Cu(II) and Zn(II) in every company which has ICP-AES for analysis.

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