*Asian Journal of Chemistry* Vol. 20, No. 5 (2008), 3633-3640

# Simultaneous Preconcentration and Determination of Trace Amount of Lead and Copper in Water Samples by Flame Atomic Absorption Spectrometry

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In the present paper, a simple and sensitive method for simultaneous preconcentration and determination of lead and copper by flame atomic absorption spectrometry was developed. This method was based on solid phase extraction of lead and copper with 1-nitroso-2-naphthol-3,6-disulfonic acid chelate on naphthalene column. After preconcentration stage, the column was eluted by 5 mL of 1.2 mol $L^{-1}$ nitric acid solution and metal ions directly determined by flame atomic absorption spectrometry. The effect of different variables such as pH, sample volume, amount of chelate, flow rate and eluent solution on the recovery of the analyte was investigated. The detection limits were 0.7 and 0.5 μg $L^{-1}$ for lead and copper, respectively. The relative standard deviations of the determinations for analyte ions were below 4 %. This procedure was applied to the determination of lead and copper in water samples. The results demonstrated that the procedure can be applied for analysis of waters with satisfactory accuracy.

**Key Words: Lead, Copper, Preconcentration, 1-Nitroso-2-naphthol-3,6-disulfonic acid, Flame atomic absorption spectrometry.**

## INTRODUCTION

The main threats to human health from heavy metals are associated with exposure to lead, cadmium, copper, nickel *etc.*[1]. The positive or negative effects of these metals for human health have been studied and reviewed by the researchers and environmental foundation like WHO[1-4]. Heavy metal ions should be accurately evaluated in order to prevent the occurrence of harmful effects. The cycle of trace metal ions from environment to human

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is also an important part of environmental studies[5,6]. Various analytical techniques have been used for determination of trace metal ions including spectrophotometry, atomic absorption spectrometry (AAS), electroanalytical techniques, inductively coupled plasma mass spectrometry (ICP-MS), inductively coupled plasma optical emission spectrometry (ICPOES), *etc.*[7,8].

Flame atomic absorption spectrometry (FAAS) has been widely selected and used as the technique of choice to analysis of trace heavy metal ions owing to its high sensitivity, reproducibility, wide dynamic concentration range and its relatively low cost. However, the determinations of elements at μg $L^{-1}$ concentration level by FAAS are not possible and also interferences caused by coexisting components are often serious problems. In order to solve these two problems, analytical chemists used to combination of preconcentration and separation methods[9-11]. Preconcentration and separation methods should provide a large enrichment factor, make the composition of the sample the same as that of standard by eliminating basic components effects, can be used in routine analysis and be simple, rapid and inexpensive[12,13]. Various separation/preconcentration methods including evaporation, solvent extraction, solid phase extraction, ion exchange, electrodeposition, cloud point extraction and coprecipitation have been used before the atomic absorption spectrometric determinations of traces of heavy metal ions[14,15].

In this work, lead and copper have been preconcentrated from water samples by using 1-nitroso-2-naphthol-3,6-disulfonic acid on naphthalene column as the solid phase extractor. Various parameters, *i.e.* pH, type and volume of eluent, flow rate of sample, volume of sample and interfering ions have been evaluated. Analytical parameters such as precision and accuracy of the method have also been studied. The procedure has been successfully employed for the determination of trace lead and copper in water samples.

## EXPERIMENTAL

The evaluation of ions content were carried out on a Shimadzu 680 A (Tokyo, Japan) atomic absorption spectrometer with a hollow cathode lamp and a deuterium background corrector, at respective resonance line using an air-acetylene flame. The absorption measurements were made under conditions described in Table-1. A Metrohm, E-632 pH meter with glass electrode was used to adjust the pH of solutions.

The column was manufactured in the laboratory using a funnel glass tubing (10 cm long 1 cm i.d.), sealed at the ends with little glass wool plugs to avoid material losses. This column packed with naphthalene adsorbent through which solution containing the metals is passed.

TABLE-1
HOLLOW CATHODE LAMP CONDITIONS AND FLAME CONDITIONS FOR FLAME ATOMIC ABSORPTION SPECTROMETRY

| | Lead(II) | Copper(II) |
|---|---|---|
| Wavelength (nm) | 283.3 | 324.8 |
| Lamp current (mA) | 5.0 | 3.0 |
| Spectral bandwidth (nm) | 1.0 | 0.5 |
| Sample volume (mL) | 5.0 | 5.0 |
| Air flow rate (L $min^{-1}$) | 8.0 | 8.0 |
| Acetylene flow rate (L $min^{-1}$) | 2.0 | 1.8 |

All the reagents used were of analytical reagent grade. Deionized-distilled water was used throughout the experimental work. Working standard solutions of Pb(II) and Cu(II) were prepared by stepwise dilution of 1000 mg $L^{-1}$ stock standard solution (Titrisol, Merck) to the required μg $L^{-1}$ levels. 1-Nitroso-2-naphthol-3,6-disulfonic acid solution (0.01 mol $L^{-1}$) was prepared by dissolving 0.9433 g of the disodium salt hydrate of 1-nitroso-2-naphthol-3,6-disulfonic acid (Aldrich) in 250 mL of water. Tetraoctyl-ammonium bromide and naphthalene purchased from Fluka (Switzerland) and Merck, respectively.

**Sorbent preparation:** A solution of naphthalene was prepared by dissolving 20 g of naphthalene (Merck) and 1 g tetraoctylammonium bromide in 45 mL of acetone with stirring on a hot-plate at 40 °C. This solution was transferred with constant stirring at room temperature into *ca.* 1000 mL of water. It was stirred for 1-2 h and allowed to stand for 0.5 h. The supernatant solution of naphthalene was drained off by decantation and washed twice with water in same way. The slurry of naphthalene adsorbent in water was stored in a bottle for further use.

**Column preparation:** A glass column (10 cm long 1 cm i.d.) with a fine bore and with a glass wool plug over its stopcock was used as a preconcentration column. It was filled with the adsorbent slurry to a height of 3 cm after slightly pressing the adsorbent in the column with a flat glass rod.

**Preconcentration procedure:** An aliquot of the solution containing 3-160 μg $L^{-1}$ of copper, 5-100 μg $L^{-1}$ of lead and 3 mL of 0.01 mol $L^{-1}$ 1-nitroso-2-naphthol-3,6-disulfonic acid was added to form the their chelates. The pH of the solution was adjusted to 2 and the total volume were completed

to 100 mL with water. This solution was passed through the column at a flow rate of *ca.* 3 mL $min^{-1}$. The metal ions retained on the column were eluted into a 5 mL calibrated flask by using 5 mL of 1.2 mol $L^{-1}$ $HNO_3$ solution (Merck). The metals content in the eluent were determined by FAAS.

## RESULTS AND DISCUSSION

pH is a very important factor for metal-chelate complex formation. Therefore, the effect of the pH on the retention of metal-1-nitroso-2-naphthol-3,6-disulfonic acid complexes on the naphthalene column was studied by applying of the proposed procedure at different pH values. The results indicate that the recoveries, ≥ 95 %, are quantitative for Cu and Pb in the pH range 2-6. Therefore, pH 2 was found suitable for the preconcentration of these metal ions and was selected for further experiments.

**Influence of flow rates of sample solution:** Since the retention of elements on an adsorbent depends on the flow rate of the metal solution, the influence of flow rate for sample solutions on the retention of the trace metals was investigated over the range 0.5-6.0 mL $min^{-1}$ by using a constant sample volume of 100 mL under the optimum conditions. The maximum retention was obtained between 0.5-3.0 mL $min^{-1}$. Metals retention decreased dramatically at flow rates > 3 mL $min^{-1}$ owing to very short residence time of the sample in the column, which results in incomplete metal retention at elevated flow rates. In further studies, the flow rate was kept constant at 3 mL $min^{-1}$ in order to increase sample output (Table-2).

TABLE-2
EFFECT OF SAMPLE FLOW RATE

| Flow rate (mL $min^{-1}$) | Recovery (%) | Flow rate (mL $min^{-1}$) | Recovery (%) |
|---|---|---|---|
| 0.5 | 100 | 4 | 73 |
| 1 | 100 | 5 | 65 |
| 2 | 100 | 6 | 50 |
| 3 | 100 | – | – |

Conditions: Aqueous phase, 100 mL of 50 μg $L^{-1}$ of lead and copper, pH 2, eluent = 5 mL of 1.2 mol $L^{-1}$ $HNO_3$. Average of six replicate analysis, RSD < 0.4 %.

**Effect of type and volume of eluent:** The other important factor that affects the preconcentration procedure is the type, volume and concentration of the eluent used for the removal of metal ions from the sorbent. Optimiz-

ation of the elution conditions was performed in order to obtain the maximum recovery with the minimal concentration and volume of the elution solution. The different concentrations of nitric acid, hydrochloric acid and sulfuric acid were tested to remove the metal ions from the column, 5 mL of 1.2 mol $L^{-1}$ $HNO_3$ solution was found to be satisfactory (Table-3).

TABLE-3
EFFECTS OF VARIOUS ELUENTS ON THE RECOVERIES OF THE ANALYTES FROM NAPHTHALENE COLUMN

| Eluent type (mol $L^{-1}$) | Recovery (%) |
|---|---|
| 0.5 HCl | 75 |
| 1.2 HCl | 90 |
| 0.5 $H_2SO_4$ | 80 |
| 1.2 $H_2SO_4$ | 92 |
| 0.5 $HNO_3$ | 90 |
| 1.2 $HNO_3$ | 99 |

**Effect of sample volume on recovery:** In order to explore the possibility of enriching low concentrations of the analytes from the large sample volume, the effect of the sample solution volume on the metal sorption was studied by passing 25-500 mL volumes through the naphthalene column at a 3 mL $min^{-1}$ flow rate. In this work, the amounts of analyte added were constant. The adsorption of the metal ions was not affected by sample volume below 450 mL. Above this volume the per cent sorption decreased for the analytes. In the present study 450 mL of sample solution was adopted for the preconcentration of the investigated ions from water samples, the adsorbed metals can be eluted with 5 mL of 1.2 mol $L^{-1}$ $HNO_3$ and a preconcentration factor of 90 is achieved by this technique.

**Height of column:** The height of adsorbent packing was optimized by using different amount of height and was found that copper is quantitatively adsorbed using an adsorbent height of 3 cm in a funnel-tipped glass tube.

**Effect of amount of tetraoctylammonium bromide:** The amount of tetraoctylammonium bromide loaded on naphthalene was optimized and the results are showed that a loading of 1 g of tetraoctylammonium bromide on 20 g of naphthalene gave highest absorbance for the two ions.

**Effect of foreign ions:** Common cations such as sodium, calcium and magnesium are always found in water samples and have the capability to compete with many metal ions to complex with ligands and common anions

such as nitrate and chloride have the ability to bind with metal ions. Therefore, in their presence the efficiency of the ligand to bind metal ions may be reduced resulting in a reduction of the recovery. The effects of matrix ions in water samples on the recovery of Cu and Pb were also investigated. There are no interferences in the presence of large amounts of alkaline, alkaline earth metals and main anions in the water samples. The effect of each species was considered as interfering when the signal in the presence of the species resulted in deviation of the absorption measurement more than 5 %. The esults showed that in the indicated concentration calcium(II) (50 mg $L^{-1}$), magnesium(II) (50 mg $L^{-1}$), strontium(II) (50 mg $L^{-1}$), sodium (500 mg $L^{-1}$), iron(III) (20 mg $L^{-1}$), nickel(II) (40 mg $L^{-1}$), cobalt(II) (30 mg $L^{-1}$) and cadmium(II) (10 mg $L^{-1}$), $Cl^-$, $F^-$, $NO_3^-$ and $SO_4^{2-}$ (50 mg $L^{-1}$) did not interfere in copper and lead determination by this procedure.

**Analytical features:** The analytical performance of the procedure can be calculated for the results from FAAS measurements. The calibration curves for analyte ions were drawn after setting various parameters of FAAS including wavelength, slit width, lamp current at an optimum level. The optimum linear concentration ranges for Pb(II) and Cu(II) were 5-100 and 3-160 μg $L^{-1}$, respectively. The statistical calculations are based on the average of triplicate readings for standard solution analyte ions. The reproducibility of the preconcentration and separation method was evaluated by passing 50 mL of solution containing 50 μg $L^{-1}$ of Pb(II) and Cu(II) ions through naphthalene-tetractyammonium bromide column and repeating this procedure ten times. The relative standard deviations (RSD) were 3.1 % for Pb(II) and 3.7 % for Cu(II). The detection limits for analytes were calculated after presented preconcentration procedure was applied to the blank solutions. The detection limits of the investigated elements based on three times the standard deviations of the blank (k = 3, n = 10) on a sample volume of 150 mL were 0.7 μg $L^{-1}$ for lead and 0.5 μg $L^{-1}$ for copper.

**Application of the method:** The application of the method was verified by the analyses of tap and river water samples from the city of Semnan and its neighborhood. The water samples were collected in polyethylene bottles and kept in a refrigerator before use. An appropriate volume of sample solutions was adjusted to the optimum pH and subjected to the recommended column procedure for the preconcentration and determination of metal ions. The results reported in Table-4 with a confidence interval for the 95 % confidence level show the applicability of the proposed method to water analysis. The analytes were determined with a relative error lower than 5 % in all samples. The accuracy of the results was verified by analyzing

the spiked water samples. These results clearly prove the validity of the method described in this work.

TABLE-4
DETERMINATION OF LEAD(II) AND COPPER(II) IN WATER SAMPLES

| Sample | Lead concentration (μg $L^{-1}$) | | | Copper concentration (μg $L^{-1}$) | | |
|---|---|---|---|---|---|---|
| | Added | Found* | Recovery | Added | Found | Recovery |
| River water** | 0 | 30 ± 1 | – | 0 | 22 ± 2 | – |
| | 10 | 42 ± 2 | 105 | 15 | 39 ± 1 | 105 |
| | 45 | 77 ± 3 | 102 | 50 | 75 ± 2 | 104 |
| University tap water | 0 | 10 ± 1 | – | 0 | 63 | – |
| | 30 | 42 ± 2 | 105 | 10 | 75 ± 1 | 103 |
| | 60 | 73 ± 1 | 104 | 20 | 85 ± 3 | 102 |

*Mean ± Confidence interval (p = 0.05, n = 5); **From Hable Rood river.

## Conclusion

The proposed procedure provides a simple, precise, reliable and accurate technique for the preconcentration and determination of lead and copper. The recoveries of analytes studied were nearly quantitative (> 95 %). The accuracy of the results was verified by analyzing the spiked water samples and the results were shown in the Table-4. The recoveries for these elements were satisfactory and it is evident for the reliability of the proposed method for the analysis of water samples. The detection limits achieved were lower and linear range of proposed method is wider than some previous methods[16,17]. The analyte ions can be sensitively determined by FAAS without any influence of matrix ions. In addition this method is sensitive, low cost and applicable when sophisticated techniques such as ICP-OES or GFAAS are not available.

## ACKNOWLEDGEMENT

The financial support of this work by Semnan University Research Council is greatly acknowledged.

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(*Received*: 11 August 2007; *Accepted*: 4 February 2008) AJC-6296