SIMULTANEOUS PRECONCENTRATION OF Cu(II), Cd(II) AND Mn(II) ON SILICA-POLYETHYLENE GLYCOL AND DETERMINATION BY FLAME ATOMIC ABSORPTION SPECTROMETRY

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A simultaneous solid phase extraction procedure for enrichment of Cu(II), Cd(II) and Mn(II) has been developed. The method is based on adsorption of Cu(II), Cd(II) and Mn(II) ions on polyethylene glycol-silica gel pre-conditioned with acetate buffer (pH 5.5). The adsorbed metal ions are eluted with nitric acid (1 mol L^{-1}) and determined by flame atomic absorption spectrometry. The calibration graph was linear in the range of 2-140 ng mL^{-1} for Cu(II), 1-40 ng mL^{-1} for Cd(II) and 4-100 ng mL^{-1} for Mn(II). The limits of detection were 0.66, 0.33 and 1.20 ng mL^{-1} for Cu(II), Cd(II) and Mn(II), respectively.

Keywords: Cu(II); Cd(II); Mn(II).

INTRODUCTION

High concentrations of heavy metals may have severe toxicological effects on living organisms. Large amounts of heavy metals can enter the environment from metallurgy industries, combustion of coal, and automobiles. Heavy metals can easily enter the food chain through a number of pathways, and long-term exposure in a contaminated environment can cause progressive toxic effects for living organisms. Therefore, controlling heavy metal discharges and their measurement in different samples has become a challenge for analytical chemists.[1,2] The flame atomic absorption spectrometry technique is extensively employed for the quantification of metallic species because of its desirable characteristics, such as low cost, ease of operation, high analytical frequency and good selectivity. However, the direct determination of trace metals by this technique is limited because of matrix interference problems and low concentration of metals in samples. However, these problems can easily be overcome by applying separation and/or preconcentration procedures before performing the detection procedure. Different methods exist for the separation and isolation of metal ions such as liquid-liquid extraction,[3] ion exchange,[4] flotation,[5] solid phase extraction[6-10] and cloud point extraction.[11-13] The inherent limitations of the methods based upon solvent extraction are the high costs of solvents and the environmental concerns regarding their disposal. Hence, solid phase extraction methods were proposed as an alternative to overcome these drawbacks of liquid-liquid extraction. The separation, preconcentration, and determination of metal ions at trace levels has been successfully accomplished using different adsorbents such as polymeric resins modified with selective ligands.

Solid phase extraction is an attractive separation and preconcentration technique for trace metal ions with advantages such as simplicity, flexibility, and high enrichment factors. Various solid phase materials have been introduced for the preconcentration and separation of heavy metal ions at trace levels, including chemically--modified silica-gel with amino thioamidoanthraquinone,[14] polyurethane foam functionalized with a-naphthol,[15] cellulose functionalized with 8-hydroxyquinoline,[16] zeolite,[17] Amberlite XAD.4 coated with dithiocarbamates,[18] carboxylic acid (COOH) bonded to silica gel,[19] naphthalene[20] and PAN-naphthalene.[21]

In this work, a solid phase extraction procedure for preconcentration of Cu(II), Cd(II) and Mn(II) using silica gel-polyethylene glycol (Silica-PEG) as an adsorbent is described.

EXPERIMENTAL

Instrumentation

Analysis of the metal ions was performed by a GBC atomic absorption spectrometer model Cintra 101 (Australia) with air--acetylene flame. All instrument settings were those recommended by the manufacturer. The selected wavelengths for the determination of copper, cadmium and manganese were 324.7, 228.8 and 279.5 nm, respectively. The lamp current was 3 mA for copper and cadmium, and 5 mA for manganese. The spectral band pass was 0.5 nm for copper and cadmium, and 0.2 nm for manganese.

A digital pH-Meter model 632, Metrohm (Switzerland) with a combined glass electrode was used for pH adjustments. A Teb Azma vacuum pump (Iran) was used for pumping the solutions.

Reagents

Analytical reagent-grade chemicals and doubled distilled water were used throughout. Stock solutions of 1000 µg mL^{-1} of Cu(II), Cd(II) and Mn(II) were prepared by dissolving 0.3929 g of CuSO$_4$.5H$_2$O (Merck, Darmstadt, Germany), 0.2282 g of 3CdSO$_4$.8H$_2$O (Merck) and 0.3076 g of MnSO$_4$.H$_2$O (Merck) in water and diluting to 100 mL in a volumetric flask, respectively. The working solutions were prepared by appropriate dilution of the stock solution. An acetate buffer pH 5.5 was prepared by adding 2 mol L^{-1} NaOH to 0.1 mol L^{-1} acetic acid and adjusting its pH to 5.5 using a pH meter. Phosphate buffer pH 7.0 was prepared by adding 2 mol L^{-1} NaOH to 0.1 mol L^{-1} phosphoric acid and adjusting its pH to 7.0 using a pH meter. Silica gel (Aldrich 70-270 mesh, 60 surface area > 500 m^2/G) was activated by treatment with HCl (5 mol L^{-1}) and dried in vacuum at 120 °C. Polyethylene glycol, PEG (Merck) was heated at 80 °C under vacuum for 30 min before use to remove traces of moisture.

Adsorbent preparation by immobilization of polyethylene glycol on silica gel

The adsorbent was prepared by immobilization of polyethylene

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glycol on silica gel according to a previously reported procedure.[22] 20 g of activated silica was placed in a dried 250 mL flask equipped with a magnetic stirrer under nitrogen atmosphere. Subsequently, freshly distilled $SOCl_2$ (45 mL) was added slowly to the flask through an addition funnel and the reaction mixture was stirred at room temperature. Evolution of copious amounts of HCl and SO_2 occurred instantaneously. After stirring for 4 h, the excess unreacted thionyl chloride was distilled off and the resulting grayish silica chloride was flame dried and stored in an airtight container before use.

PEG (10 g) was added dropwise to a well-stirred silica chloride (20 g) in dry CH_2Cl_2 (40 mL), under a nitrogen atmosphere at room temperature. HCl was instantaneously evaluated. After stirring for 2 h, the obtained silica-gel supported PEG was removed by filtration. For elimination of any additional PEG, the resultant mixture was washed several times by acetone (3-30 mL). Silica-gel supported PEG was dried in a vacuum oven overnight.

Recommended procedure

A tipped glass funnel (7 cm in length and 7 mm i.d) with a very fine bore was packed with 0.35 g of the adsorbent and used as a preconcentration column. The prepared column was conditioned by passing 5 mL of acetate buffer pH 5.5. 200 mL of the solution containing 1-140 ng mL^{-1} of Cu(II), 1-40 ng mL^{-1} of Cd(II) and 2-100 ng mL^{-1} of Mn(II) and 3 mL of phosphate buffer pH 7.0, was passed through the mini column at a flow rate of 10 mL min^{-1}. The adsorbed metal ions were eluted with 3.0 mL of 1.0 mol L^{-1} of nitric acid. The metal content of the eluent was determined by FAAS and percent recoveries were calculated from the amount initially present and amount eluted from the column. A blank solution was also run under the same analytical conditions without adding any Cu(II), Cd(II) and Mn(II).

Sample preparations

The surface water samples were collected after rain in the local area, acidified, boiled, filtered and kept in a refrigerator before use. An aliquot of water samples was then treated under the recommended procedure. 0.2 g of sugar sample was dissolved in water, phosphate buffer was added and the recommended procedure was applied.

RESULTS AND DISCUSSION

We recently reported the use of Silica-PEG for preconcentration and determination of Co(II) and Ni(II).[23] The analytes are probably adsorbed through interaction with OH groups of the PEG and it seems that this polymeric compound could form complexes with cations much like crown ether. Our preliminary investigations showed that if Silica-PEG adsorbent is conditioned with acetate buffer pH 5.5 in the column, it can also be used for simultaneous preconcentration of Cu(II), Cd(II) and Mn(II) prior to their determination by flame atomic absorption spectrometry. It should be mentioned that the recoveries were around 10% for these metal ions without pretreatment. Therefore, different parameters were optimized in order to apply this adsorbent for simultaneous preconcentration and sensitive determination of Cu(II), Cd(II) and Mn(II).

Effect of pH

It was found that if Silica-PEG adsorbent is conditioned with acetate buffer it can be used for simultaneous preconcentration of Cu(II), Cd(II) and Mn(II) while the untreated adsorbent has very low tendency towards these ions. The pHPZA of the adsorbent which

corresponds to the pH value of the liquid surrounding oxide particles, when the sum of surface positive charges balances the sum of surface negative charges[24], was determined by the Noah and Schwarz method[25] and found to be 2.2.[23] This means that the surface of the adsorbent is acidic and if the pH of the solution is higher than pHPZC, the negative charge on the surface provides electrostatic interactions that are favorable for adsorbing cationic species. Therefore, first the pH for the conditioning of adsorbent was investigated in order to make the adsorbent less acidic and acetate buffers with pH values of 4.50, 5.00, 5.50 and 5.75 were used to pass through the column filled with the adsorbent before passing the sample solution. It was observed that 5 mL of acetate buffer pH 5.5 was adequate for pre-conditioning of the column for quantitative retention of Cu(II), Cd(II) and Mn(II) and, by increasing the pH for the conditioning of the adsorbent, the recoveries were decreased again.

The effect of pH of the sample solution was also studied in the range of 5-8 by adjusting the pH of the solution with HCl or NaOH (0.1 mol L^{-1}) using a pH meter. The results shown in Figure 1 indicate that highest recoveries are obtained for all metal ions at pH 7. Therefore pH 7 was selected as the optimum value and 3 mL of phosphate buffer pH 7 was added to the solutions to maintain this value.
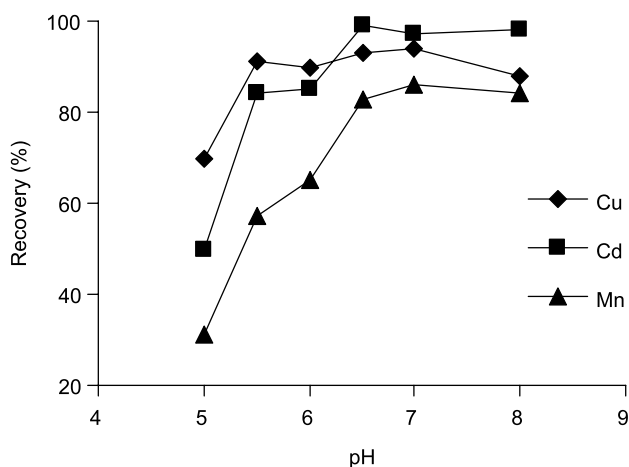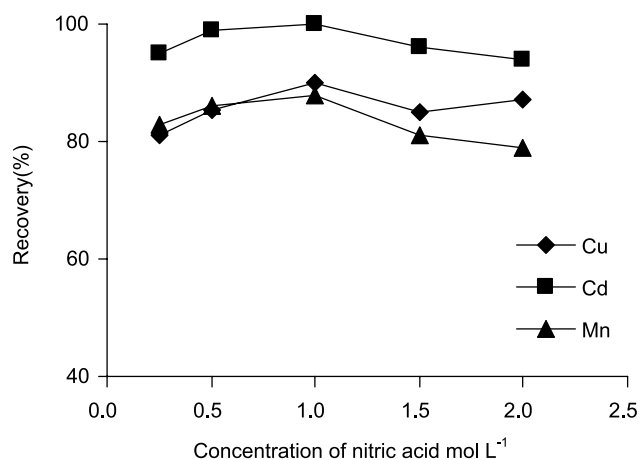

Figure 1. Effect of pH on the recovery of 100 ng mL^{-1} of Cu(II), and Mn(II) and 50 ng mL^{-1} of Cd(II). Each number is the average of 3 replicate measurements

Effect of eluent type and eluent concentration

Different acid solutions such as sulfuric, nitric and hydrochloric were investigated for the elution of adsorbed metal ions from the column. The highest recoveries were obtained when nitric acid solution was used as an eluent. Thus, the effect of nitric acid concentration was evaluated. The results given in Figure 2 show that the highest recoveries are achieved for desorbed metal ions when nitric acid concentration was 1.0 mol L^{-1}. Therefore, 3 mL of nitric acid solution (1.0 mol L^{-1}) was selected for the elution of Cu(II), Cd(II) and Mn(II) ions from the column. 2 mL was not adequate for determination of three metal ions whereas 4 mL would decrease the preconcentration factor.

Effect of sample flow rates

One of the parameters affecting the recovery and preconcentration time is sample flow rate. At fast flow rates there is insufficient time for equilibration between the analytes and the adsorbent while at slow flow rates, the analysis time is increased. Therefore, the effect of the sample flow rate on the adsorption of the metal ions was investigated. This study was carried out by pumping 200 mL of the solution containing 100 ng mL^{-1} Cu(II) and Mn(II) and 50 ng mL^{-1} at different flow
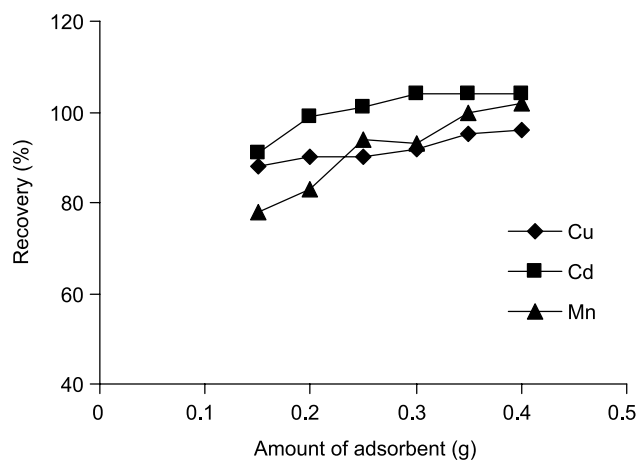
Figure 2. Effect of nitric acid concentration as the eluent on the recovery 100 ng mL^{-1} of Cu(II), and Mn(II) and 50 ng mL^{-1} Cd(II). Each number is the average of 3 replicate measurements

rates. The results indicated that all the analyte ions were quantitatively retained and recovered in the range of 2-10 mL min^{-1}. In posterior experiments, the flow rate was kept constant at 10 mL min^{-1} in order to increase the sample throughput.

### Effect of adsorbent amount and reusability

Several experiments were carried out for the selection of the amount of adsorbent. The results in Figure 3 show that quantitative recoveries were obtained for all the analytes when an adsorbent amount of 0.35-0.40 g was used. Thus, 0.35 g was selected as optimum for further work.

Figure 3. Effect of amount of adsorbent on the recovery of 100 ng mL^{-1} of Cu(II), and Mn(II) and 50 ng mL^{-1} Cd(II). Each number is the average of 3 replicate measurements

The regeneration of the column was investigated to determine the reusability of the adsorbent. The column filled with 0.35 g of solid adsorbent was reused at optimum experimental conditions for the separation and preconcentration of Cu(II), Cd(II) and Mn(II) ions from aqueous samples. Each column was washed with water after each elution and the general procedure was applied again. The results depicted in Figure 4 indicated that each column can be used six times without serious loss in the recoveries for all metal ions. Moreover, the used adsorbents can be collected and recycled by a simple procedure. Used Silica-PEG was stirred with 100 mL of 5%

hydrochloric acid for 2 h, filtered and dried. The recycled adsorbent can be reused in the same way three times. This means that only a small amount of the adsorbent is used per analysis and the adsorbent has very low consumption and is highly economical.
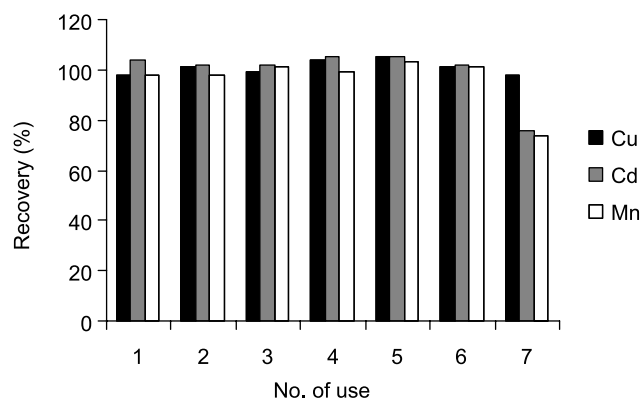
Figure 4. Number of reusing the column. Each number is the average of 3 replicate measurements

Effect of sample solution volume

In order to achieve a high preconcentration factor, the maximum applicable volume of sample solution must be established. Therefore, the effect of sample solution volume was studied by passing 50-250 mL solutions containing 10 μg of Cu(II) and Mn(II) and 5 μg of Cd(II) through the column. The results showed that all the analytes studied could be recovered quantitatively up to sample volumes of 200 mL. At higher sample volumes, the recoveries decreased gradually with increasing volume of sample solution. By analyzing 3 mL of the final solution after preconcentration of 200 mL of sample solution, a preconcentration factor of 66.6 can be achieved for all of the analytes.

Analytical performance

The calibration graph was obtained using the general procedure under optimum conditions. The graphs were linear in the range of 2-140 ng mL^{-1} for Cu(II), 1-40 ng mL^{-1} for Cd(II) and 4-100 ng mL^{-1} for Mn(II) in the initial solution. The equations of the lines are $A = 0.004C+0.008$, $A = 0.0126C+0.0189$ and $A = 0.0085C+0.0189$ for Cu(II), Cd(II) and Mn(II), respectively, where A is the absorbance and C is concentration of metal ions in ng mL^{-1}. The regression coefficients for the lines are 0.9990, 0.9993 and 0.9980 for Cu(II), Cd(II) and Mn(II), respectively. The limits of detection based on $3S_b$ were 0.66, 0.33 and 1.20 ng mL^{-1} for Cu(II), Cd(II) and Mn(II), respectively. The relative standard deviations (RSD) for 10 replicate measurements of 20 ng mL^{-1} of Cu(II), Mn(II) and 10 ng mL^{-1} of Cd(II) were 4.91, 3.79 and 3.42%, respectively.

Effect of interfering ions

Interference studies were performed by spiking some ions to the solutions containing 50 ng mL^{-1} of Cu(II), Mn(II) and 25 ng mL^{-1} of Cd(II) and applying the proposed procedure. The recoveries obtained from these solutions were compared with those of standards. Variation of over ±5% in the recoveries resulting from the presence of interfering ions was taken as interference. The results are shown in Table 1.

Adsorbent capacity

The adsorption capacity is the maximum metal quantity taken

Table 1. Effect of various ions on the determination of 50 ng mL^{-1} of Cu(II) and Mn(II) and 25 ng mL^{-1} of Cd(II)

Interfering ion	Tolerance ratio
I$^-$	1000
Br$^-$, PO$_4^{3-}$	500
NH$_4^+$, SCN$^-$, NO$_2^-$, Cl^{-1}, CO$_3^{2-}$	500
F$^-$, Pb^{2+}	50
Ca^{2+}, Zn^{2+}, Ni^{2+}, Cr^{3+}, Co^{2+}	10
Mg^{2+}, Fe^{3+}, Fe^{2+}	1

up by 1 g of adsorbent. In order to study the adsorptive capacity of Silica-PEG, the batch method was used. 0.5 g of the adsorbent was added to 100 mL solution containing 0.5 mg of Cu(II), and Mn(II) and 0.1 mg of Cd(II). After shaking for 24 h, the mixture was filtered and the metal ions remaining in the filtrate were determined by flame atomic absorption spectrometry. The capacity of adsorbent for Cu(II), Cd(II) and Mn(II) was found to be 490, 69 and 102 µg g^{-1} for Cu(II), Cd(II) and Mn(II) ions, respectively.

Application and recovery tests

In order to check the applicability of the procedure, it was applied for the determination of Cu(II), Cd(II) and Mn(II) in different samples such as sugar and water samples. In these samples, the analyte concentration was below the detection limit of the method. Thus, different amounts of the investigated metal ions were also spiked to the samples and the resulting solutions were submitted to the preconcentration procedure. The results are given in Table 2 and 3 where it can be seen that good agreement was obtained between the added and found analyte content using the recommended procedure.

Table 2. Determination of Cu(II), Mn(II) and Cd(II) in sugar

Metal ion	Added (ng mL^{-1})	Found^a (ng mL^{-1})	Recovery (%)
Cu	-	ND^b	-
	10	10.5±0.6	105.0
	20	20.9±1.2	104.5
Mn	-	ND	-
	10	10.5±0.5	105.0
	20	20.3±0.9	101.1
Cd	-	ND	-
	5	5.1±0.2	102.0
	10	9 .7±0.4	97.0

a. $\bar{x}$ ± ts / $\sqrt{n}$ at 95% confidence (n=5), b. Not detected

Table 3. Determination of Cu(II), Mn(II) and Cd(II) in surface water

Metal ion	Added (ng mL^{-1})	Found^a (ng mL^{-1})	Recovery (%)
Cu	-	ND^b	-
	50	50.7±2.8	104.5
Mn	-	ND	-
	50	41.8±1.5	83.6
Cd	-	ND	-
	25	23.8±0.9	95.2

a. $\bar{x}$ ± ts / $\sqrt{n}$ at 95% confidence (n=5), b. Not detected

CONCLUSION

The developed SPE procedure allowed the direct determination of Cu(II), Cd(II) and Mn(II) ions at the level of µg L^{-1} to be carried out by FAAS. Due to the preconcentration step, it was possible to obtain low limits of detection for these ions. The adsorbent is ecofriendly and a very small amount is consumed per analysis rendering it highly economical. A comparison with some of the different adsorbents available for preconcentration of metal ions is given Table 4.

Table 4. Comparative data about adsorption of metal ions on different adsorbent material**s** and determination by FAAS reported in literature

Adsorbent	Elements	PF	DL (ng mL^{-1})	Ref.
Penicillium digitatum immobilized on pumice stone	Cu(II) Pb(II)	50	1.30–5.80	1
Activated carbon modified by dithioxamide	Cu(II) Ni(II) Co(II)	330	0.50-0.80	9
Saccharomyces carlsbergensis immobilized on silica gel	Cu(II) Zn(II) Cd(II)	50	1.14–1.66	10
Chemically modified silica gel with aminothioamido anthraquinone	Pb(II) Cd(II) Cu(II) Ni(II)	50	0.95-22.50	12
Polyethylene glycol silica gel	Cu(II) Cd(II) Mn(II)	66.6	0.33-1.20	This work

As observed, Silica-PEG adsorbent is comparable to, or better than, some of the previously reported adsorbents for metal ions in terms of preconcentration factor and detection limits achieved. Moreover, Silica-PEG is a very promising adsorbent and has potential for use in different applications. The proposed procedure was applied to the determination of Cu(II), Cd(II) and Mn(II) in surface water and sugar samples with good recoveries for spiked samples.

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