

## 메조다공성 유기-실리카를 이용한 구리(II)의 예비농축과 불꽃원자 흡수분광법으로의 정량

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## Preconcentration of Copper(II) Using Mesoporous Organo-Silicas and Determination by Flame Atomic Absorption Spectrometry

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**요 약.** 메조다공성 유기-실리카 이용한 잔유 구리(II)의 양을 빠른 추출을 위한 간단하고 재현성을 가지는 방법과 불꽃원자 흡수분광법으로의 검출에 대해 연구하였다. 공통으로 존재하는 이온은 분리와 검출에 간섭받지 않았다. 예비농축인지는 100 ml 시료 용량에 대해 100 (1 ml 추출용량) 이 었다. 제안된 방법의 검출한계는 1.0 ng ml<sup>-1</sup>이다. 최적조건 하에서 흡착제의 최고흡수용량은 5 mg 구리/g 흡착제 었다. 최적조건하에서 상대표준편차는 2.8% ( $n=10$ )을 얻었다. 다양한 양의 구리(II)이온은 스파이크한 자연수와 합성수를 시험 시료로 하여 정확도 등을 시험하였다.

**주제어:** 예비농축, 구리, 메조 유기-실리카, 고상 추출, 불꽃원자 흡수분광법(FAAS)

**ABSTRACT.** A simple and reproducible method for the rapid extraction and determination of trace amounts of copper(II) ions using mesoporous organo-silicas mesoporous silica and atomic absorption spectrometry is presented. Common coexisting ions did not interfere with the separation and determination. The preconcentration factor was 100 (1 ml elution volume) for a 100 ml sample volume. The limit of detection of the proposed method is 1.0 ng ml<sup>-1</sup>. The maximum sorption capacity of sorbent under optimum conditions has been found to be 5mg of copper per gram of sorbent. The relative standard deviation under optimum conditions was 2.8% ( $n=10$ ). Accuracy and application of the method was estimated by using test samples of natural and synthetic water spiked with different amounts of copper(II) ion.

**Keywords:** Preconcentration, Copper, Mesoporous Organo-Silica, Solid Phase Extraction, Flame Atomic Absorption Spectrometry (FAAS)

### INTRODUCTION

Copper is an essential micronutrient for living organisms, playing an important role in several ecosystems. The chemistry of copper in aquatic systems has a complex pattern involving precipitation, complexation and redox reactions. It is well known that the free cupric ion (Cu(II)) is highly toxic for marine organisms and its determination is an important analytical task.<sup>1-4</sup> The natural content of

Cu(II) in seawaters is very low and varies in unpolluted regions in the range from 1 µg L<sup>-1</sup> to 20 µg L<sup>-1</sup>. Strong matrix interferences due to the complex nature of seawater samples, together with this low natural Cu(II) content restricted its direct determination even with highly sensitive methods, such as ETAAS or ICP-MS. In the common case, a preconcentration and separation procedure should be used to ensure the accurate and reliable determination of Cu(II) in seawater.

A great variety of analytical procedures for Cu(II) enrichment have been proposed, based mainly on liquid-liquid extraction,<sup>5-7</sup> coprecipitation,<sup>8,9</sup> and solid phase extraction (SPE).<sup>10-12</sup> The advantages of the SPE procedures is that they are faster, more reproducible cleaner extracts are obtained, emulsion formation is not an issue, solvent consumption is reduced, and smaller sample volumes are required.

The increasing use of copper compounds and copper-containing preparations in industry and medicine, has resulted in an increased copper content of environmental samples.<sup>13,14</sup> Copper also enters the environment in industrial waters because it often occurs as an impurity in copper, zinc, arsenic and antimony ores.<sup>15</sup> Low level exposure to copper compounds is widespread due to the use of soluble copper compounds to disinfect water used for drinking.<sup>24</sup> On the other hand, recent information about the interaction of copper with essential nutrients, especially selenium, copper, vitamin E and vitamin B12, have focused attention on its potential toxicity.<sup>16,17</sup> Due to the very low concentration of most elements, including copper, in environmental samples (i.e. less than 10  $\mu\text{g l}^{-1}$ ), their separation and sensitive determination urgently necessitate the use of a preconcentration or trace enrichment method.<sup>18-20</sup> The liquid-liquid extraction and separation of copper in the presence of classical<sup>21-23</sup> and macrocyclic ligands<sup>26-28</sup> are frequently reported in the literature. However, classical extraction methods are usually time consuming and labor extensive and require relatively large volumes of high-purity solvents. Of additional concern is disposal of the solvents used, which creates a severe environmental problem.

Solid phase extraction (SPE) or liquid-solid extraction is popular and growing techniques that are used to sample preparation for analysis. It is an attractive alternative for classical liquid-liquid extraction methods that reduce solvent usage and exposure, disposal costs and extraction time for sample separation and concentration purposed.<sup>29-31</sup> In recent years, the octadecyl-bonded silica SPE disks have been utilized for the extraction and separation of different organic compounds from environmental

matrices.<sup>32-35</sup> Moreover, the SPE disks modified by suitable ligands are successfully used for selective extraction and concentration of metal ions.<sup>36-41</sup>

In a recent series of papers,<sup>38-40</sup> we have described the application of metal-DNA conjugates to nucleic acid sequence determination with catalytic signal amplification; the assay relies on the esterase activity of a DNA-linked Cu complex. For optimization of the system and exploration of structure- activity relationships, a sensitive probe would be useful, which allows straightforward detection of esterase activity of ligated  $\text{Cu}^{2+}$  in low concentration. For this purpose, we used mesoporous organo-silicas in order to react with amine group of N as active donor atoms. In this study, we report the synthesis of this new sorbent and its application as a selective sorbent for separation, preconcentration and determination of  $\text{Cu}^{2+}$  ions by AAS determination.

## EXPERIMENTAL

### Apparatus

Determination of  $\text{Cu}^{2+}$  contents in working samples were carried out by a Varian spectra A.200 model atomic absorption spectrometer equipped with a high intensity hollow cathode lamp (HI-HCL) according to the recommendations of the manufacturers. These characteristics are tabulated in (Table 1).

Separation of sorbent was assisted using a centrifuge (centurion scientific model: K 240R, West Sussex, U.K.). The pH measurements were carried out by an ATC pH meter (EDT instruments, GP 353).

### Reagents and solutions

All reagents were of the highest purity available from Merck and were used as received. Analytical grade nitrate salts of lithium, sodium, potassium,

Table 1. The operational conditions of flame for determination of copper

Slit width	0.7 nm
Operation current of HI-HCL	15 mA
Resonance fine	324.8 nm
Type of background correction	Deuterium lamp
Type of flame	Air/acetylene
Air flow	7.0 mL.min <sup>-1</sup>
Acetylene flow	1.7 mL.min <sup>-1</sup>

magnesium, calcium, strontium, barium, zinc, cadmium, lead, nickel, cobalt(II), and copper(II) were of the highest purity. Ultra pure organic solvents were obtained from E.Merck, Darmstat, Germany, and High Purity double distilled deionized water was used throughout the experiments.

The stock standard solution of  $\text{Cu}^{2+}$  was prepared by dissolving 0.1000g of the copper powder in 10 mL concentrated nitric acid and diluted to 1000 mL with water in a calibrated flask. Working solutions were prepared by appropriate dilution of the stock solution.

The chemicals used for the preparation of mesoporous silica-based materials were used as received: tetraethoxysilane TEOS (>98% Merck), c-aminopropyltriethoxysilane APTES (99% Sigma-Aldrich), cetyltrimethylammonium bromide (CTAB) (98% Fluka), ethanol (95-96% Merck) and aqueous ammonia (28% Prolabo).

#### Preparation and characterisation of the mesoporous organo-silicas

The mesostructured amine-functionalised silica material was prepared according to a previously published procedure.<sup>44,45</sup> First 2.4 g of CTAB was dissolved in a solution containing 50 mL distilled water + 50 mL ethanol + 13 mL ammonia 28%. Then, the precursors APTES and TEOS were introduced according to an APTES/(APTES+TEOS) molar ratio of 10%. The mixture was left under stirring at ambient condition for 2 h, then filtered on a Büchner funnel, rinsed alternatively with distilled water and ethanol, and dried under vacuum ( $<10^{-2}$  bar) for 24 h. Surfactant extraction was achieved by refluxing 1 g of the as-synthesised solid into 100 mL of 1 M HCl in ethanol for 18 h. The final product was recovered by filtration after washing three times with ethanol. It will be denoted "APS" (aminopropylsilica) afterwards. The particles have been characterized by powder X-ray diffraction (XRD), the resulting XRD patterns being collected with an XPERT PRO from Philips equipped with a Cu anode ( $K\alpha_1$  radiation,  $k=1.54056 \text{ \AA}$ ). Their porosity was analysed by the BET method on the basis of nitrogen adsorption-desorption measurements carried out at 77 K using a Coulter SA3100 apparatus

after outgassing overnight at 323 K. Particle size distribution was measured using a light scattering analyser (model LA920, Horiba), based on the Mie scattering theory.

For some experiments, an amorphous silica material functionalised with the dipeptide carnosine was used as a solid-phase extractant for Cu(II) species. It was obtained by allowing TEOS to co-condensate with a precursor synthesised by amide coupling between the amino group of APTES and the carboxyl group of carnosine, using ethanol as co-solvent and ammonia in a catalytic amount.<sup>43,46</sup> The copolymer precipitates several hours after mixing 1.21 g of the (triethoxysilyl) alkylamido-carnosine precursor with 1.95 g TEOS, in a solution containing 1.22 g water and 6.42 g ethanol, with 0.06 g  $\text{NH}_3$  as the catalyst. The solvents are slowly evaporated to recover a dry white solid after about five days of reaction, the solid particles being washed thoroughly with dichloromethane and methanol before use. They are noted "Scar" (silica-carnosine) hereafter.

#### Procedure

A batch-wise process was employed for the extraction and preconcentration of copper. Extraction was performed in test tubes containing  $\text{Cu}^{2+}$  in 10 ml acetate buffered solution (pH 3.5). Sixty milligrams mesoporous organo-silicas was added into the solution. After that, the mixture was shaken manually for an appropriate time to extract copper completely from the solution. Finally, test tubes were placed in centrifuge and separation of sorbent was achieved by centrifugation for 2.5 min at 3500 rpm. The bulk aqueous phase was removed with a pipette and any residual aqueous phase was easily decanted. The back extraction was performed using 1.0 ml of  $1.0 \text{ mol l}^{-1}$  methanol solution. The copper concentration was determined by Flame Atomic Absorption Spectrometry (FAAS).

## RESULTS AND DISCUSSION

Some preliminary experiments were carried out in order to investigate the extraction of copper by the mesoporous organo-silicas from solution. The

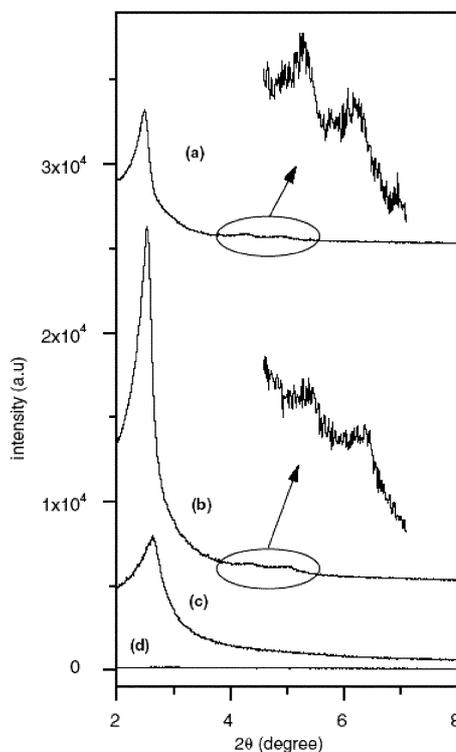


Fig. 1. Powder XRD patterns for: (a) as-synthesised APS, (b) surfactant-extracted APS, (c) surfactant-extracted APS after deprotonation in alkaline ethanol, and (d) surfactant-extracted APS after deprotonation in alkaline aqueous medium (0.01 M NaOH).

results showed that mesoporous organo-silicas can extract it quantitatively.

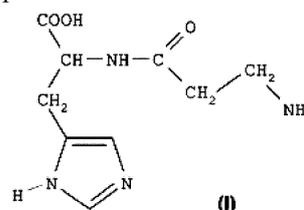
#### Characterisation of silica-based materials

The physico-chemical characteristics of both APS and Scar materials are as expected from previous studies.<sup>43,45</sup>

X-ray diffractogram of APS (Fig. 1, curve 'a') reveals the existence of an ordered structure at the mesoporous scale, typical of a hexagonal MCM-41 structure, featuring one main correlation reflection at a  $2\theta$  angle of 2.49 and two weaker reflections at higher  $2\theta$  angles (diffraction planes indexed as 1 0 0, 1 1 0 and 2 0 0). The regular mesostructure was maintained after template removal (Fig. 1, curve 'b'), this step resulting however in slight lattice contractions ( $2\theta$  angle of main line at 2.54) as previously observed for mesoporous organo-silicas

prepared by the co-condensation route.<sup>52</sup> Nitrogen adsorption-desorption isotherms were of type IV (not shown here but similar as in<sup>44</sup>), in agreement with what was usually observed with mesoporous materials.<sup>53</sup> A specific surface area of  $950 \text{ m}^2 \text{ g}^{-1}$  and pore size of 22 Å were determined by BET and BJH analyses, respectively. The synthetic method applied to prepare the mesoporous APS material led to the production of spherical particles of an average diameter of 600 nm, but most of them were in the form of bigger aggregates displaying a particle size distribution centred at  $6.5 \pm 1.4 \text{ }\mu\text{m}$ . The content of aminopropyl groups in APS was  $1.1 \text{ mmol g}^{-1}$ , as determined from elemental analysis. These groups, however, were in the form of propylammonium chloride as a consequence of template extraction performed in HCl/ethanol medium.

The silica-carnosine hybrid material, Scar, was described in reference<sup>43</sup> as an amorphous solid (flat XRD pattern) characterised by a specific surface area of  $62 \text{ m}^2 \text{ g}^{-1}$ , a total pore volume of  $0.279 \text{ cm}^3 \text{ g}^{-1}$ , and an average pore diameter of about 160 Å. Due to a treatment of Scar with gaseous HCl during the synthesis protocol,<sup>43,46</sup> the carnosine groups (b-alanyl-L-histidine I) attached to the silica framework were also protonated.



These materials are potentially good candidates for the extraction of Cu(II) species from dilute aqueous medium because of the well-known tendency of amine derivatives to form stable complexes with Cu(II). Indeed, both aminopropyl-grafted silica gels<sup>42</sup> and carnosine functionalised silica<sup>43</sup> have been incorporated in carbon paste electrodes and successfully applied to electrochemical sensing of Cu(II) after preconcentration. In the present case, however, APS and Scar contain a great majority of their N centres in a protonated form. This is expected to limit their binding properties (decreasing stability of amine-copper (II) com-

plexes at pH below 7<sup>42</sup>), thus requiring deprotonation of the material prior to use.

Deprotonation of APS without damage to the structural and chemical integrity of the material is not an easy task. As shown in curve 'd' on Fig. 1, a treatment of APS in aqueous NaOH (0.01 M) resulted in the complete crashing of the mesostructure, which was accompanied by dramatic leaching of aminopropyl groups and silicon moieties in solution. A similar treatment in 95% ethanol was less destructive as some order was maintained (Fig. 1, curve 'c') but the mesostructure was by far less ordered as the diffraction line corresponding to the 1 0 0 plane dropped significantly in comparison to the non treated solid while the weaker reflections at higher 2θ angles disappeared. This XRD pattern also revealed a shift of the diffraction line at higher 2θ values, indicating a significant contraction of the lattice with possible partial structure collapsing, as otherwise confirmed by BET measurements (specific surface area dropping by a factor of about 2.5 and pore volume by a factor 3).

**Effect of pH**

Basically, the approach described above for Cu(II) detection at APS-MCPE should be applicable to any modified electrode system involving N-bearing ligands that would require a modulation of their properties by a pH change. To point out this generalisation aspect, we have revisited an earlier work dealing with the use of an amorphous silica sample functionalised with carnosine groups (Scar), which was applied as modifier of a carbon paste electrode (Scar-MCPE) to Cu(II) preconcentration and detection.<sup>43</sup> The synthetic protocol to get the Scar material involved protection/deprotection processes resulting in N-bearing ligands under their protonated form, counter-balanced by chloride anions (compound II).

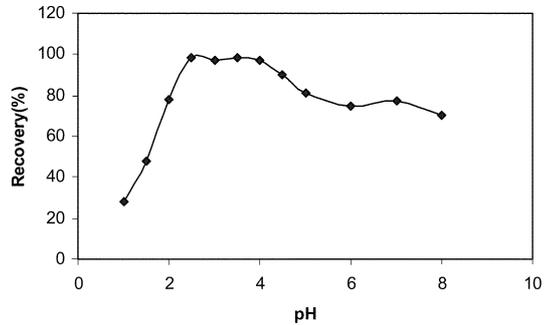
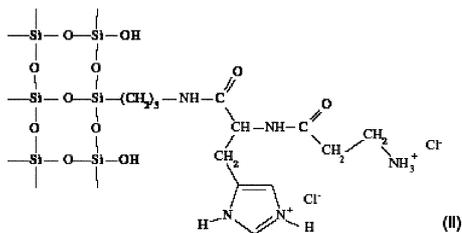


Fig. 2. Effect of pH on the extraction of copper. Experimental conditions: source, 10 ml of 0.1 μgml<sup>-1</sup> Cu<sup>2+</sup> solution; amount of sorbent, 50.0 mg.

The effect of pH on the extraction of Cu<sup>2+</sup> from water samples was studied in the pH range of 1.0-8.0. The higher pH values were not studied because functionalized mesoporous silicates were not stable in alkali solutions due to the breaking of the Si-O-Si bonds by hydroxide ions attack<sup>54</sup>. pH of the solution was adjusted at the required value by adding 1.0 mol l<sup>-1</sup> sodium hydroxide and/or 1.0 mol l<sup>-1</sup> nitric acid. As can be seen in Fig. 2, extraction was nearly constant and quantitative in the pH range of 2-8.0. At lower pH (<2.5), the nitrogen atoms in mesoporous organo-silicas are protonated, so the stability of complex formation between the sorbent and Cu<sup>2+</sup> is reduced. Therefore, the extraction of copper decreased. Hence, pH of 3.5 was chosen as the optimum pH for extraction.

**Choice of eluent**

In order to choose the most effective eluent for desorbing copper ion from the sorbent surface aliquots of 10 ml of 0.1 μg ml<sup>-1</sup> copper ion solution was contacted with 50.0 mg of mesoporous organo-silicas. A series of selected eluent solution such as nitric acid, formic acid, acetic acid, sodium thiosulfate, ethanol and methanol was used. A total of 10.0 ml of 0.1 mol l<sup>-1</sup> of the above mentioned eluents were used for desorbing the adsorbed copper ion. The amount of copper ion back-extracted into the liquid phase by each eluent was measured using Flame Atomic Absorption Spectrometry (FAAS). Percent recoveries of copper ion were calculated for each sample. The results (Fig. 3) showed that recov-

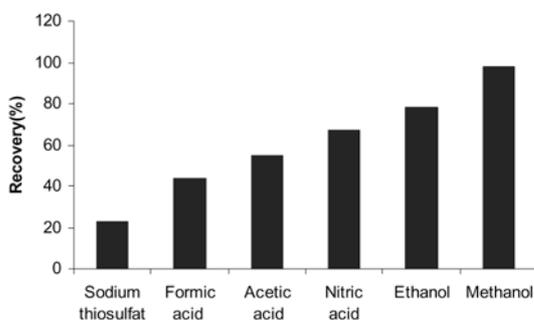


Fig. 3. Effect of nature of eluent on the recovery of copper. Experimental conditions: source, 10 ml of  $0.1 \mu\text{gml}^{-1}$   $\text{Cu}^{2+}$  solution at pH 3.5; sorbent 50.0 mg.

ery was the best when methanol was used as eluent. Also, higher concentrations of hydrochloric and nitric acid ( $0.5$  and  $1.0 \text{ mol l}^{-1}$ ) solutions were tested and the results showed the recovery of copper was not quantitative. Therefore, methanol was selected as eluent.

#### Effect of eluent concentration

The influence of the concentration of methanol on desorption of copper ion was studied. For desorbing  $1.0 \mu\text{g}$  copper ion, already adsorbed on 50.0 mg of sorbent, 1.0 ml of different concentration of eluent (methanol) have been used. At a concentration of more than  $0.7 \text{ mol l}^{-1}$ , methanol desorbs (recovery of almost 100%) copper ion completely from the sorbent surface. A concentration of  $1.0 \text{ mol l}^{-1}$  of methanol was selected for further studies.

#### Effect of the sample volume

In order to explore the possibility of concentrating low concentrations of copper from large volumes, the maximum applicable volume must be determined. For this purpose, the effect of the sample solution volume on the recovery was studied by keeping the total amount of  $\text{Cu}^{2+}$  uptake constant ( $1.0 \mu\text{g}$ ). The quantitative recoveries were obtained for sample volume of 100 ml. Therefore, the concentration factor was 100 for  $\text{Cu}^{2+}$  since the final elution volume was 1.0 ml.

#### Effect of the amount of mesoporous organo-silica

To test the effect of the amount of mesoporous organo-silicas on quantitative retention of analyte different amounts of sorbent (range from 2.0 to

200.0 mg) were added into the solution following the experimental method. The results showed that the extraction of  $\text{Cu}^{2+}$  was quantitative by using only 10.0 mg of mesoporous organo-silicas. Subsequent extraction experiments were carried out with 50.0 mg of mesoporous organo-silicas in order to achieve higher capacity and to account for other extractable species.

#### Adsorption capacity

The capacity of the sorbent is an important factor that determines how much sorbent is required to remove a specific amount of metal ions from the solution quantitatively. For investigation of adsorption isotherm of copper ion, the same volumes of copper ion solution with different concentrations of copper ion were contacted with 0.1 g of sorbent in the batch mode. Then, the concentration of the remaining copper in the solution was determined by Flame Atomic Absorption Spectrometry (FAAS). The adsorption isotherm that is the number of microgram absorbed per gram of adsorbent ( $N_f$ ) versus the equilibrium concentration of cation ( $C_e$ ) is shown in Fig. 4. According to these results, the maximum amount of copper that can be sorbed by mesoporous organo-silicas was found to be  $5 \text{ mg g}^{-1}$  at pH 3.5.

#### Effect of equilibrium time

In order to investigate the effect of shaking time on the extraction efficiency, extraction for a series of solutions containing  $1.0 \mu\text{g}$   $\text{Cu}^{2+}$  were carried out. The results showed that the shaking time (from 20 to 350 s) has no effect on the extraction efficiency of copper and the extraction was quantitative. Although the extraction process can be continued during the centrifugation, however, the

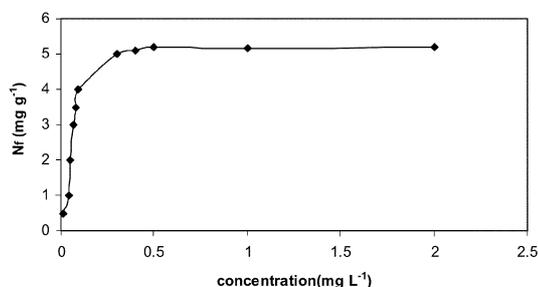


Fig. 4. Adsorption isotherm of copper(II) ion on sorbent.

results showed that extraction was quantitative and very fast in all cases. Thus, the mixtures have been shaken for 20 s to reach equilibrium in the subsequent experiments.

**Effect of ionic strength**

The influence of ionic strength on the extraction of copper was studied in the potassium nitrate solution with various concentrations from 0.01 to 1.0 mol l<sup>-1</sup>. Results have shown that ionic strength has no considerable effect upon extraction efficiency up to 1.0 mol l<sup>-1</sup> of KNO<sub>3</sub>. These observations showed the specific tendency of mesoporous organo-silicas for Cu<sup>2+</sup> and the possibility of using this method for separation of copper from highly saline solutions.

**Effect of coexisting ions**

The effects of common coexisting ions in natural water samples on the recovery of copper were studied. In these experiments, 10 ml of solutions containing 0.1 µg l<sup>-1</sup> of copper and various amounts of interfering ions were treated according to the recommended procedure. An ion was considered to interfere when its presence produced a variation in the extraction recovery of sample more than ±5%. The results showed that, in excess of 10,000-fold Li<sup>+</sup>, K<sup>+</sup>, Na<sup>+</sup>, Ca<sup>2+</sup>, Mg<sup>2+</sup>, Ba<sup>2+</sup>, Sr<sup>2+</sup> and 1000-fold Cl<sup>-</sup>, Br<sup>-</sup>, SO<sub>4</sub><sup>2-</sup>, Ag<sup>+</sup>, Co<sup>2+</sup>, Cd<sup>2+</sup>, Ni<sup>2+</sup>, Zn<sup>2+</sup>, Mn<sup>2+</sup>, Pb<sup>2+</sup>, Al<sup>3+</sup>, Cr<sup>3+</sup>, Fe<sup>3+</sup> and Hg<sup>2+</sup> ions had no significant interferences in the extraction and determination of copper. As can be seen, mesoporous organo-silicas has shown a high tolerance limit for alkali and alkaline earth metals. This is particularly useful for the analysis of copper in natural water samples, for example, seawater, which contain large amounts of alkali and alkaline earth metal ions.

**Reusability and stability of mesoporous organo-silicas**

Reusability is one of the key parameters to assess the effectiveness of a sorbent. A series of sorption/desorption experiments were performed to understand the reusability of the synthesized mesoporous organo-silicas. After sorption, the sorbent was treated with 1.0 mol l<sup>-1</sup> methanol to desorb Cu<sup>2+</sup> and this sorption/desorption procedure was repeated five times. After each desorption step, the sorbent was washed with doubly distilled water to remove

methanol and condition sorbent. On storing for a year under dark and dry conditions, the stability of sorbent was excellent and adsorption capacity did not change significantly.

**Analytical Performance**

The limit of detection (LOD) and the limit of quantification (LOQ) were calculated as the amount of analyte necessary to yield a signal equal to three times (3σ) and ten times (10σ) the standard deviation of the blank signals, respectively. Using sample volume of 100 ml a LOD of 1.0 µg l<sup>-1</sup> and a LOQ of 1.2 µg l<sup>-1</sup> were obtained for the determination of copper. Ten replicate extraction and measurement of 1.0 µg of Cu<sup>2+</sup> ion in 100 ml water solution gave a R.S.D. of 2.8%. Calibration graph was obtained using preconcentration of 100 ml of standard solutions buffered at pH 3.5 with 50 mg of sorbent. For this purpose, standard solutions containing copper ion in the range of 1-1000 µg l<sup>-1</sup> were examined by the proposed procedure and it

Table 2. Recovery of copper(II) added to 100 mL of different water samples (containing 0.1 M buffer acetic acid / acetate at pH= 3.5).

Sample	Cu <sup>2+</sup> spiked (ng ml <sup>-1</sup> )	Cu <sup>2+</sup> detected (ng ml <sup>-1</sup> )	Recovery (%)
Sample 1 <sup>a</sup>	5.0	4.9 (2.0) <sup>b</sup>	98.3
	10.0	9.8 (2.5)	98.4
	5.0	5.0 (2.8)	99.0
Sample 2 <sup>c</sup>	10.0	9.9 (2.8)	98.2
	0.0	2.3 (2.4)	98.5
	5.0	7.2 (2.9)	98.5
Tap water <sup>d</sup>	10.0	12.3 (3.3)	98.8
	0.0	N.D.	-
	5.0	5.0 (2.1)	98.6
Rain water <sup>e</sup>	10.0	10.1 (2.6)	98.9
	0.0	14.0(2.0)	99.3
	5.0	18.9 (2.3)	98.6
Sea water <sup>g</sup>	10.0	24.1 (2.8)	99.2

<sup>a</sup>Hg<sup>2+</sup>, Co<sup>2+</sup>, Cd<sup>2+</sup>, Fe<sup>3+</sup>, Ni<sup>2+</sup>, Cr<sup>3+</sup>, 5000 ng ml<sup>-1</sup> of each cation; K<sup>+</sup> and Li<sup>+</sup>, 10,000 ng ml<sup>-1</sup> of each.

<sup>b</sup>R.S.D of three replicate experiments.

<sup>c</sup>Hg<sup>2+</sup>, Co<sup>2+</sup>, Cd<sup>2+</sup>, Fe<sup>3+</sup>, Ni<sup>2+</sup>, Cr<sup>3+</sup>, 2500 ng ml<sup>-1</sup> of each cation; K<sup>+</sup> and Li<sup>+</sup>, 5000 ng ml<sup>-1</sup> of each.

<sup>d</sup>From drinking water system of Tehran.

<sup>e</sup>Not detected.

<sup>f</sup>Tehran, 26January, 2007, Iran.

<sup>g</sup>Caspian sea water.

was observed that calibration curve were linear in this range. The regression equation was  $I=0.0083C$  ( $\mu\text{g l}^{-1}$ ) + 0.0045 and the correlation coefficient was 0.9993.

#### Analysis of water samples

To assess the applicability of the method to real samples, it was applied to the extraction and determination of copper from 100 ml of different water samples. Tap water (Tehran, taken after 10 min operation of the tap), rain water (Tehran, 26 January, 2007), and Sea water (taken from Caspian sea, near the Mahmoud-Abad shore) samples were analyzed (Table 2). As can be seen from Table 2 the added copper ions can be quantitatively recovered from the water samples used.

### CONCLUSION

Results presented in this work demonstrate well the tremendous possibilities offered by the solid phase extraction of trace amounts of Cu(II) in water samples using of mesoporous organo-silicas and its determination by FAAS. The method developed was simple, reliable, high capacity, good stability and fast adsorption and desorption kinetics for determining copper in water. Also, the proposed method was free of interference compared to conventional procedures to determine copper.<sup>50-54</sup> The method can be successfully applied to the separation and determination of copper in binary mixtures.

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