# Solid Phase Extraction of Copper Ions using a Chemically Modified SBA-15 Mesoporous Silica

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*A new method was proposed for the preconcentration of copper ions using a column packed with SBA-15 mesoporous silica functionalized with N-Propylsalicylaldimine. The effects of various parameters such as pH, flow rate of sample, elution conditions, sample volume and enrichment factor, and the influence of some matrix elements have been studied. The dynamic adsorption capacity for $Cu^{2+}$ under optimized conditions was 985.6 $\mu g \cdot g^{-1}$. The adsorbed metal ions were quantitatively eluted by 2 mL of 1M HCl (enrichment factor of 200).Common coexisting ions did not interfere with the separation. Copper was determined from spiked tap water and mineral water by flame atomic absorption spectrometry (FAAS) after preconcentration on this new solid-phase extraction (SPE) material. The obtained recoveries were 103 ± 3% and 97 ± 2%, respectively. The LOD and LOQ values of the proposed method were found to be $6.0 \times 10^{-6}$ and $1 \times 10^{-5}$ mM. For three preconcentration experiments the relative standard deviation was found to be ≤ 5% in all cases proving high accuracy and precision of the presented method.*

*Keywords: SBA-15 silica, N-propylsalicylaldimine, solid-phase extraction (SPE), Cu (II)*

Copper is known as an important element in industry and biological systems as well. It is an essential nutrient to high plants and animals and is a co-factor in various enzymes. This element can be poisonous even at very low concentration. Copper concentration in potable water is usually very low (≤ 20 μg/L) [1]. The average copper concentration in lakes and rivers is 10 μg/L. In groundwater the average of copper concentration (5 μg/L) is similar to that in lakes and rivers. Some groundwater contains up to 2800 μg/L, which is above the standard level for drinking water [2]. The presence of heavy metals in the environment is of serious concern as the number of ecological and health problems associated with them is very high [3,4]. Consequently, a great attention has been paid in the last years to determine and/or remove these contaminants from aqueous systems. For humans, the main sources of Cu(II) are water and food, so a precise, accurate and rapid measurement of copper must be accessible for its determination in these samples. Flame and graphite furnace atomic absorption spectrometry [5] and spectrophotometric methods [6] are known as the most common methods for determination of copper in various samples. However, these methods suffer from their insufficient sensitivity for very low concentration of metal in environmental and biological samples. Therefore, preconcentration and selective separation of trace or ultra trace Cu(II) is sometimes required before applying the above-mentioned techniques. The traditional separation and preconcentration methods for metal ions include liquid-liquid extraction [7], co precipitation [8] and ion-exchange [9], etc. These methods often require large amounts of high purity organic solvents, some of which are harmful to health and cause environmental problems. Recently solid-phase extraction (SPE) technique has become known as a powerful tool for separation and enrichment of various inorganic and organic analytes. The SPE has several major advantages that include (i) higher enrichment factor, (ii) simple operation, (iii) safety with respect to hazardous samples, (iv) high selectivity, (v) lower cost and less time, (vi) the ability to combine with different modern detection techniques. Chemically modified silica gel is one of the most successful adsorbents, because the silica gel supports do not swell or shrink like the polymeric resin. The adsorbents based on mesoporous silica functionalized with organic groups are considered as the best adsorbents for heavy metal ion trapping [8-11].

SBA-15 silica, prepared by using poly(alkylene oxide) triblock copolymer as structure directing agent [12] shows one of the largest pore size for siliceous mesostructured materials, good hydrothermal and chemical stability. SBA-15 was selected in many works as the ideal support for anchoring organic chains that contained functional groups for metal ions adsorption. Functional groups such as thiol [13], imidazole [14], 5-mercapto-1-methyltetrazole [15] amino [16], polyol [17], iminodiacetic [18] were incorporated into the inorganic SBA-15 network and used for selective adsorption of different heavy metal ions.

We have previously reported that MCM-41 and SBA-15 silica functionalized with N-propylsalicylaldimine in a two-step post-synthesis method showed high adsorption capacity and high selectivity for copper ions [19a,b]. In this study we report the application of SBA-15 mesoporous silica functionalized with this organic groups as an efficient sorbent for copper preconcentration and its determination by flame atomic absorption spectrometry The optimum analytical conditions for adsorption and quantitative recoveries of metal ions were investigated. The prepared material was then applied to preconcentrate trace copper ions from tap and mineral water samples with satisfactory results.

## Experimental part

### *Synthesis of functionalized SBA-15 silica*

SBA-15 material was synthesized as described in [20]. The organic–inorganic hybrid materials were obtained by a two-step post-grafting procedure with 3-aminopropyl-triethoxysilane (APTES) and salicylaldehyde (SA),

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respectively. Firstly, the calcined SBA-15 was silanized with APTES. One gram of SBA-15 silica, freshly activated overnight at 453 K under vacuum, and 1 mL of APTES (99% Aldrich) was added to 50 mL of dry toluene. After stirring the solution (reflux, 2 h), the released ethanol was distilled off and the mixture was kept under reflux for 90 min. The $NH_2$-functionalized mesoporous silica (referred as $NH_2$–SBA-15) was filtered and washed with toluene, ethanol and then diethyl ether. It was then submitted to a continuous extraction run overnight in a Soxhlet apparatus using diethyl ether/dichloromethane (v/v, 1/1) at 373 K and dried overnight at 403 K. In the second step, the $NH_2$–SBA-15 solid (1 g), activated under vacuum at 403 K for 1 h, was dispersed in dry toluene (50 mL) before adding 1 mL of SA. The mixture was refluxed at 398 K overnight and the obtained yellow solid (denoted as SA–SBA-15) was collected by filtration and washed successively with toluene, ethanol and diethyl ether. The SA excess was removed by Soxhlet extraction using diethyl ether/dichloromethane (v/v, 1/1). The obtained SA–SBA-15 was dried overnight at 313 K.

Small-angle XRD patterns of SBA-15 and SA-SBA-15 mesoporous silica were acquired on a Bruker diffractometer using Cu Kα radiation. $N_2$ adsorption–desorption isotherms were measured at 77 K with a Micromeritics ASAP 2010 instrument. Specific surface area was calculated by the BET method, the mesopore volume was determined by nitrogen adsorption at the end of capillary condensation, and pore size distribution was determined from the desorption isotherms. FTIR spectra of self-supported wafers previously heated at 423 K under vacuum were performed on a Bruker Vector 22 spectrometer. C, H, and N contents were evaluated by combustion on a Fisons EA1108 elemental analysis apparatus. Thermogravimetric analysis was carried out in a Netzsch TG 209C thermobalance.

*Column SPE procedure*

A glass column (10 cm x 1cm i.d.) was filled with 0.1 g of dried SA-SBA-15. Before use, the column was washed with doubly distilled deionized water. The *p*H of optimized volume of metal ion solution was adjusted by the drop-wise addition of dilute $HNO_3$ or NaOH. The solution was then passed through the column with a peristaltic pump at a flow rate of 4 mL/min. The column was thereafter washed with 20 mL deionized water to remove the metal ions that were not adsorbed. Metal ion adsorbed on the column was then eluted with 1 mol·L$^{-1}$ HCl at an elution rate of 1 mL/min. The concentration of the metal ions in the eluate was determined by FAAS.

*FAAS determination of heavy metals*

Atomic absorption spectrophotometry (FAAS) measurements were performed on a Spectra AA-220 Varian spectrophotometer equipped with Varian multi-element hollow cathode lamps and air–acetylene burner. Copper, nickel, cobalt and zinc were determined according to the standard guidelines of the manufacturers. Working standard stock solutions of $Cu^{2+}$, $Ni^{2+}$, $Co^{2+}$ and $Zn^{2+}$ were prepared by diluting an AA stock solution (1000 mg L$^{-1}$) of each metal.

*Copper determination in natural and mineral water samples*

Tap water (*p*H 6.4, conductivity 150 μS/cm) and commercial mineral water (*p*H 6.6, conductivity 460 μS/cm) were used without any pretreatment. A glass column (10 cm x 1cm i.d.) was filled with 0.1 g of dried SA-SBA-15. 100 mL of tap or mineral water with the *p*H adjusted to 5 was passed through the column at a flow rate of 4 mL/min. Then the column was washed with 20 mL deionized water. The adsorbed copper was eluted with 2 mL of 1 mol·L$^{-1}$ HCl and determined by FAAS.

## Results and discussion

*Adsorbent characterization*

In a previous paper [19] we have presented the physico-chemical properties of the SA-SBA-15 material that was used in this study for copper preconcentration from water samples before its FAAS determination.

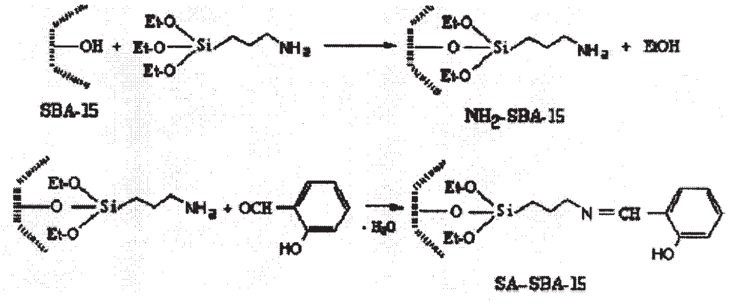
The organic functional groups were sequentially grafted on the SBA-15 surface by a two-step post-synthesis procedure (scheme 1).

Based on the elemental and thermogravimetric analysis, the amount and the density of the grafted salicylaldimine was determined (1.36 mmol g$^{-1}$ and 1.01 molecules nm$^{-2}$, respectively).

The XRD measurements confirmed the SBA-15 structure for both unmodified and grafted samples.

All materials exhibited irreversible type IV $N_2$ adsorption-desorption isotherm with a H1 hysteresis loop in the partial pressure range 0.65 to 0.75, characteristic of materials with 7-8 nm pore diameter. The textural results (table 1) confirm the grafting of the organic moieties inside the mesopores.

In the FTIR spectrum of the SA-SBA-15 material were observed the characteristic bands for the organic functional



Scheme 1. Schematic illustration of the SBA-15 functionalization

**Table 1**
TEXTURAL PROPERTIES OF CALCINED AND MODIFIED SBA-15

| Material | $S_{BET}$/m$^2$g$^{-1}$ | $V_{mezo}$/ml g$^{-1}$ | $D_{BdB}$/nm |
|---|---|---|---|
| SBA-15 | 697.23 | 1.49 | 8.28 |
| SBA-15 $NH_2$ | 367.75 | 0.77 | 7.83 |
| SBA-15 $NH_2$ SA | 316.73 | 0.73 | 6.85 |

groups: the first one, at about 1650 cm$^{-1}$ was assigned to –C=N stretching vibration of the imine group, which is the principal band for the Schiff base ligand; the second one, at 1250 cm$^{-1}$ can be attributed to the phenolic C–O bond. The medium intensity bands at 2922 and 2885 cm$^{-1}$ correspond to the $\nu_{as}$ ($CH_2$) and $\nu_s$ ($CH_2$) vibrations.

*Copper preconcentration on the SA-SBA-15 mesoporous silica*

The ability of SA-SBA-15 to be used as a solid-phase extraction material for $Cu^{2+}$ ions from water samples was tested. Different parameters were optimized. The effect of sample solution *p*H, sample flow rate, sample volume and elution conditions on the extraction efficiency, effect of coexisting ions, dynamic adsorption capacity, enrichment factor and reusability of the sorbent were studied. The optimization procedure was carried out by varying a parameter while the others were kept constant.

*Effect of pH*

Solution acidity has two effects on metal adsorption: proton in acid solution can protonate binding sites of the chelating ligand, and hydroxide in basic solution may complex and precipitate many metal ions. Therefore, *p*H is the first parameter to be optimized According to the batch procedure [19], Cu(II) adsorption was investigated in the *p*H range of 1-7 and then analyzed by FAAS. The effect of the solution *p*H on the adsorption of Cu(II) onto SA-SBA-15 are shown in figure 1. The $Cu^{2+}$ removal efficiency increases as the solution *p*H increase from 1 to 5, then it slightly decrease with further increase in *p*H. At *p*H around 5, the copper in aqueous solution exists as $Cu^{2+}$, $Cu(OH)^+$ and $Cu_2(OH)_2^{2+}$ forms [21] which are favorable for the Cu(II) adsorption. When *p*H is higher than 6, precipitation of the metal hydroxid is expected [22]. As seen in figure 1, the optimum *p*H value for the removal of Cu(II) from aqueous solution was 5.

*Effect of sample flow rate*

The flow rate of sample solution through the packed volume is a very important parameter for controlling the time of adsorption and analysis. Therefore, the effect of the flow rate of sample solution was examined under the optimum conditions by passing 10 mL of standard solution through the column with a peristaltic pump. The flow rates were adjusted in range 1-6 mL·min$^{-1}$. The adsorption values were not very much affected by flow rate (fig.2). Quantitative recoveries were obtained with 4.0-5.0 mL·min$^{-1}$. Above 5.0 mL·min$^{-1}$ the copper recovery was less than 95%. Flow rate of less than 4.0 mL·min$^{-1}$ were not employed to avoid the long extraction time. Thus, a flow rate of 4 mL·min$^{-1}$. was selected for copper preconcentration.

*Elution condition*

Studies were carried out to investigate the influence of different acids as eluents for desorbing retained copper ions. $HNO_3$ caused decomposition of the mesoporous silica support. Since this material showed good stability in HCl solutions, this acid was used for the elution of the adsorbed ions from the solid. The elution condition was studied by using various concentrations and volume of HCl solution. It was found that 2.0 mL of 1.0 mol·L$^{-1}$ were sufficient for complete elution of copper ions. Therefore, 2.0 mL of 1.0 mol·L$^{-1}$ HCl solution was used as eluent in further experiments. The flow rate of eluent was 1 mL·min$^{-1}$.

*Maximum sample volume and enrichment factor*

In order to explore the possibility of adsorbing low concentrations of analytes from large volume of solution, the effect of sample volume on the retention of metal ions was also investigated. For this purpose, 50, 100, 200, 300, 400 and 500 mL of sample solutions containing the same amount of metal ion (25 µg) were passed through the

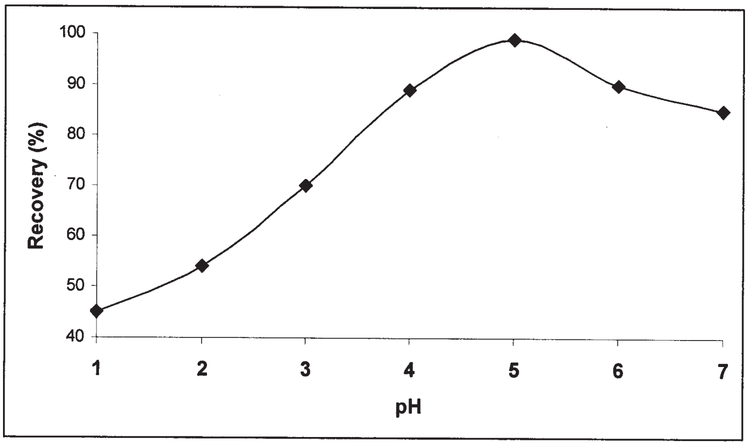


Fig. 1 Effect of pH on adsorption of 10 µg ·mL$^{-1}$ Cu(II) on SA-SBA-15

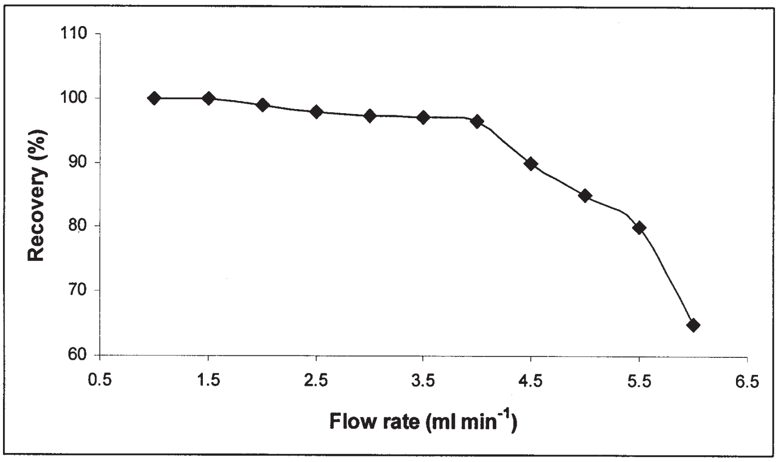


Fig. 2. Effect of solution flow rates on adsorption of 10µg ·mL$^{-1}$ Cu(II) on SA-SBA-15. Other conditions: 0.1 g adsorbent, volume 10 mL, *p*H 5, temperature 25$^0$C

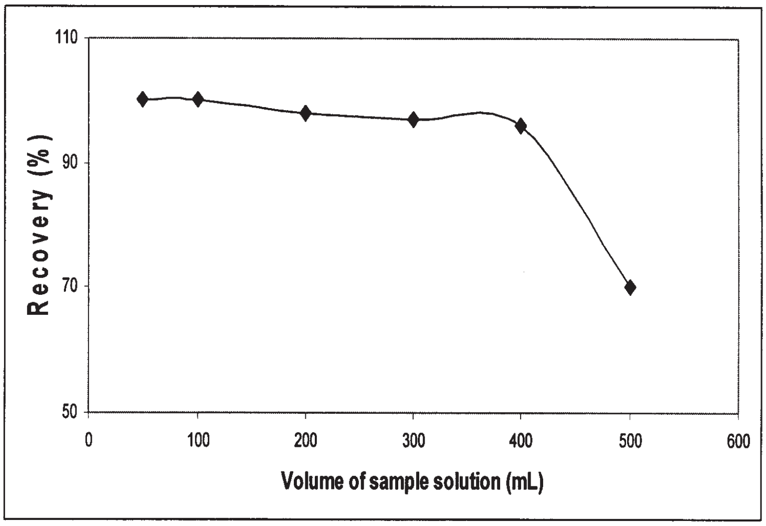


Fig. 3. Effect of sample volume on Cu(II) recovery at *p*H 5; temperature 25°C

**Table 2**
DETERMINATION OF COPPER IONS IN WATER SAMPLES

| Sample | Spiked (μg $L^{-1}$) | Found (μg $L^{-1}$)[a] | Recovery (%) |
|---|---|---|---|
| Deionized water | 0 | n.d. | - |
| | 10 | 10.20 ± 1.08 | 102 |
| Tap water | 0 | 6.54 ± 0.60 | - |
| | 10 | 15.27±1.05 | 92 |
| Mineral water | 0 | 0.93 ± 0.65 | - |
| | 10 | 10.71 ± 0.45 | 98 |

[a] Average of three determination ± standard deviation, n.d. = not detectable

column with the optimum flow rate. As shown in figure 3, the quantitative recovery (>95%) was obtained for the sample volume of 400 mL. The adsorbed metal ions could be eluted with 2.0 mL 1.0 mol·$L^{-1}$ HCl, so the enrichment factor achieved by this method was 200. The enrichment factor for $Cu^{2+}$ obtained in this work is comparable to those of the most other important silica-based materials previously used. Therefore, the SA-SBA-15 material is suitable for the preconcentration of trace concentration of $Cu^{2+}$ ions.

*Dynamic adsorption capacity*

The capacity of the adsorbent is an important factor that determines how much sorbent is required to quantitatively remove specific amount of metal ions from the solutions [23]. For investigation the adsorption capacity, a standard Cu(II) solution was passes through the column packed with 0.10 g of sorbent until the initial and final copper concentration are the same. The maximum amount of $Cu^{2+}$ taken up by the SA-SBA-15 ($N_{max}$) was calculated as follows:

$$N_{\max} = \frac{n_r}{m}$$

where $n_r$ is the amount of $Cu^{2+}$ retained by the solid and $m$ is the mass in grams of the adsorbent. For comparation, the same adsorption experiment was carried out with the unmodified SBA-15 mesoporous silica.

Based on the obtained results, the functionalization of SBA-15 with the N-propylsalicylaldimine leads to a significant increase in the binding capacity for $Cu^{2+}$ ($N_{max}$ = 985.6 μg·$g^{-1}$ and 5.2 μg·$g^{-1}$ for SA-SBA-15 and SBA-15, respectively).

Comparing the copper adsorption capacity of the SA-SBA-15 with those of other hybrid materials [24-26] it can be concluded that this material could be successfully used for copper preconcentration from water samples.

*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 1μg $mL^{-1}$ 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 of more than 5% in the extraction recovery of the sample. Some of the tested: ions, $F^-$, $Cl^-$, $Br^-$, $I^-$, $ClO_4^-$, $SO_4^{2-}$, $PO_4^{3-}$, $Li^+$, $K^+$, $Ca^{2+}$, $Mg^{2+}$, $Ba^{2+}$, $Sr^{2+}$, $Sn^{2+}$, $Al^{3+}$, $Cr^{3+}$ and $Fe^{3+}$, (Ion / Cu(II) (m/m) = 1000) did not interfere with copper extraction and determination. The others ions: $Co^{2+}$, $Cd^{2+}$, $Ni^{2+}$, $Zn^{2+}$, $Mn^{2+}$, $Pb^{2+}$, $Ag^+$, $Pd^{2+}$ are tolerable only for an 10-fold excess.

*Regeneration of the sorbent SA-SBA-15*

To study the regeneration capacity of the material, a glass column was filled with the modified silica and the adsorption capacity of the material for $Cu^{2+}$ was determined after three adsorption and elution cycles. Results indicate not significant reduction in the adsorption capacity after the repeated cycles (97±2% adsorption). Thus, the material with an enhanced stability could be used in successive adsorption/elution cycles.

*Real sample analysis and analytical performance*

To demonstrate the validity of the SA-SBA-15 material, 100 mL of tap water and mineral water samples were used for $Cu^{2+}$ preconcentration under the optimized conditions and its determination of by FAAS. The data obtained with the proposed method for spiked and natural water samples are presented in table 2. The results of triplicate analysis of each water samples showed that the copper recovery was almost quantitative.

In order to evaluate the accuracy of the method, tap water and mineral water samples were spiked to achieve a final concentration of 10.0 $\mu g \cdot L^{-1}$ before passing through the column containing SA-SBA-15 material.

The results were compared with deionized water spiked with $Cu^{2+}$ to achieve the same final concentration.

Copper could not be detected in the no spiked water samples (table 2). The $Cu^{2+}$ spiked to tap water and mineral water samples was quantitatively recovered, indicating a good accuracy of the preconcentration method we have developed.

The limit of detection (LOD) and limit of quantification (LOQ) for $Cu^{2+}$ were determined by passing a blank solution through the SA-SBA-15. The LOD value (blank + $3\sigma$) and LOQ value (blank + 10 $\sigma$) , were $\sigma$ is standard deviation of blank determination (n=8), were 0.5 and 2.0 $\mu g \cdot L^{-1}$, respectively and are in accordance with the previously reported values.

The precision of the method was evaluated using spiked water samples. The relative standard deviation (RSD, %) for four preconcentration experiments of 1µg of Cu(II) ion from 100 mL water solution was found to be ≤ 5% in all cases. These results showed a good precision and reasonable RSD value, comparatively with other studies.

Calibration graph was obtained using preconcentration of 100 mL of standard solutions buffered at *p*H = 5.0 with 100 mg of sorbent. For this purpose, standard solutions containing copper ion in the range of 2-1000 $\mu g\ L^{-1}$ were examined by the proposed procedure and it was observed that calibration curves were linear in this range. The regression equation was $I = 0.0021\ C\ (\mu g\ L^{-1}) + 0.0011$ and the correlation coefficient was 0.9989.

## Conclusions

A new method for copper ions preconcentration from water samples was developed by using a hybrid material based on SBA-15 mesoporous silica and N-Propylsalicylaldimine. The dynamic adsorption capacity for $Cu^{2+}$ under optimized conditions was 985.6 $\mu g \cdot g^{-1}$ with an enrichment factor of 200. This method is accurate and $Cu^{2+}$ determination was not affected by potential interferences from the major matrix compounds of the tap and mineral waters. These results are in agreement with those obtained in other studies of metal ions preconcentration using silica-based material.

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