



Preconcentration of ultra-traces of Cu(II) in water samples using SBA-15 sorbent modified with a thiocarbohydrazide ligand prior to determination by flame atomic absorption spectrometry

MAHMOOD PAYEHGHADR*, HAMIDREZA HAGHGOO QEZELJE, FARZANEH NOURIFARD, ABDOLMOHAMMAD ATTARAN and MEHDI KALHOR

Department of Chemistry, Payame Noor University, 19395-4697 Tehran, Iran

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Abstract: A simple, reliable and rapid method for the extraction of ultra-trace copper(II) using nanoporous SBA-15 sorbent modified with a thiocarbohydrazide ligand, and determination by flame atomic absorption spectrometry is presented. The optimum parameters of the method were obtained as pH of aqueous solution 5, sorbent amount 2 mg, stirring time 20 min and 0.4 M HCl solution as the eluent solvent. This method has a breakthrough volume greater than 1500 mL with a concentration factor of more than 300, linear range 0.8–2500.0 $\mu\text{g L}^{-1}$, limit of detection 0.253 $\mu\text{g L}^{-1}$ and limit of quantification 0.844 $\mu\text{g L}^{-1}$ for copper(II). The capacity of 2 mg of modified SBA-15 was found to be $123.00 \pm 0.04 \text{ mg g}^{-1}$. Standard deviations were 3.3, 2.3 and 2.1 % for 1, 2 and 4 $\mu\text{g mL}^{-1}$, respectively ($n = 5$). This method was successfully applied for the determination of copper(II) in different real samples, especially in the food samples.

Keywords: nanoporous sorbent; thiocarbohydrazide; flame atomic absorption spectrometry; copper(II).

INTRODUCTION

The pollution of natural waters by several types of pollutants has caused great concern to modern society. Among the most hazardous pollutants, a great variety of metals, which are mainly produced by industrial, urban and agricultural activities, can be found. Once in the environment, metals may be disturbed through water, soil and the atmosphere to the most remote places in the world, posing risk to human and wild life health.^{1,2} Among the heavy metals that exist in the environment, copper is very critical because copper is known as an important element in industry and biological systems. It is an essential nutrient to high plants and animals and is a co-factor in various enzymes. This element can

* Corresponding author. E-mail: mahmood_payehghadr@yahoo.com
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be poisonous even at very low concentration. Copper concentrations in potable water are usually very low ($\leq 20 \mu\text{g L}^{-1}$). For humans, the main sources of copper are water and food. Although copper is an essential element for human health, it is toxic at high concentrations and hence, an accurate and rapid method for the determination of copper in these samples must be accessible.^{3,4} Flame atomic absorption spectrometry (FAAS),⁵ graphite atomic absorption spectrometry⁶ as well as spectrophotometric methods,⁷ are known as the most common methods for the determination of copper in various samples. However, the heavy metals concentration levels in environmental samples are fairly low and preconcentration procedures are often needed.⁸ Among the various methods, such as coprecipitation,⁹ ion exchange,¹⁰ liquid–liquid extraction (LLE),¹¹ reverse osmosis adsorption¹² and solid phase extraction (SPE),^{13,14} solid phase extraction has attracted a considerable amount of interest for the preconcentration of toxic metal ions,^{15–17} due to the higher efficiency and low use of pure organic solvents. This method is simple, efficient, selective, cost-effective and easy to automate without the need for emulsion, and it is safe concerning the reagents employed.¹⁸

According to the nature of this method, the key point is choosing a suitable sorbent, since this factor could affect the selectivity and sensitivity of the method.¹⁹ With the advent of SPE, various sorbents have been proposed, such as TiO_2 ,²⁰ activated carbon,²¹ Fe_3O_4 nanoparticles,²² micro crystalline naphthalene,²³ carbon nanotubes,²⁴ Amberlite XAD-7 resin,²⁵ activated alumina²⁶ and nanoporous silica.²⁷ Among these sorbents, nanoporous silicas, such as MCM-41, MCM-48 and SBA-15, have attracted great attention because of their adjustable morphology and porosity, potentiality of functionalization, high chemical stability in a great variety of media and temperatures, very high specific surface areas and the simplicity of their syntheses *via* the sol–gel method, which allows such materials to be obtained through mild reaction conditions.^{28,29} In spite of these advantages, their applications without surface modifications and functionalization are limited.³⁰ Furthermore, the properties of these materials depend on the functional group that is anchored to the surface of nanoporous silica. Functional groups, such as thiol,³¹ imidazole³² and amino,³³ were incorporated into the inorganic SBA-15 network and used for selective adsorption of different heavy metal ions.

In this research, newly synthesized SBA-15 nanoporous silica modified by thiocarbohydrazone ligand (SBA-15–TCH), Fig. 1, was used for the separation

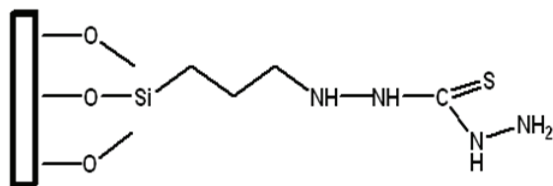


Fig. 1. Chemical structure of SBA-15–TCH.

and preconcentration of ultra trace copper(II) from different real samples, and determination by the FAAS method. Different parameters, such as pH effect, weight of sorbent, type and concentration of eluent solvents, stirring time, breakthrough volume and co-existing ions, on the separation and determination of copper(II) were investigated.

EXPERIMENTAL

Reagents and materials

All reagents were obtained from Aldrich and used as received. Commercial grade solvents were dried and deoxygenated by standard procedures (toluene over Na-benzophenone ketyl), distilled under nitrogen. All the solutions were prepared with reagent grade salts and deionized water. A stock solution (1 mg mL⁻¹) of copper(II) was prepared by dissolving an appropriate amount of the corresponding nitrate salt in double distilled water. The following buffer solutions were used for different pH values; pH 3–5, CH₃COOH/CH₃COONa; pH 6–8, Na₂HPO₄/NaH₂PO₄; pH 9, NaOH/H₃BO₃ and pH 10, NH₃/NH₄Cl.³⁴ Colloidal silica with particle size below 0.5 μm and surface area of 200 m² g⁻¹ was purchased from Merck and used as received.

Apparatus

The determination of copper(II) was performed on a PGI 990 (United Kingdom) atomic absorption spectrometer with a hollow cathode lamp and equipped with a deuterium background corrector, in an air–acetylene flame according to the user's manual, provided by the manufacturer. The determination of all other ions was realized with the same atomic absorption spectrometer under the recommended conditions for each metal ion. The pH was measured at 25±1 °C with a digital Metrohm 827 ion analyzer (Switzerland) equipped with a combined glass-calomel electrode. The IR spectra were recorded on a JASCO 4200 (Japan) FTIR spectrophotometer. Low angle X-ray diffraction patterns were obtained on a Siemens D-5000 diffractometer (Germany) with CuK_α radiation. The morphology of the silica could be obtained through scanning electron microscopy (SEM) on a Tescan VegaII (Czech Republic). The energy dispersive X-ray spectroscopy (EDX) was realized on an Oxford instrument INCA (United Kingdom).

Preparation SBA-15–TCH

SBA-15 was prepared according to a previous report,³⁵ and 3-chloro-propyltriethoxysilane was used to modify nanoporous silica surface, similar to the general procedure of the modification of nanoporous silica by amines.³⁶ In a typical reaction, 1.0 g of SBA-15 was suspended in 50 mL dry toluene and the mixture was stirred for 1 h. Then 3-chloro-propyltriethoxysilane 2.0 g was added to the mixture that was refluxed for 24 h under a nitrogen atmosphere. The resultant solid was suspended in 100 mL dry toluene and an excess amount of thiocarbonylhydrazide, 4.0 g, was added. After 48 h reflux, the yellow solid was removed from solvent by filtration, washed with toluene and acetone and then dried at room temperature.

Real sample pretreatment

Water samples were collected from the Karaj River and the drinking water of Andisheh City. Mushroom and canned tuna samples were purchased from a supermarket in Karaj. First, these samples were cleaned with double distilled water and then dried at 85 °C. Then 1.0 g of mushroom and canned tuna samples were transferred into separate crucibles. These samples were ashed by the dry ashing method in an electric furnace at 700 °C for 5 h. The ashes of the

samples were transferred into separate PTFE vessels. Afterwards, HCl (10 mL, 38 %) was added and the vessels were heated on a hot plate at 80 °C for 36 h, until a clear transparent solution was obtained. The water samples were then stored in a refrigerator in the dark before analysis.

Dispersive solid phase extraction procedure

The pH of 10 mL of standard solution containing 2 mg L⁻¹ of copper(II) was adjusted to 5.0 and 2 mg of modified SBA-15 was added to it. Then the mixture was stirred for 20 min to remove copper(II) from the solution. Finally, filtration was performed and copper(II) was eluted from the sorbent surface with 5 mL of HCl (0.4 M). Afterwards, the analyte in the eluent was determined by FAAS.

RESULTS AND DISCUSSION

Extraction and preconcentration of copper(II) on SBA-15-TCH is highly dependent on different parameters, such as pH of the sample, type and concentration of the eluent, weight of sorbent, stirring time, sample volume and concentration of co-existing ions. In this context, the procedure was optimized for the various analytical parameters.

Characterization

The FT-IR spectrum of SBA-15-TCH (KBr pellets) is presented in Fig. 2. The Si-O-Si and Si-O-H stretching vibration bands of nanoporous silica appeared at 1093.44, 809.23 and 3436.53 cm⁻¹, respectively. The band at around 1498.42 cm⁻¹ is related to stretching of the C=S bond, at 1643.05 cm⁻¹ to NH₂ in plane bend and at 3192.58 and 3267.79 cm⁻¹ related to stretching of the N-H bonds.

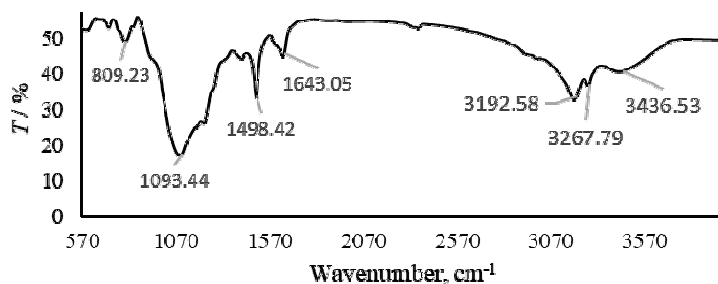


Fig. 2. FTIR spectrum of SBA-15-TCH.

The low-angle X-ray diffraction pattern of SBA-15 sorbent modified with thiocarbohydrazide ligand is shown in Fig. 3. This analysis showed that the reflections in Fig. 3 are consistent with nanoporous SBA-15 with a hexagonal lattice, as previous reported.⁸

The elemental composition of the surface of SBA-15-TCH was determined by SEM and EDX. The results of the surface analysis of SBA-15-TCH, presented in Table I, demonstrated that the surface modification was successful. The morphology of SBA-15-TCH was analyzed by SEM, and the SEM images are

presented in Fig. 4. SEM images show that the particles of SBA-15–TCH have a porous surface morphology with a particle size of 31.54 nm.

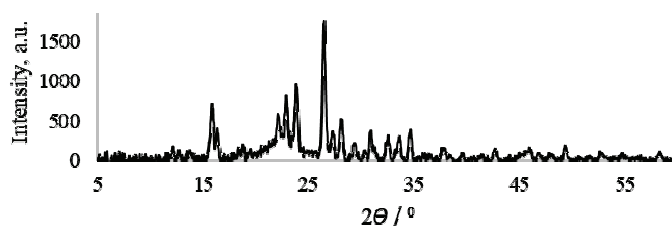


Fig. 3. XRD pattern of SBA-15–TCH.

TABLE I. Elemental analysis of SBA-15–TCH

Element	Content, wt. %	Content, at. %
C	33.92	44.54
N	23.91	26.92
O	15.02	14.81
Si	5.49	3.08
S	21.67	10.66

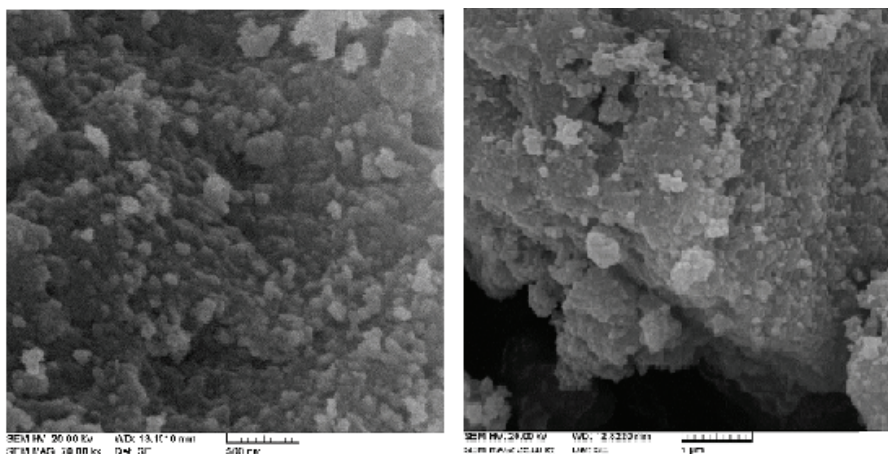


Fig. 4. SEM images of SBA-15–TCH.

Metal ion adsorption tests

Ions competitive adsorption studies were performed by treating 10 mL of a mixed metals solution containing 20, 20, 10, 40, 30 and 10 μg of Cu(II), Ni(II), Zn(II), Pb(II), Fe(III) and Cd(II) ions, respectively. After adjusting the pH (to 5.0), 2 mg of the sorbent was added and the mixture stirred for 15 min at room temperature. Finally, filtration was performed and the ions were eluted from the sorbent surface with HCl (1 M). Afterwards, the analytes in the eluent were determined by FAAS. As shown in Table II, SBA-15–TCH has the best selectivity

for Cu(II), and the percent extracted Ni(II) and Fe(III) ions were 40.3 and 73.4, respectively. On changing the pH of the solution and the amount of sorbent, the extraction efficiency for these ions did not change. Therefore, the effective parameters on the amount of copper(II) extraction were investigated.

TABLE II. Sorption of metal ions by SBA-15-TCH

Ion	Cu (II)	Ni (II)	Zn (II)	Pb (II)	Fe (III)	Cd (II)
Recovery \pm SD, %	90.1 \pm 1.5	40.3 \pm 1.3	17.1 \pm 1.3	13.9 \pm 0.9	73.4 \pm 1.1	26.1 \pm 0.7

Effect of pH

Among the tested variables, pH was found to be the most critical parameter for the sorption of metal ions onto nanoporous silica. To evaluate the effect of pH on the extraction efficiency, the pH of the 10 mL sample solutions containing 2 mg L⁻¹ of copper(II) was adjusted to fit in the range of 3–10 and added 2 mg SBA-15-TCH to the solution. Then the mixture was stirred for 15 min to remove copper(II) from the solution. Finally, the retained copper(II) was then eluted with 5 mL of HCl (1 M), and determined by FAAS. The recoveries of Cu(II) extraction as a function of pH are shown in Fig. 5, which showed that quantitative recovery was obtained at pH 5.0.

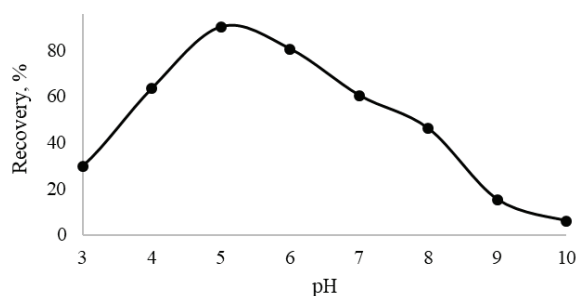


Fig. 5. The effect of pH on the recovery of Cu(II) (copper ion concentration 2 mg L⁻¹, amount of sorbent 2 mg, stirring time 15 min and 1.0 M HCl as the eluent solvent).

The percentage of copper(II) sorption increased significantly at pH 5.0 and then decreased extremely. For pH values higher than 8.0, modified nanoporous silica may be hydrolyzed in alkali solutions due to breakage of the Si–O–Si bonds by OH⁻ attack and at pH values lower than 4.0, the ligand is surrounded by H⁺ that prevents copper(II) ions from reaching the ligand to form complexes for its removal from solution. Therefore, the pH value of the sample solutions was adjusted to 5.0 in the subsequent experiments.

Effect of sorbent amount

To evaluate the effect of the amount of sorbent, 10 mL sample solutions containing 2 mg L⁻¹ of copper(II) were adjusted to pH 5.0 and different amounts

of modified sorbent (0.5, 1, 2, 4, 6, 8, and 10 mg) were added to the solutions. Then the mixture was stirred for 15 min to remove copper(II) from the solution, retained copper(II) was eluted with 5 mL of HCl (1 M) and copper(II) content in the eluent was determined by FAAS. The recoveries of Cu(II) as a function of sorbent amount are shown in Fig. 6. As could be seen, by raising the sorbent amount from 0.5 to 2 mg, the percentage of copper(II) removal increased significantly and percentage of sorbent was almost constant. Hence, 2 mg of SBA-15-TCH was used in the experiments thereafter.

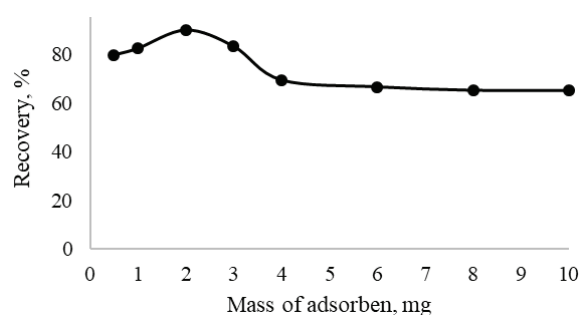


Fig. 6. The effect of sorbent mass on the recovery of Cu(II) (copper ion concentration 2 mg L^{-1} , pH 5.0, stirring time 15 min and 1.0 M HCl as eluent solvent).

Effect of the stirring time

To evaluate the effect of the stirring time, 10 mL sample solutions containing 2 mg L^{-1} of copper(II) was adjusted to pH 5.0 and about 2 mg modified SBA-15-TCH was added to the solution. Then the mixture was stirred for different times (1, 5, 10, 15, 20 and 25 min) to remove copper(II) from the solution. The retained copper(II) was eluted with 5 mL of HCl (1 M) and copper(II) content in the eluent was determined by FAAS. The obtained data as a function of time and are shown in Fig. 7. According to the results, copper(II) removal up to 20 min increased and then was nearly constant. Therefore, a 20 min stirring time was used thereafter.

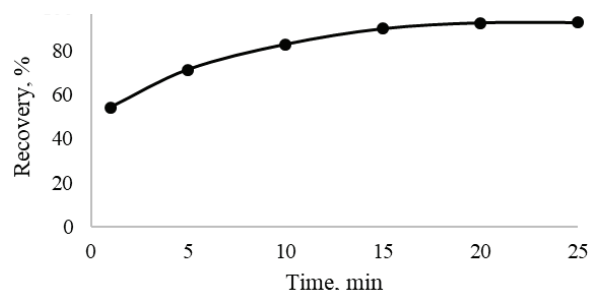


Fig. 7. Effect of stirring time on percent recovery of copper(II). (Copper ion concentration 2 mg L^{-1} , pH 5.0, amount of sorbent 2 mg and 1.0 M HCl as eluent solvent).

Effect of type and concentration of eluent

For desorption copper(II) from SBA-15-TCH, a series of selected eluent solutions, *i.e.*, HNO₃, EDTA, HClO₄, HCl and CH₃COOH, at different concentrations were used. As shown in Table III, it was eventually found that HCl (0.4 M) provided for an effective elution of copper(II) from SBA-15-TCH. Therefore, a volume of 5 mL of HCl (0.4 M) for desorption of copper(II) was used in the remaining experiments.

TABLE III. Effect of type and concentration of eluent

Eluent	Concentration, M	Recovery %
HNO ₃	0.1	48.7
EDTA	0.1	49.2
HClO ₄	0.1	57.2
CH ₃ COOH	0.1	5.1
HCl	0.1	79.1
HCl	0.2	87.6
HCl	0.4	99.3
HCl	0.6	99.3
HCl	0.8	99.3
HCl	1.0	99.3

Effect of sample volume

The preconcentration (or enrichment) factor can be calculated as the ratio of the breakthrough volume and the eluent volume. A higher preconcentration factor (PCF) could be obtained by increasing the ratio of sample to eluent volume by either decreasing the eluent volume and or increasing the sample volume. Therefore, the maximum volume of sample solution was investigated by increasing the volume of metal ion solution with a constant amount of ions. The break through volume of sample solution was tested by dissolving 20 µg copper(II) in 100, 250, 500, 1000, 1500 and 2000 mL water and the recommended procedure was followed under the optimal experimental conditions. The results, Fig. 8, demonstrated that in 1500 mL the extraction copper(II) by SBA-15-TCH was found to be quantitative. As the copper(II) in 1500 mL of the sample solution were concentrated into 5 mL, an enrichment factor of 300 was determined by this method.

Sorption capacity

The capacity of sorbent shows the weight of the sorbent which is required to remove a specific amount of analyte from the solution. To evaluate this factor, 100 mL of a solution containing 500 µg copper(II) by 2 mg of sorbent underwent the extraction procedure and the maximum capacity was calculated. The capacity of SBA-15-TCH, obtained for five replicate analyses, was found to be 123.00±0.04 mg g⁻¹ for copper(II).

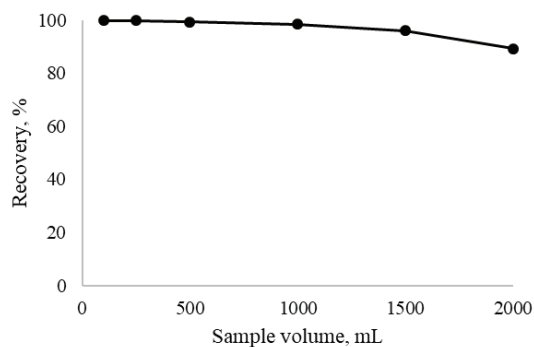


Fig 8. Effect of sample volume on percent recovery of copper(II) (20 μg copper ion per solution, pH 5.0, 2 mg of sorbent, stirring time 20 min and 0.4 M HCl as eluent solvent).

Effect of foreign ions

To investigate the effect of various ions found in natural samples, various ions were added to 10 mL of a solution containing 2 mg L⁻¹ copper(II). The degrees of tolerance for some ions are presented in Table IV. From the tolerance data, it could be seen that the foreign ions have no significant effects on the preconcentration of copper(II) at pH 5.0.

TABLE IV. Effect of diverse ions on the recovery of Cu(II)

Foreign ion	Concentration tolerance ratio foreign ion/Cu(II)	Recovery \pm SD, %
Na ⁺	8000	95.9 \pm 1.3
K ⁺	8000	96.3 \pm 1.4
Ca ²⁺	8000	97.5 \pm 1.1
Mg ²⁺	8000	95.4 \pm 1.1
Zn ²⁺	500	97.1 \pm 0.9
Co ²⁺	500	97.2 \pm 1.1
Cd ²⁺	400	95.8 \pm 0.9
Fe ²⁺	400	96.1 \pm 0.8
Au ³⁺	400	96.2 \pm 0.8
Ag ⁺	150	94.6 \pm 0.9
Ni ²⁺	150	95.6 \pm 0.9
Hg ⁺	150	94.9 \pm 1.2
Mn ²⁺	150	96.1 \pm 0.9
Cr ³⁺	150	95.8 \pm 0.8
NH ₄ ⁺	2000	94.3 \pm 1.2
CO ₃ ²⁻	4000	96.3 \pm 1.4
NO ₃ ⁻	8000	95.4 \pm 1.1
Cl ⁻	8000	96.3 \pm 1.4
ClO ₄ ⁻	8000	95.9 \pm 1.3
SO ₄ ²⁻	1000	94.3 \pm 1.2
Zn ²⁺ , Co ²⁺ , Ag ⁺	40, 20, 20	96.7 \pm 1.1
Zn ²⁺ , Co ²⁺ , Au ³⁺	40, 20, 20	97.8 \pm 0.9
Na ⁺ , Mg ²⁺ , Ca ²⁺	1000, 1000, 1000	96.9 \pm 0.8

Analytical performance

The analytical performance of dispersive-SPE-FAAS for the determination of copper(II) was evaluated under the optimized conditions (pH 5.0, amount sorbent 2 mg, stirring time 20 min and 0.4 M HCl as eluent solvent). A calibration curve was constructed for the determination of copper(II), according to the general procedure, and the calibration equation was of $Y = 0.066x + 0.0097$, with a correlation of determination (R^2) of 0.9993 and a linear range of 0.8–2500.0 $\mu\text{g L}^{-1}$ for copper(II). The quantitative parameters, including limits of detection (LOD), limits of quantification (LOQ) and relative standard deviations for this method were calculated under optimum conditions. The limits of detection ($3S_b/m$, where S_b is the standard deviation of 5 replicate blank signals and m is the slope of the calibration curve after preconcentration, for a sample volume of 1500 mL) and quantification ($10 S_b/m$) for copper(II) extraction were found to be 0.253 and 0.844 $\mu\text{g L}^{-1}$, respectively. Standard deviations were 3.3, 2.3 and 2.1 % for 1, 2 and 4 $\mu\text{g mL}^{-1}$, respectively ($n = 5$). Therefore, the relative standard deviation of this method was obtained 3.3 %.

Comparison with other methods and adsorbents

A comparison of the analytical characteristic (including LOD, RSD, PCF and sorption capacity) obtained in this research with other reported methods and sorbents for the determination of copper(II) is presented in Table V. The obtained results indicated that in the developed method, the preconcentration factor and sorption capacity were relatively high, the detection limit is low, and precision is much better than that for other methods.

TABLE V. Comparison of the various methods and sorbents for determination of copper(II)

Sorbent	Analysis method	LOD $\mu\text{g L}^{-1}$	RSD %	PCF	Sorption capacity mg g^{-1}	Ref.
SBA-15 functionalized by diphenylcarbazine	FAAS	0.45	<4	291	105	8
SBA-15 functionalized by aminobenzenesulfonamide	FAAS	0.4	2.34	200	155	37
Activated carbon functionalized by diethylenetriamine	ICP-OES	0.19	2.4	125	26.71	21
MWCNT–Bi ₂ S ₃ nanomaterial	FAAS	13.1	2.2	20	–	38
Fe ₃ O ₄ @SiO ₂ functionalized by 3-[2-(2-aminoethylamino)ethylamino]propyl-trimethoxysilane	GAAS	0.25	3	233	14.7	39
This work	FAAS	0.253	3.3	300	123.00±0.04	–

Determination of copper(II) in real samples

Since natural samples have complex matrices, non-specific background absorption could be caused by interfering species of the sample matrix. To reduce

this undesirable effect, SBA-15-TCH was applied as a selective sorbent for copper(II) extraction in pH 5. Table VI shows the copper(II) recovery in Karaj River water, drinking water of Andisheh City, mushroom and canned tuna.

TABLE VI. Analysis of copper(II) in different real samples

Sample	$c_{\text{added}} / \mu\text{g mL}^{-1}$	$c_{\text{found}}^{\text{a}} / \mu\text{g mL}^{-1}$	Recovery, %
Karaj River water	0	0.061±1.9	–
	1	1.085±2.7	102.3
	2	1.988±1.8	96.5
Andisheh water	0	0.105±1.3	–
	1	1.142±2.6	103.3
	2	2.004±2.2	95.2
Mushroom	0	0.606±1.9	–
	1	1.540±2.9	95.7
	2	2.493±2.3	95.9
Canned tuna	0	0.518±1.3	–
	1	1.461±2.9	96.2
	2	2.379±2.2	94.6

^a±Deviation in % ($n = 3$)

CONCLUSIONS

Simple, fast, reproducible and selective solid phase extraction procedures, based on modified nanoporous silica (SBA-15-TCH) for the extraction of copper(II) and its determination by flame atomic absorption spectrometry have been developed. In comparison with other solid phase methods, this technique has the advantages of high capacity factor ($123.00 \pm 0.04 \text{ mg g}^{-1}$), high enrichment factor (300) and low limit of detection ($0.253 \mu\text{g L}^{-1}$). Due to the relatively high pre-concentration factor, trace metal ion at the $\mu\text{g L}^{-1}$ level in high volume samples (1500 mL) could be determined and separated by the functionalized nanoporous silica.

ИЗВОД

КОНЦЕНТРОВАЊЕ УЛТРА-ТРАГОВА Cu(II) У УЗОРЦИМА ВОДЕ ПОМОЋУ SBA-15 СОРБЕНТА МОДИФИКОВАНОГ ТИОКАРБОХИДРАЗИДНИМ ЛИГАНДОМ, ПРЕ ОДРЕЂИВАЊА ПЛАМЕНОМ АТОМСКОМ АПСОРПЦИОНОМ СПЕКТРОМЕТРИЈОМ

MAHMOOD PAYENGHADR, HAMIDREZA HAGHGOO QEZELJE, FARZANEH NOURIFARD, ABDOLMOHAMMAD ATTARAN и MEHDI KALHOR

Department of Chemistry, Payame Noor University, 19395-4697 Tehran, Iran

Представљен је једноставан, поуздан и брз метод за екстракцију ултра-трагова бакра(II) помоћу нанопорозног сорбента SBA-15, модификованог тиокарбохидразидним лигандом пре његовог одређивања пламеном атомском апсорпционом спектрометријом. Оптимални параметри методе су: рН воденог раствора 5, количина сорбента 2 mg, време мешања 20 min, 0,4 M HCl раствор као елуентни растварач. Ова метода има граничну запремину већу од 1500 mL са факторима концентрације већим од 300, линеарни опсег 0.8–2500.0 $\mu\text{g L}^{-1}$, границу детекције 0.253 $\mu\text{g L}^{-1}$ и границу квантификације

0.844 $\mu\text{g L}^{-1}$ за бакар(II). Утврђено је да капацитет SBA-15 модификованог са 2 mg наведеног лиганда износи $123,00 \pm 0,04 \text{ mg g}^{-1}$. Стандардна девијација је 3,3, 2,3 и 2,1 % за 1, 2 и 4 μg бакра mL^{-1} , редом ($n = 5$). Ова метода се може успешно се примењивати за одређивање бакра(II) у различитим стварним узорцима, посебно у храни.

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