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## Use of Modified Nano Sorbent Materials for Extraction and Determination of Trace Amounts of Copper Ions in Food and Natural Water Samples

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### ABSTRACT

In this research, the first study on the high performance of Nanoparticled  $\gamma$ -alumina coated with sodium dodecyl sulfate and 4-2-pyridylazo-resorcinol (SDS-PAR) as a new sorbent solid phase extraction has been reported. Sorbent with adjusted nanometer-sized alumina was used to preconcentrate and separate Cu in plant belonging to the legume family and natural water samples. A microsample introduction system was employed for the nebulization micro-volume of diluted solution by FAAS (flame atomic absorption spectrometry) method. Various influencing parameters on the separation and preconcentration of trace metal, such as pH, amount of sorbent, and volume of the chelating agent, were studied. The calibration graph was linear in the range of 1-800  $\mu\text{g L}^{-1}$  with detection limit of 0.21  $\mu\text{g L}^{-1}$ . RSD for ten reproduce measurements was 1.8%. The proposed method has been applied to the decision of Cu ions at trace levels in substantial samples such as cucumber, eggplant, mint, tomato, potato, parsley, spinach, apple, mangosteen, kiwi, banana, The apple core, macaroni, pea, wheat flour, red beans, lentil, barley, tap water, river water, sea water. The proposed analytical method was successfully applied to the determination of Cu in mentioned samples.

**Key words:** Modified nano sorbent, preconcentration copper, food and natural water samples

### INTRODUCTION

The determination of trace metal elements, mainly intermediate metals has received increasing attention in pollution studies. Copper is an essential trace element at lower concentrations in biological systems. In view of plenty of it in universe, investigation of copper in various samples has been studied, so developing sensitive and selective methods to determine copper are required. In general, a daily copper intake of 1.5-2 mg is essential and copper at nearly 40  $\text{ng mL}^{-1}$  is required for biological processes. But, in higher concentration, it is toxic and severe oral intoxication will affect mainly the blood and kidneys. In these levels, copper can bind to the cell membrane and hinder the transport process through the cell wall (Ansari *et al.*, 2004; Ghiasvand *et al.*, 2004), so they affect on the taste of waters and corrosion. The copper content at trace levels in water and food must be controlled thus the European Commissioner, United States and Canada have fixed amount of Cu in drinking water, respectively 2  $\text{g mL}^{-1}$ , 1.3 and 1.0  $\mu\text{g mL}^{-1}$  (Rumori and Cerda, 2003; Szigeti *et al.*, 2005). FAAS selectivity is good and it has high sensitivity, speed, satisfactory reproducibility, wide dynamic concentration range and low cost (Soylak, 2004; Awode *et al.*, 2008;

Pantuzzo *et al.*, 2009; Khaniki *et al.*, 2007; Ezer, 2009). Anyway, determination of metals at sub-mg L<sup>-1</sup> level by FAAS is not directly possible (Soylak *et al.*, 2005; Calero *et al.*, 2009; Rofouei *et al.*, 2009; Iwegbue, 2012; Ojeda and Rojas, 2009). Also another problem in these determinations is interference of the matrix constituents of the analyzed samples (Soylak and Elci, 2000; Khosravan and Saljooghi, 2009; Tharanitharan and Srinivasan, 2009; Bakircioglu *et al.*, 2009). Various separation-preconcentration methods encompassing solvent extraction, cloud point extraction, ion-exchange, electroanalytical techniques, solid phase extraction, and chelating sorbents, etc. (Soylak and Tuzen, 2006; Burham *et al.*, 2009; Quiros, 2009; Soy lak and Dogan, 1996; Rezaei *et al.*, 2009; Shamspur and Mostafavi, 2009; Khammas, 2009; Rappoport and Liebman, 2009) have been used to overcome these problems. Among these sorbents, Nanoscale materials have gained great attention because they have special properties, because nanometer-sized alumina has high surface area, high sorption capacity and high chemical activity and it has ability for the separation and preconcentration of trace elements in biological environmental samples. Recently, the using of the surfactant-coated mineral oxide for SPE has demonstrated that for these new sorbent materials to be a favorable tool for the extraction/preconcentration of organic compounds in a wide polarity range. In this study, FAAS has been applied for the preconcentration and determination of Cu in real samples. Nanometer-sized alumina coated with SDS-PAR has been used as a new and effective sorbent. High efficiency has been shown.

## **MATERIALS AND METHODS**

**Materials:** Usually in chemistry, mainly analytical chemistry, analytical-reagent grade is used. The model compound studied were Cu(II) nitrate(Merck), nano- $\gamma$ -alumina (Sigma-Aldrich), nitric acid (Merck), SDS (Merck) and 4-(2-Pyridylazo) resorcinol monosodium salt monohydrate (PAR) (Merck). They were used without further purification. All solutions were prepared in distilled water.

**Instrumentation:** Atomic absorption analyses were performed on an M series model (Model: M5) equipped with a 50 mm burner head, deuterium background correction and using an air-acetylene flame and resonance line of 324.8 nm for copper. The buffer solutions have been applied to adjust the pH of the solutions. An expanded scale pH meter Metrohm (model 744) equipped with glass electrode for measurements. A centrifuge (Kokusen Ensinkico, model H-11N) is used to accelerate the phase separation process.

**Procedure of modified nano- $\gamma$ -alumina:** Ten milliliter solution with pH of 2 contains 0.5 g of activated nano- $\gamma$ -alumina, 0.1 mg SDS and 0.2 mL PAR. Then it was shaken for 10 min (Shemirani and Akhavi, 2001).

**General procedure:** The sample solution of Cu (II) in the range of 1-800  $\mu\text{g L}^{-1}$  was added to modified nano- $\gamma$ -alumina and the adjusted pH value was 4 for using acetic acid buffer solution. The centrifuge was used in the process of solid phase extraction at 3800 rpm for 10 min. Then, for eluting of the metal ions retained on the sorbent, were used 0.2 mL of HNO<sub>3</sub> 1 mol L<sup>-1</sup>. The determination of analytes was used FAAS in the extraction.

**Preparation of real samples:** Cucumber (2.0 g), eggplant (2.0 g), mint (2.0 g), tomato (2.0 g), potato (2.0 g), parsley (2.0 g), spinach (2.0 g), apple (3.0 g), mangosteen (2.0 g), kiwi (2.0 g), banana (2.0 g), pea (2.0 g), The apple core (2.0 g), macaroni (2.0 g) wheat flour (2.0 g), red beans

(2.0 g), lentil (2.0 g) and barley (2.0 g) samples were digested with 10 mL of HNO<sub>3</sub> (65%) and 3 mL of H<sub>2</sub>O<sub>2</sub> (30%) . Then after this action, the volume of the digested samples was made up to 25 mL with distilled water.

## RESULTS AND DISCUSSION

Investigation of all the parameters is necessary because they can influence the extraction performance. In this method, these parameters are the kind and amount of eluting solution and anti-sticking pageant, pH, Ligand amount, centrifuge conditions that were investigated and optimized in order to achieve a high recovery and enrichment factor. In all optimization steps concentration of copper was 0.5 mg L<sup>-1</sup>.

**Effect of pH:** The pH of the solutions is very important in the SPE procedure. The sorption of SDS on nano-sized alumina is highly dependent on the pH of solution. Positively charged nano- $\gamma$ -alumina surfaces effectively sorbed negatively charged SDS at lower pH values. Therefore, maintenance of organic compounds on SDS-coated nano- $\gamma$ -alumina occurs. The SDS is absorbed on the positively charged nano- $\gamma$ -alumina surfaces via formation of self-aggregates (Ghaedi *et al.*, 2009; Li *et al.*, 2008) over a wide pH range (1-6), whereas very little amount of SDS could be retained on inert surface of nano- $\gamma$ -alumina. Maximum sorption of SDS on nano- $\gamma$ -alumina was achieved at pH 1-2.9 by shaking the solution containing SDS and nano- $\gamma$ -alumina for 10 min. When solution was acidified, SDS would form hemimicelles on nano- $\gamma$ -alumina by strong sorption. The micelles could trap PAR molecules homogeneously (Fig. 1). (The low toxicological properties, commercial availability and cost are very important factors in SDS) (Shemirani and Akhavi, 2001).

The pH of the aqueous solution is an important parameter for retaining of metal ions on a solid phase materials as metal ions-chelates. The sorption behavior of Cu by modified nano- $\gamma$ -alumina in water samples was investigated in the pH range of 3-9. According to the results, a quantitative recovery of Cu (>95%) was found in the pH 4. So pH 4 was used in this working (Fig. 2).

**Effect of the amount of sorbent:** Regard to the experimental results (Fig. 3), copper ion was completely adsorbed on the sorbent in the 400 mg of the modified nano- $\gamma$ -alumina. Therefore, 400 mg was selected for all of the subsequent experiments.

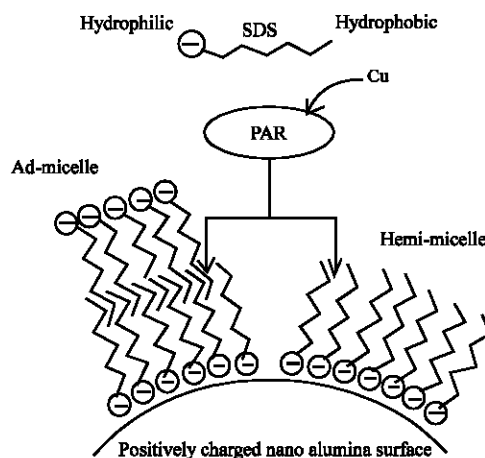


Fig. 1: A suggested binding mode of SDS-PAR to nano-alumina surface

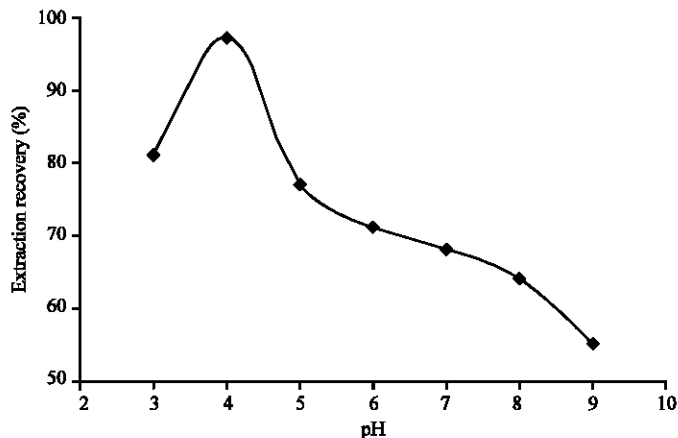


Fig. 2: Effect of pH on Cu sorption

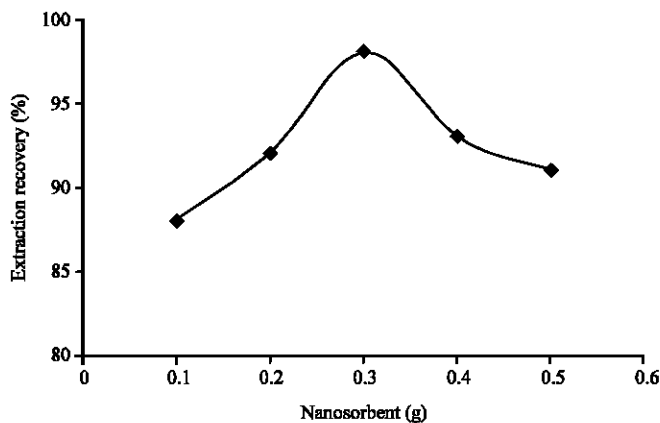


Fig. 3: Effect of the amount of modified nano- $\gamma$ -alumina on Cu sorption

**Effect of eluting solution condition:** In this experiment, a series of experiments were designed and performed to obtain a reasonable eluent to elute completely  $\text{Cu}^{2+}$  ions after their enrichment by chelation with modified nano- $\gamma$ -alumina. Various acids with various concentrations ( $0.1\text{-}1\text{ mol L}^{-1}$ ) were to obtain the optimal eluent for further experiments. The results showed that  $\text{HNO}_3$   $0.1\text{ mol L}^{-1}$  accomplish the quantitative elution of target analyte,  $\text{Cu}^{2+}$  ions chelated with from the PAR in solid phase extraction (Table 1).

**Effect of volume of ligand:** The effect of PAR volumes in the range of  $0.05\text{-}4\text{ mL}$  was evaluated on the recoveries of analytes. Figure 4 shows that the extraction recovery increases up to  $1.0\text{ mL}$  of ligand and then remains constant. So,  $1.0\text{ mL}$  of ligand  $10^{-8}\text{ M}$  was chosen as optimum.

**Effect of centrifuge conditions:** The effect of centrifugation rate on the absorbance was studied in the range of  $1000\text{-}4000\text{ rpm}$ . It was found when rpm was over 3000, solid phase completely settled, so the optimizing of rate was selected 3800 rpm. The effects of centrifugation time were investigated on the settles of solid phase in the range of  $5\text{-}15\text{ min}$  at 3800 rpm. Over 7 min, transfer of solid phase to the bottom of centrifuge tube was complete. So, the optimum centrifugation time was chosen as 10 min.

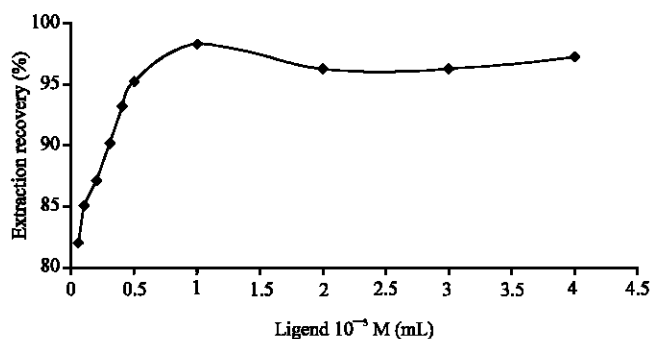


Fig. 4: Effect of volume of ligand on the sorption of Cu

Table 1: Effect of type and concentration of eluent on the adsorption of Cu

Eluent	Concentration (mol L <sup>-1</sup> )	Recovery (%)
H <sub>2</sub> SO <sub>4</sub>	0.1	59.7
	0.5	71.6
	1.0	81.8
CH <sub>3</sub> COOH	0.1	1.7
	0.5	2.8
	1.0	5.1
HNO <sub>3</sub>	0.1	84.7
	0.3	86.9
	0.5	94.3
	1.0	98.8
HCl	0.1	68.2
	0.5	81.2
	1.0	95.4

Table 2: Influences of some foreign ions on the recoveries of analytes

Ion	Added as	Interferent/Co(II) (weight ratio)	Recovery (%)
Na <sup>+</sup>	C <sub>2</sub> H <sub>3</sub> NaO <sub>2</sub> .3H <sub>2</sub> O	1000	102.5
K <sup>+</sup>	K <sub>2</sub> CO <sub>3</sub>	1000	100.6
Pb <sup>2+</sup>	Pb(NO <sub>3</sub> ) <sub>2</sub>	1000	96.2
SO <sub>4</sub> <sup>2-</sup>	CdSO <sub>4</sub> .8H <sub>2</sub> O	1000	99.4
PO <sub>4</sub> <sup>3-</sup>	Na <sub>3</sub> PO <sub>4</sub> .12H <sub>2</sub> O	1000	102.5
Mn <sup>2+</sup>	MnCl <sub>2</sub> .2H <sub>2</sub> O	500	96.9
Co <sup>2+</sup>	CoN <sub>2</sub> O <sub>6</sub> .6H <sub>2</sub> O	500	98.7
Cr <sup>3+</sup>	CrCl <sub>3</sub> .6H <sub>2</sub> O	500	103.1
Ag <sup>+</sup>	AgNO <sub>3</sub>	500	98.7
Mo <sup>2+</sup>	Mo(NO <sub>3</sub> ) <sub>2</sub>	500	96.2
Ni <sup>2+</sup>	Ni(NO <sub>3</sub> ) <sub>2</sub> .6H <sub>2</sub> O	100	97.5
Fe <sup>3+</sup>	Fe(NO <sub>3</sub> ) <sub>3</sub> .9H <sub>2</sub> O	100	95.6
Zn <sup>2+</sup>	ZnCl <sub>2</sub>	100	99.4

**Effect of other ions:** The effect of over 13 ions on the determination of Cu (II) was studied with flame atomic absorption spectrometric. Different amounts of metal ions were added to a solution containing fixed amounts Cu of ions and the present procedure was followed. The results for this study are given in Table 2. The tolerance limit was defined as the ion concentration causing a

Table 3: Analytical characteristics of proposed method

Analytical feature	Parameter
1-800	Linear range ( $\mu\text{g L}^{-1}$ )
0.21	Limit of detection ( $\mu\text{g L}^{-1}$ ) (n = 7)
1.8	Repeatability (RSD %) (n = 10)
50	Enrichment factor
0.999	Correlation coefficient ( $r^2$ )

Table 4: Determination of copper in real and spiked water samples

Sample	Cu <sup>2+</sup> spiked ( $\mu\text{g L}^{-1}$ )	Cu <sup>2+</sup> detected ( $\mu\text{g L}^{-1}$ )	Recovery(%)
Tap water <sup>a</sup>	-	114 (2.9) <sup>d</sup>	-
	500	597 (3.4)	97.2
River water <sup>b</sup>	-	51 (4.1)	-
	500	562 (3.7)	102
Sea water <sup>c</sup>	-	80 (3.6)	-
	500	551 (2.9)	95

<sup>a</sup>From drinking water system of Qaemshahr, Iran, <sup>b</sup>Telar river, Qaemshahr, Iran, <sup>c</sup>Caspian sea water, Iran, <sup>d</sup>RSD of three replicate experiments

relative error smaller than  $\pm 5\%$  related to the coprecipitation and determination of the examined elements. Most of the cations and anions examined did not show interferences at the concentration of 100 times higher than that of Cu concentration, the results are desired in view of applications to real samples including various salts at high concentration levels.

**Figures of merit:** Table 3 shows the analytical features of the optimized method. It contains limit of detection, reproducibility and enhancement factor. The limit of detection ( $\text{LOD} = 0.21 \mu\text{g L}^{-1}$ ) was calculated as  $3S_b/m$  ( $S_b$ : standard deviation of the blank signals. m: slope of calibration curve after preconcentration). A reasonable correlation coefficient ( $r^2 = 0.999$ ) was gotten and only small deviations between sequential determinations ( $\text{RSD} = 1.8\%$ ) were found. The calibration curve was investigated up to  $2000 \mu\text{g L}^{-1}$  which was linear. Enhancement factor ( $\text{EF} = 50$ ) was obtained from the slope ratio of calibration curve after and before preconcentration. The calibration equation curve after the preconcentration procedure was given in Eq. 1.

$$A = 0.3204C_{(\text{Cu})} + 0.0066 \quad (r^2 = 0.999) \quad (1)$$

**Analysis of real sample:** This method was applied to determine of Cu in water and herbal samples. In order to test the applicability and reliability of the proposed method, tap water, river water, sea water, cucumber, eggplant, mint, tomato, potato, parsley, spinach, apple, mangosteen, kiwi, banana, pea, The apple core, macaroni, wheat flour, red beans, lentil and barley samples were analyzed. For this purpose, 10 mL of each of the samples were preconcentrated with modified nano- $\gamma$ -alumina, in accordance with the proposed method. The results are shown in Table 4 and 5. In all cases the spike recoveries confirmed the reliability of the proposed method.

**Comparison other SPE studies:** The data have been compared with those of recent reported methods on preconcentration of copper (Table 6). Some parameters obtained are comparable to those presented by other methods. The present work has relatively low LOD and RSD when compared to other sorbent, activated carbon, silica gel, resine. Other parameter, PF (50) is relatively

Table 5: Determination of copper in herbal samples

Sample	Concentration of Cu ( $\times 10^{-3}$ mg g <sup>-1</sup> )	Sample	Concentration of Cu ( $\times 10^{-3}$ mg g <sup>-1</sup> )
Cucumber	0.052 ( 4.1) <sup>a</sup>	Apple	0.024 ( 3.7)
Eggplant	0.070 ( 3.9)	Mangosteen	0.055 ( 4.4)
Mint	0.034 ( 4.7)	Kiwi	0.017 ( 3.8)
Tomatoes	0.048 ( 2.8)	Banana	0.065 ( 2.9)
Potato	0.065 ( 3.5)	The apple core	0.021 ( 4.2)
Parsley	0.015 ( 2.6)	Macaroni	0.020 ( 4.5)
Spinach	0.017 ( 2.8)	Pea	0.018 ( 2.7)
Wheat flour	0.016 ( 3.4)	lentil	0.021 ( 3.6)
Red beans	0.019 ( 4.2)	Barley	0.045 ( 3.3)

<sup>a</sup>RSD of three replicate experiments

Table 6: Comparison of the proposed method with other methods reported

Method	Technique	LOD ( $\mu$ g L <sup>-1</sup> )	RSD (%)	References
Cloud point	Spectrofluorimetric	0.29	2.12	Tabrizi (2007)
Solid phase extraction	FAAS	0.23	3.7	Ferreira <i>et al.</i> (2003)
ISFME	SFIS	0.024	2.1	Zeeb <i>et al.</i> (2011)
SFODME	FAAS	0.18	2.7	Durukan <i>et al.</i> (2011)
Modified nano alumina	FAAS	0.21	1.8	This work

high enough when compared to some of the others methods. In addition, the cited methods are more complicated and use more reagents than this method, namely application of this method is simpler and takes less time.

## CONCLUSION

For determination of trace amounts of copper ions in low concentrations, the ligand loaded on the modified nano- $\gamma$ -alumina was used. These results showed that this method has high sensitivity. The proposed solid phase extraction method has important advantages such as: it is superior for having lower RSD and lower detection limits when compared to other methods (Table 6). It is simple, rapid with low cost. Therefore, this method of the determination of copper by FAAS provides a simple, easy and accurate for the preconcentration and separation of trace amounts. The method has been successfully applied to the environmental samples.

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