

# Nano-level determination of copper with atomic absorption spectrometry after pre-concentration on N,N-(4-methyl-1,2-phenylene)diquinoline-2-carboxamide–naphthalene

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## ABSTRACT

A novel, simple, sensitive and effective method has been developed for selective extraction and pre-concentration of copper on N,N-(4-methyl-1,2-phenylene)diquinoline-2-carboxamide–naphthalene. After pre-concentration, copper was eluted from sorbent with hydrochloric acid, and then flame atomic absorption spectrometry (FAAS) was used for its determination. The effect of pH, sample flow rate and the volume and concentration of eluent on the recovery of the analyte was investigated and the optimum conditions were established. A pre-concentration factor of 400, and an adsorption capacity of  $6.9 \text{ mg g}^{-1}$  of the solid-phase sorbent or  $82.8 \text{ mg g}^{-1}$  of ligand was achieved using the optimum conditions. The calibration graph was linear in the range of  $1.0\text{--}4000 \text{ ng mL}^{-1}$  with the detection limit of  $1.0 \text{ ng mL}^{-1}$ . A R.S.D. value of 2.4% was obtained by this method for  $400 \text{ ng mL}^{-1}$  of  $\text{Cu}^{2+}$  solution. This procedure has been successfully applied to separate and determine the ultra trace levels of copper in the environmental samples, free from the interference of some diverse ions.

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## 1. Introduction

Copper is an essential element that is used in a variety of industrial materials [1,2] and also it is an important bio-element present in animals, plants and microorganisms [3]. However, above a healthy limit it accumulates in the liver, causing diarrhea, vomiting, transpiration and, depending on its concentration, death from bleeding [4,5]. Its serum and urine concentrations in various conditions, such as Wilson's disease (hepatolenticular degeneration) may be useful as indicators of Cu utilization [6].

Water pollution by heavy metals is causing serious ecological problems in the world, therefore, the determination of heavy metals such as copper in the environmental samples is needful today, and requires analytical techniques exhibiting with low detection limits for this toxic element. Maximum permissible concentrations of copper in drinking water by World Health Organization (WHO) and United State Environmental Protection Agency (USEPA) are  $1.0\text{--}2.0$  and  $1.3 \text{ ng mL}^{-1}$ , respectively [7]. The permissible level of copper for industrial wastewater to be discharged to the surface water is  $3.0 \text{ ng mL}^{-1}$  [8]. Analytical chemists are searching for sample preparation procedures that are faster, easier, safer, less expensive and providing accurate and precise data with reasonable detection limits.

There are several techniques which have been used for determination of copper at low concentrations; such as inductively coupled plasma-optical emission spectrometry (ICP-OES) [9,10], microwave-induced plasma (MIP) [11], electrothermal atomic absorption spectrometry (ET-AAS) [12–17], flame atomic absorption spectrometry (FAAS) [18–23], spectrophotometry [24,25] and inductively coupled plasma-mass spectrometry (ICP-MS) [26,27]. Direct determination of metals in seawater samples or biological samples by AAS, ICP-OES or ICP-MS is not always possible due to matrix interferences and the very low concentrations of metal ions [28]. Therefore, a pre-concentration/separation step is required [29–31]. FAAS is a powerful detection technique for determining trace elements. The advantages of FAAS include well-known interferences, low operator skill required, and comparatively low cost instrumentation and operation. It is very reliable and simple to use. A lot of different analytical procedures for Cu(II) enrichment have been proposed, such as liquid–liquid extraction [32], co-precipitation [33], solid-phase extraction (SPE) [34–36], stripping voltammetry [37–41], high-performance liquid chromatography (HPLC) [42], cloud point extraction (CPE) [43,44], and flotation method [45].

Among pre-concentration methods, SPE has some advantages in view of: (i) ease regeneration of solid phase; (ii) high pre-concentration factor; (iii) reusability of the adsorbent; (iv) low consumption of reagents; (v) ease of automation; (vi) eco-friendly methods; (vii) ease usage [46]. It is noticeable that SPE not only

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separates and concentrates samples but also performs as cleaner samples.

A survey of the literature revealed that various adsorbents such as thiol cotton [47,48], silicized glass beads resin [49], silica gel [50], activated carbon [11], C<sub>60</sub>–C<sub>70</sub> fullerene [51] and microcrystalline naphthalene [52] have been investigated for pre-concentration of metal ions. In this work copper (II) is separated and pre-concentrated by adsorption on N,N-(4-methyl-1,2-phenylene)diquinoline-2-carboxamide–naphthalene ((Mebqb)–naphthalene) adsorbent, then eluted by hydrochloric acid and determined by FAAS. Some advantages of this work are simplicity, rapidity, high selectivity, being operative and cheap, ease of recovery of the solid phase, easy to usage and ability to attain a high concentration factor for pre-concentration and sensitive determination of very low levels of Cu (II) in aqueous solution.

## 2. Experimental

### 2.1. Apparatus

A PerkinElmer atomic absorption spectrometer (Waltham, Massachusetts, USA), Model 2380, furnished with a copper hollow-cathode lamp was used as detection system. The instrument was set at a wavelength of 324.8 nm and air–acetylene flame was adjusted according to the standard recommendation.

A syringe pump (model No. NE-1000, serial No. 220235 (USA)) for low flow rates, a peristaltic pump (Ismatec Model ISM 404 (Glatbrugg, Switzerland)) for high flow rates, and silicon rubber tubings (2.06 mm i.d.) were used for delivery of solutions and a Teflon tube (6.9 mm i.d.) was applied as mini-column.

pH of aqueous solutions was adjusted by means of a Metrohm (Herisau AR, Switzerland), Model 827 pH-meter with a glass electrode.

### 2.2. Reagents

A 100.0 µg mL<sup>-1</sup> standard solution of copper(II) was prepared by dissolving 0.0380 g of Cu(NO<sub>3</sub>)<sub>2</sub>·3H<sub>2</sub>O (Merck (Darmstadt, Germany)) in doubly distilled water and diluting it in a 100 mL volumetric flask. All working solutions of copper were prepared by serial dilution of the stock solution with water, and other chemical reagents were analytical reagent grade. Double distilled water was used to prepare all solutions.

Britton–Robinson buffer solutions from 2.0 to 9.0 (phosphoric acid, acetic acid, and boric acid (0.04 mol L<sup>-1</sup>) with appropriate volumes of NaOH, 0.2 mol L<sup>-1</sup>) were prepared.

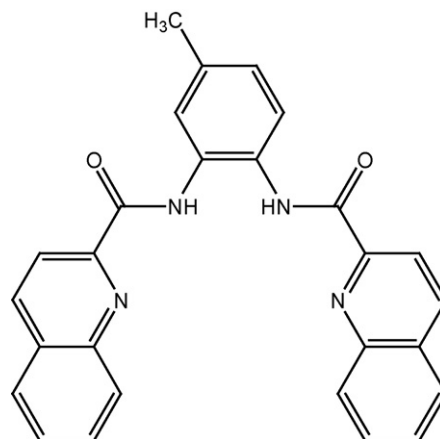
### 2.3. Preparation of adsorbent

N,N-(4-methyl-1,2-phenylene)diquinoline-2-carboxamide was synthesized in inorganic laboratory [53]. 0.3 g of synthesized ligand was dissolved in tetrahydrofuran at 40 °C, while stirring vigorously. After dissolving 12.0 g naphthalene in above solution, 500 ml double distilled water was added drop by drop to obtain adsorbent particles with suitable sizes. Stirring at this temperature was continued for 1 h. The product was filtrate and dried overnight.

### 2.4. General procedure

The mini-column was made by packing teflon tubes (6.9 mm i.d.) with N,N-(4-methyl-1,2-phenylene)diquinoline-2-carboxamide–naphthalene while a frit was placed at the end of the column to prevent material loss.

N,N-(4-methyl-1,2-phenylene)diquinoline-2-carboxamide with the following structure (Scheme 1) is a new chelating agent which



Scheme 1. The Mebqb structure.

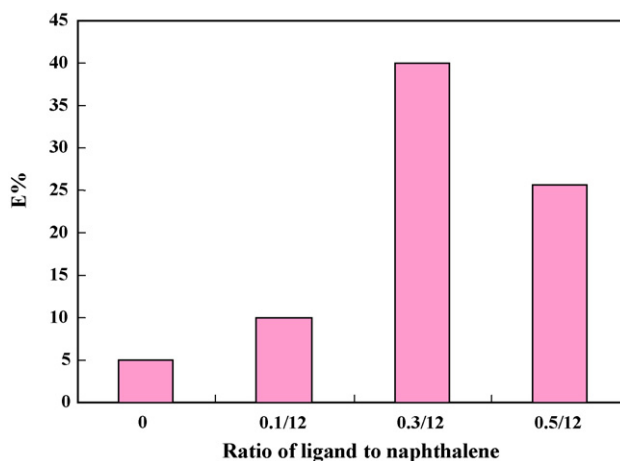


Fig. 1. Effect of ratio of ligand/naphthalene on adsorption of Cu(II).

can form a stable complex with Cu(II). By immobilizing this tetradentate-tetra amide ligand on microcrystalline naphthalene, Cu(II) can be adsorbed. Since proton has stronger affinity to interact with functional groups on the sorbent, so desorption of copper is carried out by using a strong inorganic acid. The eluent was collected and analyzed for Cu(II) by flame atomic absorption spectrometry.

To evaluate the effective parameters, the extraction percent (E%) was calculated as follows:

$$E\% = \frac{C_1 - C_2}{C_1} \times 100 \quad (1)$$

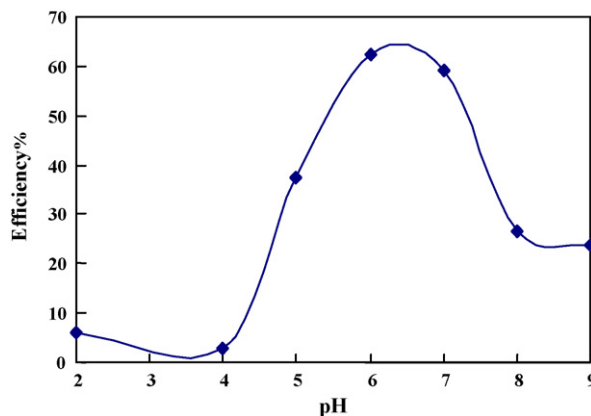


Fig. 2. Influence of pH on adsorption of Cu(II) on the Mebqb–naphthalene. Conditions: initial copper (II) value, 10 mL of 400 ng mL<sup>-1</sup>; flow rate: 0.6 mL min<sup>-1</sup>.

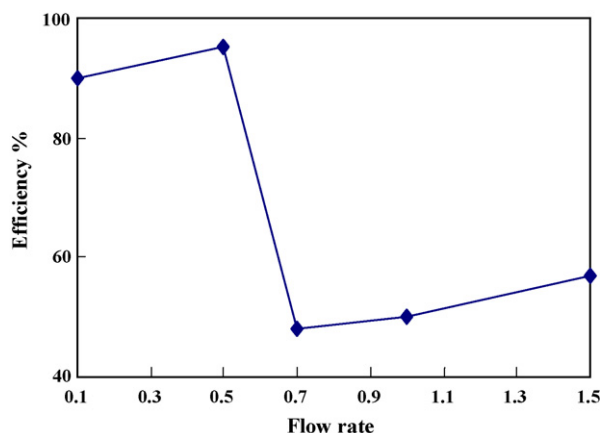


Fig. 3. Influence of flow rate on adsorption of Cu(II) on the Mebqb-naphthalene. Conditions: initial copper (II) value, 10 mL of 400 ng mL<sup>-1</sup>; pH: 6.5.

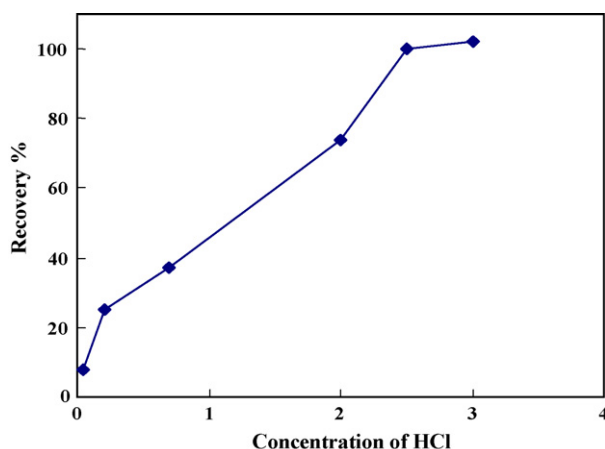


Fig. 4. Influence of concentration HCl on pre-concentration of Cu(II). Conditions: initial copper (II) value, 10 mL of 100 ng mL<sup>-1</sup>; pH: 6.5; flow rate 0.5 mL min<sup>-1</sup>.

where  $C_1$  and  $C_2$  are the concentration of copper in the initial solution and after desorption, respectively.

### 3. Results and discussion

#### 3.1. Effect of variables on the pre-concentration of copper

##### 3.1.1. The ratio of ligand to naphthalene

The ratio of ligand to naphthalene can be important in raising the efficiency of pre-concentration and separation by sorbent. So this parameter was studied by preparation of sorbents by different ligand to naphthalene ratios and passing specific amounts of copper solution through them. The results depicted in Fig. 1 revealed that the best ratio for ligand to naphthalene is 0.3 to 12.0.

##### 3.1.2. The influence of pH

The effect of pH on pre-concentration of Cu(II) was examined in range of 2.0–9.0 and the results are shown in Fig. 2. The results show that the maximum adsorption recovery was obtained in the pH of 6.0–7.0. At more acidic media, active sites of ligand will be protonated and at higher pH values, copper hydroxide will be formed on the column (precipitation will occur instead of adsorption). So pH of 6.5 was selected as optimum pH.

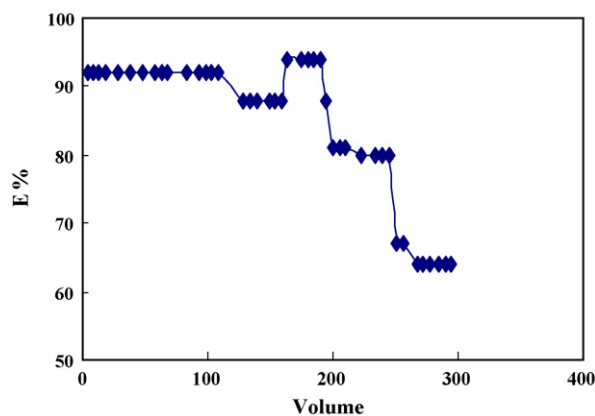


Fig. 5. Breakthrough volume study. Conditions: initial copper (II) value, 10–300 mL of 500 ng mL<sup>-1</sup>; pH: 6.5; flow rate 0.5 mL min<sup>-1</sup>.

##### 3.1.3. The effect of flow rate

By passing 10.0 mL of Cu(II) 2.0 μg mL<sup>-1</sup> solution in the pH 6.5 with different flow rates, the influence of analyte retention time was investigated. The results (Fig. 3) show that in the high flow rates, copper cannot be quantitatively adsorbed on microcrystalline naphthalene. The best flow rate was selected to be 0.5 mL min<sup>-1</sup>.

##### 3.1.4. The effect of type, concentration and volume of elution solvent

As Mebqb-Cu(II) complex is unstable in high acidic solutions, therefore an organic acid can be used to separate Cu(II) from its ligand on naphthalene. Three types of acids, including nitric acid, sulfuric acid and hydrochloric acid were tested, and observations showed that hydrochloric acid is better than else to desorb the analyte. The influence of concentration of HCl on removal of Cu(II) from sorbents was also investigated (Fig. 4) and HCl, 2.5 mol L<sup>-1</sup>, was selected as optimum elution solvent.

The volume of washing solution (0.5–3.0 mL) was investigated, too. Over 90% of adsorbed copper was desorbed from column by 0.5 mL of 2.5 mol L<sup>-1</sup> hydrochloric acid. Therefore 0.5 mL of HCl

Table 1

Effect of some matrix ions on the selectivity of method (1000 ng mL<sup>-1</sup> Cu(II)).

Metal ion	Tolerance ratio ( $W_{ion}/W_{Cu(II)}$ )
Co <sup>2+</sup>	500
Fe <sup>2+</sup> , Ag <sup>+</sup> , Ni <sup>2+</sup> , Pb <sup>2+</sup>	100
Zn <sup>2+</sup> , Cd <sup>2+</sup>	50
Fe <sup>3+</sup> , Sn <sup>2+</sup> , Hg <sup>2+</sup>	10

Table 2

Determination of Cu(II) in water samples.

Sample	Cu(II) added (ng mL <sup>-1</sup> )	Cu(II) found (ng mL <sup>-1</sup> )	Recovery (%)
Tap water	–	6.7 ± 0.9 <sup>a</sup>	–
	20	27.6 ± 1.2	103.4
	30	36.1 ± 1.3	98.4
	40	46.7 ± 1.2	100.0
Zayanderood river	–	9.9 ± 0.9	–
	20	29.4 ± 0.6	98.3
	30	41.2 ± 1.0	103.2
	40	49.1 ± 1.10	98.4
Waste	–	71.7 ± 1.5	–
	40	112.0 ± 1.5	100.3
	80	152.8 ± 1.5	100.2
	120	190.9 ± 1.3	99.6

<sup>a</sup> Standard deviation for four replicated measurements.

**Table 3**  
Comparative analytical characteristics some systems on pre-separation of copper.

Technique	Detection method	Sample	System	PF	DL (ng mL <sup>-1</sup> )	References
SPE	TS-FF-AAS	Biological samples	Amberlite XAD-4 functionalized with 3,4-dihydroxybenzoic acid	91	0.1	[54]
Precipitation	FAAS	Biological samples	2-[2-(6-Methyl benzothiazolylazo)]-4-aminophenol	40	0.5	[55]
CPE	FAAS	Tap water	4-(Phenyl diazenyl) benzene-1,3-diamine/Triton X-114	30	0.6	[56]
SPE	FAAS	Waters and vegetables	<i>Penicillium digitatum</i> immobilized on pumice stone.	50	1.3–5.8	[57]
SPE	FAAS	Vegetable and dam, lake and tap waters	<i>Saccharomyces carlsbergensis</i> immobilized on silica gel 60	50	1.14–1.66	[58]
SPE	FAAS	Water, dust and black tea	<i>Aspergillus fumigatus</i> immobilized on Diaion HP-2MG	50	0.3–0.72	[59]
SPE	FAAS	Tea, mushroom, wheat, rice, and soil	<i>Bacillus sphaericus</i> immobilized on Diaion SP-850 resin	50	0.2–0.75	[60]
SPE	FAAS	Water and waste	N,N-(4-methyl-1,2-phenylene)diquinoline-2-carboxamide immobilized on naphthalene	400	1.0	Proposed method

SPE: solid-phase extraction; CPE: cloud point extraction; TS-FF-AAS: thermo spray flame furnace atomic absorption spectrometry; FAAS: flame furnace atomic absorption spectrometry; PF: pre-concentration factor; DL: detection limit.

was chosen as optimum volume for eluent and in order to provide enough time for 0.5 mL of acid to break complex, the flow rate of 0.1 mL min<sup>-1</sup> was applied.

### 3.2. Analytical features

Under optimum conditions for the recommended procedure, the calibration graph was linear in the range of 1.0–4000 ng mL<sup>-1</sup> copper. The regression equation is  $A = 0.0258C + 0.0029$  ( $R^2 = 0.9992$ ), where  $A$  is the absorbance and  $C$  is the concentration of copper in the initial solution. The detection limit (taken as three times the standard deviation of the blank) was 1.0 ng mL<sup>-1</sup>. The repeatability of the method was evaluated by measuring the signal for three samples with the concentration of 400 ng mL<sup>-1</sup>, and the relative standard deviation was obtained to be 2.4%.

### 3.3. Breakthrough volume

Different volumes of copper solution (500 ng mL<sup>-1</sup>) from 10.0 to 300.0 mL were passed through the column and their recoveries were measured. It was found that the analyte could be recovered quantitatively when volumes up to 200 mL of the sample solution was used. At higher volumes the column will be saturated and the recovery is decreased. Results are shown in Fig. 5. A pre-concentration factor of 400 can be achieved by this SPE procedure when using 200 mL of sample and eluting the column with 0.5 mL of 2.5 M hydrochloric acid.

### 3.4. Evaluation of sorbent reproducibility

For investigating the ability of microcrystalline naphthalene to adsorb Cu(II) after sequential elutions, the pre-concentration process was repeated for many times. It was indicated that the recoveries were significantly decreased after three repeated adsorption–desorption cycles.

### 3.5. Retention capacity of the adsorbent

The retention capacity of Mebqb–naphthalene adsorbent was determined by a batch method. First, equal volumes of Cu(II) solution with different concentrations were passed through the column to determine that in which concentration this amount of sorbent will be saturated with analyte. Observations showed that in concentration up to 4000 ng mL<sup>-1</sup>, adsorption of Cu(II) decreases. Then, 0.35 g of Mebqb–naphthalene was added to 200 mL solution of 4000 ng mL<sup>-1</sup> Cu(II) in pH 6.5. After stirring vigorously for 4 h, the suspension was filtrate and the concentration of copper in the filtrate was determined with FAAS. The reten-

tion capacity (mg adsorbed copper/g adsorbent) was obtained to be 6.9 mg of copper per g of adsorbent or 82.8 mg g<sup>-1</sup> of lig-

### 3.6. Interference study

The effect of various ions on the pre-concentration and determination of 1.0 µg mL<sup>-1</sup> copper was investigated. A given species was considered to interfere if it resulted in a ±5% variation of the AAS signal and the obtained results are presented in Table 1. Since atomic absorption spectroscopy is a selective method, therefore determination of Cu(II) can be done free of the interference of diverse ions.

## 4. Application to environmental samples

In order to evaluate the applicability of the proposed method for the analysis of real samples it was applied to the determination of copper in tap, river and sewage water samples. The Zayanderood river, tap (fresh) and Galvanized water samples were subjected to the recommended procedure for the pre-concentration and determination of copper directly and after standard addition. The results are shown in Table 2 and as can be seen the proposed method has good recoveries for determination of copper in water samples which is important in evaluating their pollution.

## 5. Conclusions

Since the application of copper as an industrial element is increasing; so there is extraordinary requirement to evaluate this analyte as environmental pollutant. Solid-phase extraction with microcrystalline naphthalene is an effective, simple, and selective separation and pre-concentration technique for copper. The proposed method will be applied for the sensitive determination of trace amounts of this heavy metal.

The linear range is wider than some of the previously reported methods. High speed, selectivity and freedom from interferences are likely to make this method suitable for the determination of copper in sea water. The experimental procedure is easy to carry out, and the method has good recoveries. In Table 3, some merit of this work compared with some others work. The results show that pre-concentration factor of proposed method was better than same works so admissible detection limit.

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