



Solid Phase Extraction for Trace Amount Cu (II) by C₁₈ Modified Carbon Nano Tube and Cupferron Ligand in Waste Water Sample and Determination it by Flame Atomic Adsorption

ALI MOGHIMI^{1*}, SEYED ALI HOSSEINI ²and ALI MAZLOMI FAR²

¹Department of Chemistry, College of Science, Varamin (Pishva) Branch, Islamic Azad University, Varamin, Iran.

²Department of Chemistry, College of Science, Yadegar-e-Imam Khomeini (RAH) Shahr-e-rey Branch, Islamic Azad University, Tehran, Iran.

*Corresponding author: kamran9537@yahoo.com

<http://dx.doi.org/10.13005/ojc/310129>

(Received: December 26, 2014; Accepted: January 20, 2015)

ABSTRACT

A novel, simple method has been developed for the preconcentration of Cu(II) based on the adsorption of its Schiff's cupferron complex on a multi walled carbon nanotubes (MWCNTs) onto C₁₈ cartridge. A new technique using a solid phase extraction (SPE) cartridge with modified Schiff's Cupferron complex on a multi walled carbon nanotubes (MWCNTs) onto C₁₈ cartridge as sorbent was developed for the preconcentration of trace amounts of Cu and was determined by flame atomic absorption spectrometry (FAAS). Cupferron play a key role as chelating reagent on ultrahigh specific surface of multi walled carbon nanotubes (MWCNTs). Some of the important parameters on the preconcentration and complex formation were selected and optimized. Under the optimized conditions the limit of detection (LOD) and limit of quantification (LOQ) were 0.167, 0.562 and the proposed method has a good reproducibility 0.81% (RSD %). The enrichment factor was 200 and the percentage of recovery was in the range of 95-100%. The method was successfully applied to the recovery of Cu²⁺ in different type of water samples.

Key words: Multi walled carbon nanotubes (MWCNTs); Cupferron; SPE; Preconcentration; FAAS; copper.

INTRODUCTION

The Direct determination of trace metals especially toxic metal ions such as copper, tin, copper and metalloids arsenic, antimony and selenium from various samples requires mostly an initial and efficient pre-concentration step (Leyden

et al., 1976). This pre-concentration is required to meet the detection limits as well as to determine the lower concentration levels of the analyte of interest (Jones *et al.*, 1983). This can be performed simply in many ways including liquid and solid phase extraction techniques (Nambiar *et al.*, 1998; Caroli *et al.*, 1991). The application of solid phase

extraction technique for pre-concentration of trace metals from different samples results in several advantages such as the minimal waste generation, reduction of sample matrix effects as well as adsorption of the target species on the solid surface in a more stable chemical form (Alexandrova *et al.*, 1993).

The normal and selective solid phase extractors are those derived from the immobilization of the organic compounds on the surface of solid supports which are mainly nano polyurethane forms, filter paper (Leyden *et al.*, 1975), cellulose (Gennaro *et al.*, 1983) and ion exchange resins (Shamsipur *et al.*, 2005). Silica gel, alumina, magnesia and zirconia are the major inorganic solid matrices used to immobilize the target organic modifiers on their surfaces (Unger *et al.*, 1979) of which silica gel is the most widely used solid support due to the well documented thermal, chemical and mechanical stability properties compared to other organic and inorganic solid supports

(Boudreau *et al.*, 1989). The surface of silica gel is characterized by the presence of silanol groups, which are known as weak ion exchangers, causing low interaction, binding and extraction of the target analytes (Kvitek *et al.*, 1982). For this reason, modification of the silica gel surface with certain functional groups has successfully been employed to produce the solid phase with certain selectivity characters (Bruening *et al.*, 1991). Two approaches are known for loading the surface of solid phases with certain organic compounds and these are defined as the chemical immobilization which is based on chemical bond formation between the silica gel surface groups and those of the organic modifier, and the other approach is known as the physical adsorption in which direct adsorption of the organic modifier with the active silanol groups takes place (Unger *et al.*, 1979).

Selective solid phase extractors and pre-concentrators are mainly based on impregnation of the solid surface with certain donor atoms such as oxygen, nitrogen and sulfur containing compounds (Mahmoud 1979; Mahmoud *et al.*, 1997). The most successful selective solid phases for soft metal ions are sulfur-containing compounds, which are widely used in different analytical fields. Amongst these

sulfur-containing compounds are dithiocarbamate derivatives for selective extraction of copper(II) (Mahmoud 1999; Mahmoud 1998) and pre-concentration of various cations (Leyden *et al.*, 1976; Moghimi *et al.*, 2009; Tehrani *et al.*, 2005) and 2-mercaptobenzothiazol-modified silica gel for on-line pre-concentration and separation of silver for atomic absorption spectrometric determinations (Moghimi *et al.*, 2009). Ammonium hexa-hydroazepin-1-dithiocarboxylate (HMDC)-loaded on silica gel as solid phase pre-concentration column for atomic absorption spectrometry (AAS) and inductively coupled plasma atomic emission spectrometry (ICP-AES) was reported (Alexandrova *et al.*, 1993). Mercapto-modified silica gel phase was used in pre-concentration of some trace metals from seawater (Moghimi *et al.*, 2009). Sorption of copper(II) by some sulfur containing complexing agents loaded on various solid supports (Moghimi *et al.*, 2011) was also reported. 2-Amino-1-cyclopentene-1-dithiocarboxylic acid (ACDA) for the extraction of silver(I), copper(II) and palladium(II) (Moghimi 2009), 2-[2-triethoxysilyl-ethylthio] aniline for the selective extraction and separation of palladium from other interfering metal ions (Tehrani *et al.*, 2005) as well as thiosemicarbazide for sorption of different metal ions (Moghimi *et al.*, 2011) and thioanilide loaded on silica gel for pre-concentration of palladium(II) from water (Tehrani *et al.*, 2005) are also sulfur containing silica gel phases.

Ion adsorption onto solid chelating nano polymer materials is now considered as one of the most promising techniques for selective concentration, removal and recovery of metal ions from a wide variety of sources. Among different types of polymer adsorbent, polymer fibers have attracted great interest in recent years (Tahaei *et al.*, 2008; Moghimi, 2006). In our previous attempts, we modified SPE membrane disks with suitable compounds for selective determination of copper (Tuzen *et al.*, 2009). Meanwhile, other investigators have successfully utilized these sorbents for quantitative extraction and monitoring trace amounts of copper (Tahaei *et al.*, 2008).

Recently, CNTs have been shown to be excellent classes of sorbent materials for SPE (Moghimi 2013). Since the first application of CNTs in SPE by Cai *et al.* that he use multi-walled

carbon nanotubes (MWCNTs) (Moghimi 2013), In recent years many reports have been distributed focusing on progress of use CNTs-based SPE methods for a great variety of analytes, , inorganic ions (Moghimi *et al.*, 2009), organometallic compounds (Kaiss *et al.*, 2007).

In this study, we report the synthesis of this new sorbent and its application as a selective sorbent for separation. preconcentration of Cu^{2+} ions is done by C18 modified multi walled carbon nanotubes (MWCNTs) and Cupferron ligand and was determinate by FAAS.

EXPERIMENTAL

Apparatus

The concentration of the metal ion solutions was determined by using the Varian model spectra AA-240 (Mulgrara, Victoria, Australia). The pH-measurements of the metal ion and buffer solutions were carried out by an Orion 420. Infrared spectra of Multi walled carbon nanotubes (SWCNTs) were carried out from KBr by a Perkin-Elmer 1430 ratio recording spectrophotometer.

Materials and reagents

Multi walled carbon nanotubes (MWCNTs) and Schiff's Cupferron were prepared from Merck (Darmstadt, Germany). All solutions were prepared with doubly distilled deionized water from Merck (Darmstadt, Germany). C_{18} powder for chromatography with diameter of about 50 μm obtained from Katayama Chemicals from Supelco. It was conditioned before use by suspending in 4 M nitric acid for 20 min, and then washed two times with water.

Preparation of Multi walled carbon nanotubes (MWCNTs) cartridge

A glass column 1.5 cm in diameter and 15 cm in length was used for the preconcentration of Copper(II). About 5 g of Multi walled carbon nanotubes (MWCNTs) cartridge was mixed with 25mL of HCl 1M to form slurry and then loaded on to the column. Cotton was placed at the bottom for allowing Multi walled carbon nanotubes (MWCNTs) cartridge to settle properly. The column was packed up to a height of 3 cm.

Procedure for preconcentration

A 50mg SDS and 30 mg Cupferron of 50mL was loaded on to the column of neutral Multi walled carbon nanotubes (MWCNTs) cartridge maintaining a flow rate of 5mL min^{-1} . Then 250 ml volume of 10 μg m Cu(II) solution was loaded on to the column. The sample solution was loaded on to the column of neutral Multi walled carbon nanotubes (MWCNTs) cartridge maintaining a flow rate of 0.5mL min^{-1} . The complex was adsorbed as a narrow band on the top of the column. The adsorbed complex was eluted using 10mL of HNO_3 4M at a flow rate of 0.5mL min^{-1} and the concentration of Copper(II) was determined by FAAS.

Sampling

Tap water (Tehran, taken after 10 min operation of the tap), rain water (Tehran, 20 January, 2014), and Sea water (taken from Caspian sea, near the Mahmoud-Abad shore) samples were analyzed (Table 2). Tap water samples used for development of the method were collected in glasses containers. Before the analysis, the organic content of the water samples was oxidized in the presence of 7% H_2O_2 and then concentrated nitric acid was added. These water samples were then filtered through a $0.45\mu\text{m}$ Millipore cellulose membrane to remove suspended particulate matter and stored in a refrigerator at $4\text{ }^\circ\text{C}$ in the dark before analysis.

RESULTS AND DISCUSSION

The treatment of Multi walled carbon nanotubes (MWCNTs) (Fig.1 a,b,c,d) can lead to the Cupferron functional groups via adsorption (Fig.1 e,f,g,h,i). The formation of MWCNTs was followed by Raman Spectroscopy. Initially, in the spectrum of MWCNTs the carbonyl vibration appears at 1580 cm^{-1} , while there are fingerprints at 1100 cm^{-1} and 1300 cm^{-1} due to the presence of hydroxyl species at the carbon nanotubes. (Fig.2). Optimization of SPE procedures

Effect of pH

The metal chelate stability constant and its chemical stability considerably influence the SPE recovery. The pH plays a very important role

Table 1: Separation of Cu from binary mixtures ^a

Diverse ion	added	Amounts taken(mg)	%Recovery of Cu ²⁺ ion
	NaNO ₃	100	97.6(0.5) ^b
	KCl	100	98.1(0.3)
Ca ²⁺	Ca(NO ₃) ₂	100	99.7(0.9)
Mg ²⁺	Mg(NO ₃) ₂	100	99.2(1.3)
Fe ³⁺	Fe(NO ₃) ₃	80	98.8(1.1)
Cd ²⁺	Cd(NO ₃) ₂	80	98.9(0.7)
Cr ³⁺	Cr(NO ₃) ₃	80	99.1(1.3)
Co ²⁺	Co(NO ₃) ₂	50	97.6(0.6)
Ni ²⁺	Ni(NO ₃) ₂	50	99.5(1.1)
	NaCl	50	98.3(0.8)
	NaBr	20	97.4(0.5)
	NaF	20	97.3(0.9)
Mn ²⁺	MnCl ₂	20	98.7(1.2)
Zn ²⁺	ZnCl ₂	20	99.7(0.8)

^a Initial samples contained 10µg Cu²⁺ and different amounts of various ions in 100 mL water.

^b Values in parentheses are RSDs based on five individual replicate analysis

Table 2: Recovery of Cu(II) added to 100mL of different water samples (containing 0.1M buffer acetic acid / acetate at pH= 3.0)

Recovery (%)	Cu ²⁺ detected (ng ml ⁻¹)	Cu ²⁺ spiked (ng ml ⁻¹)	Sample
97.5	4.8 (2.0) ^b	5	Sample 1 ^a
98.4	9.7 (2.5)	10	
98.3	4.4 (3.0)	5	Sample 2 ^c
97.2	9.2 (3.0)	10	
98.5	2.5 (2.4)	0	Tap water ^d
97.5	7.5 (2.9)	5	
98.3	12.3 (2.4)	10	
—	N.D.	0	Rain water ^f
96.4	4.9 (2.3)	5	
97.6	10.1 (2.6)	10	
97.3	14.0(2.0)	0	Sea water ^g
98.9	18.9 (2.3)	5	
98.9	24.0 (3.0)	10	

^a Hg²⁺, Co²⁺, Fe³⁺, Ni²⁺, Cr³⁺, 5000 ng ml⁻¹ of each cation; K⁺ and Li⁺, 10,000 ng ml⁻¹ of each.

^b R.S.D of three replicate experiments.

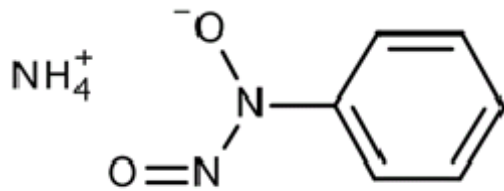
^c Hg²⁺, Co²⁺, Fe³⁺, Ni²⁺, Cr³⁺, 2500 ng ml⁻¹ of each cation; K⁺ and Li⁺, 5000 ng ml⁻¹ of each.

^d From drinking water system of Tehran.

^e Not detected.

^f Tehran, 20 January, 2014, Iran.

^g Caspian sea water.



Schematic 1 Synthesis and Molecular structure of Schiff's Cupferron

on metal chelate formation and following extraction. Therefore, pH was the first optimized parameter. pH of the analyte solutions was adjusted to desired values with diluted hydrochloric acid (0.1 mol L^{-1}) and/or ammonia solution (0.1 mol L^{-1}). The variation in recovery of Cu(II) with pH is shown in Fig.4. According to the results shown in Fig 3 up to pH 2-2.5, complete recoveries are obtained. However, at higher pH values, percentage recovery decreases.

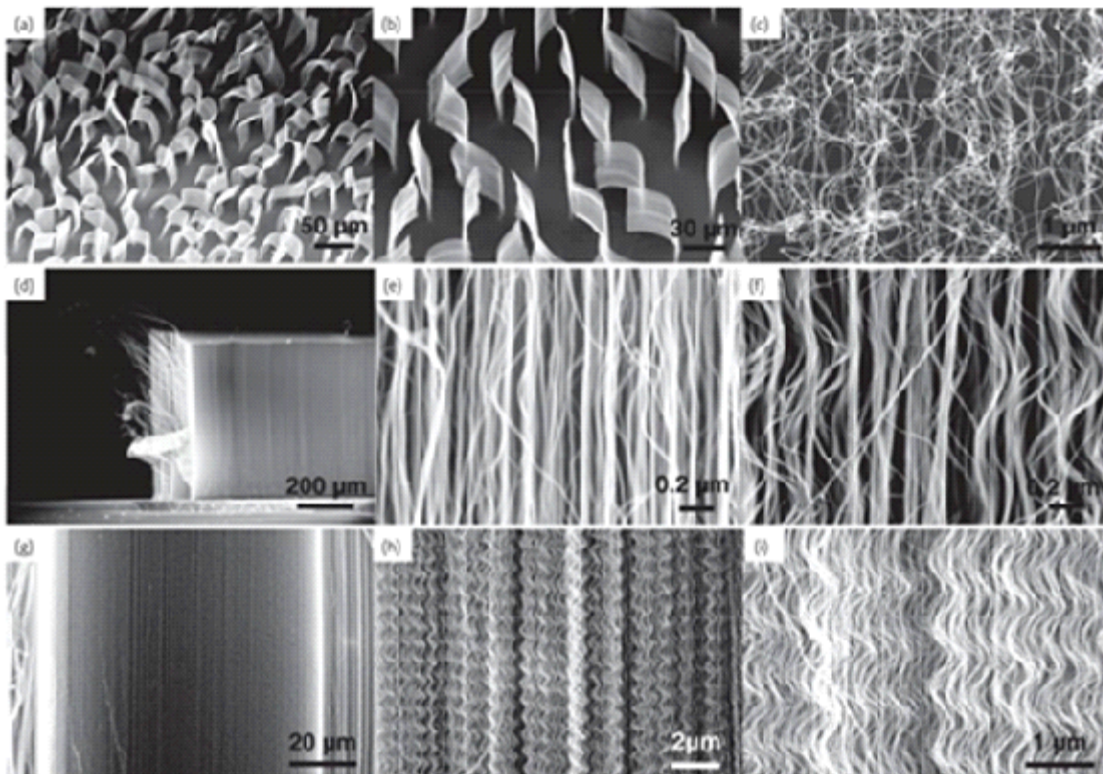


Fig. 1: SEM image of Multi walled carbon nanotubes (MWCNTs)

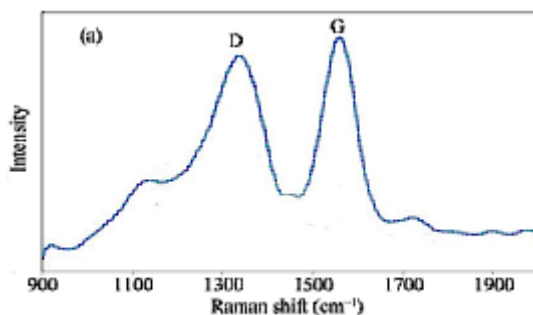


Fig. 2: Raman Spectroscopy image Multi walled carbon nanotubes (MWCNTs)

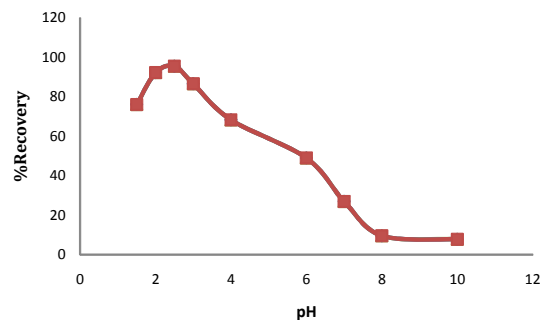


Fig. 3: Effect of pH on the extraction of Cu. Experimental conditions: source, 10 ml of $0.1 \mu\text{gml}^{-1}$ Cu^{2+} solution; amount of sorbent, 50.0 mg

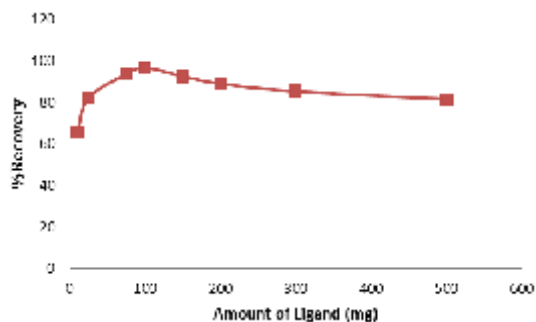


Fig. 4. Removal percentages of Cu (II) at different amounts of adsorbent, of Cu (II), pH= 2.5

This is due to fact that in an acidic solution the protonation of Cupferron occurs and there is a weak tendency for retention between Cu (II) and C18 modified multi walled carbon nanotubes (MWCNTs) and Cupferron ligand, whereas at higher values (pH>5), Cu (II) reacts with hydroxide ions to produce Cu (OH)₂. Accordingly, pH 2.5 was selected for subsequent work and real sample analysis.

Effect of flow rates of sample and eluent solution

The effects of flow rates of sample solution and eluent solution on the recovery of Cu (II) was also examined between under the optimum conditions in the range of 1–10.0 mL min⁻¹ by controlling the flow rate with peristaltic pump. The recovery of the ions were independent of flow rate in the range of 0.5–2.0 mL min⁻¹ for eluent solution and range of 1–5.0 mL min⁻¹ for sample solution.

Effect of sample solution volume

Another parameter studied to find the best experimental conditions is the volume of sample solution and/or analyte concentration. For this purpose, 50.0–1100.0 mL of sample solutions containing 5ppm Cu (II) were processed according to the suggested procedure. The recovery of Cu(II) was quantitative (>96%) obtained up to a sample volume of 1000.0 mL and the adsorbed Cu(II) can be eluted with 5 mL eluent. Therefore, an enrichment factor of 200 was achieved by this technique. Finally In our suggested procedure, a sample volume of 50.0 mL was chosen for preconcentration method.

Effect of amount of sorbent

To achieve a high extraction recovery, different amounts of multi walled carbon nanotubes

(MWCNTs) and Cupferron ligand ranging from 50 to 300 mg were applied to extract the target compounds from the sample solutions. The results are shown in Fig 4 from which it can be seen that the extraction recovery achieved by 100 mg, but almost the same as obtained with 300 mg or more than of the adsorbent. Based on the above results, 100 mg of multi walled carbon nanotubes (MWCNTs) and Cupferron ligand was selected for the following experiments.

Eluent type and its volume

Another important factors which affect the percent of recovery are the type, volume, and concentration of the eluent solution used for the removal of metal ions from the sorbent. For this purpose, various type of eluents were examined according to the suggested procedure. 4.0 mol L⁻¹ HNO₃ was found to be adequate for quantitative elution (≤95%). The results show the best quantitative recovery is 5.0 mL of 4.0 mol L⁻¹ HNO₃. As a result 5.0 mL of 4.0 mol L⁻¹ HNO₃ was selected in the subsequent preconcentration method.

Reusability of Column

The stability and potential regeneration of the column were studied. After every time extraction, the column was washed with 10 mL of MeOH and 10mL of deionized water. Thus, the column was available for a next extraction immediately at least 50 adsorption elution cycles without significant decrease in the recovery of Cu (II) ions.

Effect of foreign ions

The influence of common foreign ions on the adsorption of Cu (II) on C18 modified multi walled carbon nanotubes (MWCNTs) and Cupferron ligand were studied. In these work, 50.0 ml solutions containing 5ppm of Cu and various amounts of interfering ions were treated according to the suggested procedure. The tolerance level was defined as the maximum concentration of the foreign ion causing a change in the analytical signal no higher than 5%, when compared with the signal of 5ppm Cu alone. The results, listed in Table 1, demonstration that the presence of major cations and anions in natural water has no important influence on the adsorption of Cu (II) ions under the designated conditions.

Analytical figures of merits

Under optimized conditions, a calibration curve for Cu (II) was found by preconcentrating a series of Cu (II) standards according to the procedure mentioned. The curve was linear from 1.0 mg/l to 7.0 mg/l for Cu.

Determination of Copper in real water samples

Three type of water samples (information described in section 2.6 sampling) were used for the determination of Copper. The analytical results, are given in Table 2. The percent of recoveries for the addition of different concentrations of Cu (II) to water samples were 97 and 98.9%. These satisfactory percent of recoveries indicate no significant effects from the matrix composition of the real water samples.

CONCLUSION

In conclusion, the proposed SPE possesses the following advantages: the

technique is rapid when compared with the previously reported procedures for the separation and determination of Copper, the time taken for the separation and determination of Copper in a 500 mL sample is at the most 30 min. Furthermore, it is a simple, highly sensitive, selective and reproducible method for the separation of Cu^{2+} and in this work the recovery yields obtained with *C18 modified multi walled carbon nanotubes (MWCNTs)* and Cupferron ligand were about 95-100% then it show C18 and its derivation e.g. in this work C18 modified multi walled carbon nanotubes (MWCNTs) and Cupferron ligand is full of potential for use as a adsorbent in the extraction method like SPE and SPME .consequently it can be applied to the preconcentration and determination of Copper and the large number of heavy metal that are dangers for human from real samples.

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