

# New electrochemical sensor for sensitive quantification of copper in river, city, bottled and drinking water samples

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## ABSTRACT

In the present study, a reliable and very sensitive sensor for the determination of ultra-trace of Cu(II) is proposed. Copper was determined by anodic differential pulse stripping voltammetry based on the adsorption collection of the Cu(II) on an encapsulated Schiff base onto multiwalled carbon nanotube paste working electrode. The variation of peak current with pH and several instrumental parameters such as accumulation time, accumulation potential and scan rate, were optimized. Under optimized condition, the relationship between the peak current and copper ion concentration is linear which is used as analytical signal. The method was applied to the determination of copper ion in river water, city water, and bottled water and drinking water samples with satisfactory results.

**Key words** | anodic stripping voltammetry, bottled water, city water, copper, drinking water, multiwalled carbon nanotube

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## INTRODUCTION

Copper, an important essential metal, is considered as a micronutrient for human health, which plays an important role in lipid and carbohydrate metabolism and in the maintenance of heart and blood vessel activity. Acute symptoms from excessive ingested copper include salivation, epigastria pain, nausea, vomiting, diarrhoea, intravascular haemolytic anaemia, acute hepatic and renal failure, shock and coma (Walsh *et al.* 1997; Ohta *et al.* 2001; Tisato *et al.* 2010). The requirement of an adult human is about 1–5 mg/day of copper, but excess amounts in the body can be toxic. It is therefore extremely important to develop a cost-effective, sensitive, selective and rapid analytical method for trace determination of copper. At this time, a number of methods, such as atomic absorption spectrometry (AAS) (RahnChique *et al.* 2012; Azeem *et al.* 2013; Prkic *et al.* 2013), cold vapour AAS or flame AAS–electrothermal atomization (Alvarez & Carrillo 2012; Acar *et al.* 2013), inductively coupled plasma-optical emission spectroscopy (ICP-OES) (Hagen & Sneddon 2009; Sereshti *et al.* 2011), stripping voltammetry (Zhang *et al.* 2012; Figueiredo-Filho *et al.* 2013;

Martiniano *et al.* 2013), chromatography (Sardella *et al.* 2012; Rybak & Ruzik 2013), gravimetric detection (Sherif 2012) or photometry (Dengqing & Wusong 2012) are used for monitoring the concentration of copper at trace levels. However, maintenance and operational costs of inductively coupled plasma mass spectrometry, ICP-OES, AAS and chromatography techniques are expensive and require adequate expertise (these methods are not sufficiently sensitive for the direct determination of copper so that a pre-concentration stage is necessary). Therefore, the analysis is often limited to laboratory level since reliable, low cost, quick and, of course, ultra-sensitive analytical techniques are necessary. However, such requirements are greatly met by electrochemical methods (Gozzo *et al.* 1999).

As an electrochemical technique, stripping voltammetry has been accepted as being one of the most sensitive and convenient tools for the determination of trace metals. Conventionally, hanging mercury drop electrodes and mercury film electrodes (Goudarziafshar *et al.* 2013) have been used as the working electrodes for stripping voltammetric

analysis of metals. Owing to the high toxicity of mercury, much effort has recently been directed into developments of the so-called 'mercury-free' electrodes (Wang *et al.* 2000; Honeychurch *et al.* 2002; Legeai *et al.* 2005). Over the past decades, the main mercury-free electrode, carbon paste, has become one of the most popular electrode materials used for the laboratory preparation of various electrodes, sensors and detectors. Such a consequence is undoubtedly the result of the optimum constellation of physico-chemical and electrochemical properties of this carbonaceous substrate.

To prepare more sensitive electrodes, carbon paste is used as a support for plating with metallic films which is able to offer more sensitive results similar to those of well-established solid electrodes. In addition, their easy and inexpensive preparation with no risk of mechanical damage of the electrode surface is very advantageous. Carbon nanotubes with unique electronic properties can mediate the electron transfer reaction with electroactive species. These carbon nano composites have the advantages of high conductivity and large surface area, which allows the production of ultra-sensitive sensors. Electrochemical sensors based on carbon nanotubes (CNTs) represent a new and interesting alternative for quantification of different analytes. Multiwalled carbon nanotubes (MWCNTs) have attracted enormous interest because of their unique structural, mechanical, electronic and chemical properties. Some of these properties include high chemical and thermal stability, high elasticity, high tensile strength and, in some instances, metallic conductivity. The subtle electronic properties suggest that CNTs have the capability of promoting electron transfer reactions and improving sensitivity in electrochemistry, and thus they are widely used as electrodes (Kang *et al.* 2007; Choong *et al.* 2008; Jiang *et al.* 2011). CNT modified electrodes have been proved to have excellent electroanalytical properties, such as wide potential window, low background current, low detection limits, high sensitivities, reduction of over potentials and resistance to surface fouling. There are reports that reveal that CNT modified electrodes have shown electrocatalytic behaviour with excellent performance in the study of a number of biological species (Kang *et al.* 2007; Choong *et al.* 2008; Crespo *et al.* 2009; Morton *et al.* 2009; Jiang *et al.* 2011; Senthilkumar & Saraswathi 2011; Janegitz *et al.* 2009; Soleimani & Ghahraman Afshar 2013). In this paper, a multiwalled carbon

nanotube electrode is prepared. To obtain a more sensitive and selective electrode, a synthesized Schiff base was used as encapsulated into the multiwalled carbon nanotube. The sensitivity and selectivity of electrode is examined by analysing city water, river water, bottled water and drinking water samples.

## EXPERIMENTAL

### Apparatus and reagents

All voltammetric measurements were performed using a Metrohm (Herisau, Switzerland) Autolab equipped with PGSTAT-12 and GPES software. Measurements were carried out with a Schiff base modified multiwalled carbon nanotube electrode in a three-electrode arrangement. The auxiliary electrode was a wire of platinum with a considerably larger surface area than that of Schiff base modified multiwalled carbon nanotube electrode. A silver-silver chloride (KCl 3 M) was used as reference electrode. Stirring was carried out by a large Teflon rod at a speed of 1,000 rpm. A Metrohm-780 digital pH meter was used for pH measurement. Solutions were deoxygenated with high-purity nitrogen for 5 minutes prior to each experiment, and experiments were performed under a nitrogen atmosphere.

Stripping voltammetric experiments were carried out with a Metrohm Autolab equipped with PGSTAT-12 and GPES software. A three-electrode electrochemical cell (20 mL) was used in all experiments. A platinum rod and an Ag/AgCl, KCl salt electrode were used as auxiliary and reference electrodes, respectively. pH measurements were made with a Metrohm Model 780 pH meter. Solutions were prepared by dissolving analytical-grade reagents in double distilled water. Cu(II) standard solution, 1,000 mg/L, appropriate amount of  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  (Merck) was dissolved in water acidified by 0.1 mL of concentrated  $\text{H}_2\text{SO}_4$  and the solution was diluted with water to 100 mL. When needed, the Cu(II) stock solution was diluted with water to use as working solution. Multiwalled carbon nanotubes were purchased from Sigma-Aldrich (>95%, O.D.: 10–15 nm, I.D.: 2–6 nm, length: 0.1–10  $\mu\text{m}$ ). Borate buffer was prepared by mixing boric acid solution with sodium hydroxide.

## Characterization of the MWCNTs

Specific surface areas (SSA) is obtained using the Brunauer–Emmett–Teller (BET) method (Brunauer *et al.* 1938; Walton & Snurr 2007). Briefly, monitoring the adsorption of N<sub>2</sub> on the surface of MWCNTs by measuring the amount of adsorbed gas was related to monomolecular layer adsorbed on the MWCNTs surface. The SEM image of the MWCNTs surface is shown in Figure 1. The results of the BET method showed that the SSA of oxidized MWCNT was 158 m<sup>2</sup> g<sup>-1</sup>.

The BJH method (Li *et al.* 2003; Yavari *et al.* 2011) was used to obtain the pore size distribution of oxidized MWCNTs. The results of this experiment showed that the average pore diameter and pore volume were 36 nm and 0.24 cm<sup>3</sup>g<sup>-1</sup>, respectively.

## Synthesis of Schiff base

Exactly 1.2 g terephthalaldehyde was dissolved in 150 mL acetonitrile (free of water). Drops of the solution were added to 0.972 mL of 2-etylen-3-amin (solved in 280 mL acetonitrile). The solution was kept at room temperature for 2 days. The resulting Schiff base was used to prepare the sensor (see Figure 2).

## Preparation of working electrode

To prepare the sensor, typically multiwalled carbon nanotube (60% w/w) and a specific quantity of Schiff base (8% w/w) were added to an appropriate amount of methyl

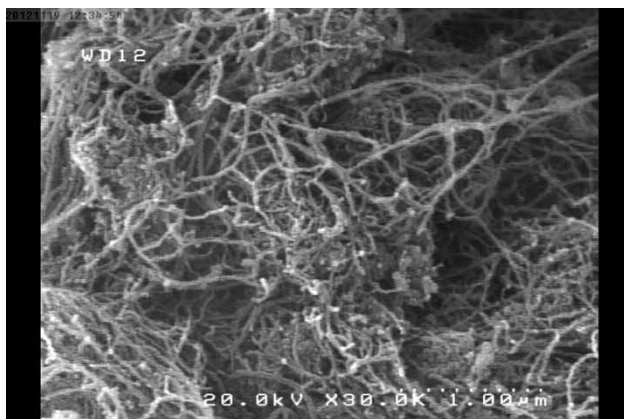


Figure 1 | The SEM image of oxidized MWCNTs surface.

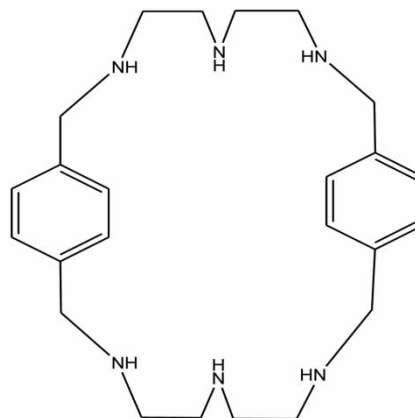


Figure 2 | Structural formula of Schiff base.

alcohol and mixed to form a uniform mixture. Excess solvent was evaporated at room temperature. The mineral oil (32%) was added to the multiwalled carbon nanotube–Schiff base composite. A copper wire was used as external electrical contact between electrode and nanocomposite. The surface of the electrode was polished with a piece of weighting paper and then thoroughly rinsed with distilled water.

## Anodic stripping voltammetry with modified multiwalled carbon nanotube

The electrode was immersed in the voltammetric cell containing the sample solution (20 mL) as borate buffer (pH = 6.8) and a known amount of copper. The stirrer was switched on and the solution was purged with nitrogen gas for 4 minutes while the accumulation potential of –100 mV vs. Ag/AgCl electrode was applied to the solution. At the end of the experiment, the stirrer was switched off and the stripping voltammograms were scanned in the negative direction in the differential pulse mode from –0.10 to –0.30 V.

## RESULTS AND DISCUSSION

The anodic stripping voltammetric behaviour of 30 µg L<sup>-1</sup> of copper was studied by employing the modified multiwalled carbon nanotube electrode as the working electrode in pH 6.8 of borate buffer as supporting

electrolyte. After 4 minutes accumulation potential of  $-100$  mV vs. Ag/AgCl electrode, a large anodic stripping peak at around  $-0.19$  V was obtained (Figure 3).

### Effect of operational parameters

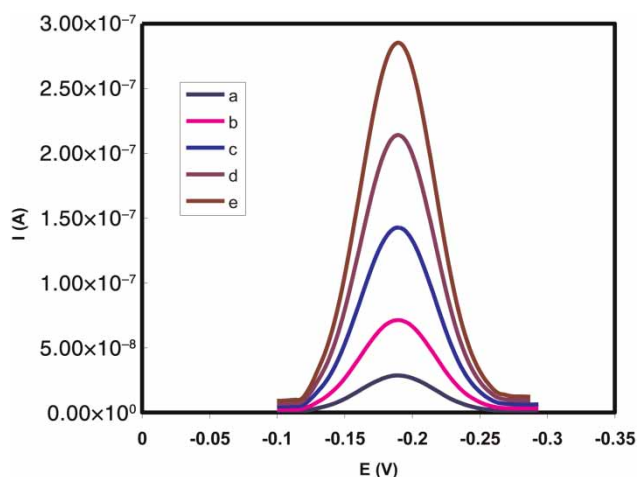
The influence of effective parameters such as supporting electrolyte, accumulation potential and accumulation time on the sensitivity and selectivity of the modified multiwalled carbon nanotube electrode was studied.

### Effect of supporting electrolyte

Among various electrolytes examined for the anodic stripping study, the best results were obtained in borate buffer media. The influence of pH on the anodic stripping peak currents of copper was studied in the pH range of 5.5–9.0. It was found that at pH 6.8 the peak currents of copper were at their maximum values. Thus, pH 6.8 was adopted for further studies.

### Effect of accumulation potential

The effect of accumulation potential on the peak currents of copper was studied over the range of  $-300$  to  $+100$  mV. The results show that in the potential of  $-100$  mV the peak currents of copper were independent of accumulation potential



**Figure 3** | Differential pulse voltammograms of different concentrations of copper ion and borate buffer (pH = 6.8) for Schiff base modified multiwalled carbon nanotube electrode.

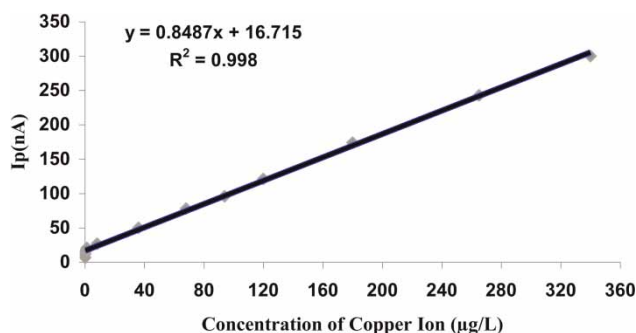
and had the maximum value. An accumulation potential of  $-175$  mV was used for the optimized analytical procedure.

### Linear range and detection limit

To obtain the linear range, a series of different amounts of Cu(II) standard solution were, respectively, added to the electrochemical cell and related voltammograms were recorded. The results showed that the linear range determined by the present procedure was  $0.09$ – $340.0$   $\mu\text{g L}^{-1}$  with the regression equation of  $I_p(\text{nA}) = 0.8487C_{\text{Cu(II)}} (\mu\text{g L}^{-1}) + 16.715$  (correlation coefficient  $R^2 = 0.998$ ) (see Figure 4). For three replicate determinations of  $30$   $\mu\text{g L}^{-1}$  Cu(II), the relative standard deviation determined was 1.86%. This indicated that the present sensor has good precision. The precision of the sensor for real samples was checked by repetitive analyses ( $n = 13$ ) of real samples. The results indicate satisfactory precision for the proposed method. With 10 replicate blank experiment determinations the detection limit of the method was calculated to be  $0.01$   $\mu\text{g L}^{-1}$ .

### Real sample analysis

The electrode was used for the determination of copper in city water, river water, drinking water and bottled water samples. The water samples were filtered using a  $0.45$   $\mu$  membrane filter and acidified to pH close to 2 using Supra-pure  $\text{HNO}_3$  and then digested by UV irradiation for 3 h. The results are presented in Table 1. The recovery of the method was in the range of 96.8–101.2%.



**Figure 4** | Calibration curve.

**Table 1** | Determination of copper in water samples

Sample	Add ( $\mu\text{g L}^{-1}$ )	Found ( $\mu\text{g L}^{-1}$ )	Recovery
River water	0	5.0	–
	25	29.3	97.2
	50	55.1	100.2
City water	0	3.6	–
	25	27.8	96.8
	50	54.8	100.8
Drinking water	0	3.2	–
	25	28.5	101.2
	59	52.2	98.0
Bottled water	0	2.8	–
	25	27.2	97.6
	50	52.4	99.2

## CONCLUSION

The present study demonstrates that stripping voltammetric determination of copper using encapsulated Schiff base onto multiwalled carbon nanotube can be used to determine trace amounts of this element in the water samples. The results of this study show that the copper content of river water, city water, drinking water and bottled water are 5.0, 3.6, 3.2 and 2.8  $\mu\text{g L}^{-1}$ , respectively (see Table 1). The results of real sample analysis are in agreement with other studies, which indicate that the copper content of water samples are in the range of  $\mu\text{g L}^{-1}$ . The electrode offers a practical potential for trace determination of copper with high selectivity, sensitivity, simplicity and speed. In comparison with other reports, the average recovery of this method for analysis of copper ion in water samples is 98.8 with standard deviation of 1.86%, which is more acceptable than the results of Morton *et al.* (2009) who reported an average recovery of 94.5% with relative standard deviation of 7.53%. The linear range and detection limit of this method are more acceptable than the results of Janegitz *et al.* (2009) who obtained a linear range of  $7.90 \times 10^{-8}$  to  $1.60 \times 10^{-5}$  mol  $\text{L}^{-1}$  with the detection limit of  $1.00 \times 10^{-8}$  mol  $\text{L}^{-1}$ . A comparison between our results with those of Senthilkumar & Saraswathi (2011) shows that detection limit of their sensor for analysis of copper ion is 0.72  $\mu\text{g L}^{-1}$ , and detection limit of our sensor is 0.01  $\mu\text{g L}^{-1}$ . Also, the linear range of sensor reported by Senthilkumar & Saraswathi (2011) is 3.2–642.8  $\mu\text{g L}^{-1}$ , but

in this work is 0.09–340  $\mu\text{g L}^{-1}$ . This indicates that the linear range of sensor reported in this work is better (one order) than that of Senthilkumar & Saraswathi (2011). Also, in terms of sensitivity, the results of this study are more sensitive than the results of Soleimani & Ghahraman Afshar (2013), who reported a detection limit of  $1.1 \times 10^{-6}$  M for Cu(II). In addition, an advantage of this method in comparison with that of Ohta *et al.* (2001) is analysis of a real sample without any pre-concentration step.

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First received 25 April 2014; accepted in revised form 27 April 2015. Available online 5 June 2015