

Preparation and application of a simple electrochemical sensor for the determination of copper in some real and standard samples

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Abstract In this study, anodic stripping voltammetry was optimized and used for the trace determination of copper ions using modified carbon paste electrode with dicyclohexyl-18-crown-6 and multi-walled carbon nanotubes. The important and critical parameters such as pH, electrolyte type, electrode composition, deposition time, and reduction potential was studied and optimized. Copper shows a sharp peak at +0.095 V that was used for its determination from 4.0 to 200 ng mL⁻¹. With the application of the suggested method, the detection limit and relative standard deviation were obtained as 1.1 ng mL⁻¹ and ±2.3 %, respectively. This electrochemical sensor has several advantages such as simple and low cost preparation, good reproducibility, low LOD, and high speed. The suggested sensor was applied successfully for the determination of copper ions in environmental, biological, and standard samples.

Keywords Anodic stripping voltammetry · Modified carbon paste electrode · Multi-walled carbon nanotubes · Copper

Introduction

Heavy metals such as Cu, Cd, Co, As, Ni, Hg, and Pb have been extensively applied in several fields of human activities such as industrial, technological, and agricultural

improvements. All of these ions can present toxic effects at high concentration levels on human and ecosystems health, so diverse techniques were applied to the determination of these metals [1–4]. Among these metals, copper is mostly used in diverse fields such as electronics and related devices, architecture, antimicrobial and antibiofouling applications, jewelry, and etc. [5].

Copper is an important and fundamental element, plays a vital role in many living organisms' functions as an enzyme co-factor and participates in the formation process of red blood cells [6]. However, high concentration of this ion may be detrimental and can cause irritation of the throat and nose, anemia, bone disorders, vomiting, and diarrhea [7]. For this reason, the United States Environmental Protection Agency (USEPA) exclaimed the maximum contamination level of copper in drinking water at 1.30 ppm [8]. So, according to the above subjects, the monitoring of trace amounts of Cu²⁺ in different samples is necessary.

Some analytical techniques have been used for the determination of copper in different samples such as graphite furnace atomic absorption spectrometry (GFAAS) [9], flame atomic absorption spectrometry (FAAS) [10], near-infrared reflectance spectroscopy (NIRS) [11], fluorescence [12], and inductively coupled plasma mass spectrometry (ICP-MS) [13].

Until today, several ligands were used to modify the different types of electrodes and electrochemical determination of copper such as phenanthroline–tetraphenyl borate ionophore [14], 2,2'-(1E,1'E)-1,1'-(2,2'-azanediylbis (ethane-2,1-diyl) bis (azan-1-yl-1-ylidene)) bis (ethan-1-yl-1-ylidene) diphenol [15], dimethyl 4,4'-(o-phenylene) bis (3-thioallophanate) [16], and etc. Among the analytical techniques, the stripping voltammetry (SV) is a beneficial technique for the determination of trace ions and biological compounds due to its advantages such as high sensitivity, accuracy, selectivity, high speed, and

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low cost of apparatus [17–20]. Stripping voltammetry needs the presence of a suitable ligand for the fast and quantitative complex formation at the surface of electrode and then, the ligand or the metal ion are oxidized or reduced [21].

In the present work, we reported the performance of a carbon paste electrode modified with dicyclohexyl-18-crown-6 (as ligand) and multi-walled carbon nanotubes (to increase the conductivity, peak current, and sensitivity) for detecting trace levels of copper in different samples using differential pulse anodic stripping voltammetry (DPASV). The premier performance of mentioned modified carbon paste electrode (MCPE-CNT) is demonstrated by the determination of copper in water samples, human hair, and certified reference materials with satisfactory results.

Experimental

Materials and reagents

Cu(II) stock solution (1000.0 mg L^{-1}) was prepared by dissolving an appropriate amount of $(\text{CuNO}_3)_2 \cdot 3\text{H}_2\text{O}$ (Merck, Darmstadt, Germany) into a 100.0-mL volumetric flask and was diluted to the mark with deionized water. Working standard solutions of Cu(II) were prepared at different concentrations by diluting the stock solution with deionized water, and their concentrations were checked by an atomic absorption spectrometer (Perkin-Elmer model 2380). Multi-walled carbon nanotubes with 3–20-nm diameter, core diameter 1–10 nm, SBET $350 \text{ m}^2 \text{ g}^{-1}$, and 95 % purity were purchased from Plasma Chem (Plasmachem, Germany). The graphite powder, dicyclohexyl-18-crown-6, hydrochloric acid, acetic acid, phosphoric acid, and nitric acid were purchased from Merck (Darmstadt, Germany). Acetate buffer solution (pH=5) was prepared with NaAc and HAc. Also, pure nitrogen was applied for the deaeration process.

Instruments

Voltammetric determinations of copper were carried out using a Metrohm electroanalyzer (Model 757 VA Computrace). The measurements were done using VA Computrace version 2.0 (Metrohm, Herisau, Switzerland) run under the Windows 98 operating system. All voltammograms were recorded with a three electrode system consisting of an Ag/AgCl electrode (as the reference electrode), a platinum wire (as the counter electrode), and the modified or unmodified CPEs (as the working electrodes). A RH B-KT/C (IKA, Staufen, Germany) magnetic stirrer was employed to stir the sample solution. Also, a Metrohm 827 pH meter was applied for adjustment the pH. All electrochemical experiments were performed under pure N_2 gas atmosphere at room temperature.

Samples treatment

Water samples

Three water samples, including tap water (Kerman drinking water, Kerman, Iran), well water (Shahid Bahonar University of Kerman, Kerman, Iran), and river water (Sarcheshmeh, Kerman, Iran) were selected. These water samples were filtered to remove suspended particulate matter, their pH was adjusted to pH=2.0 with HNO_3 to inhibit adsorption of the ions at the surface of the flask walls [22], and stored at 4°C in a refrigerator. For carrying out the recommended method, the pH of the samples was adjusted to 5.0.

Human hair

The human hair sample was immersed in acetone for 30 min, eluted by deionized water, and dried. 0.5 g of this prepared sample was weighed exactly, digested by 20.0 mL of solution containing perchloric and nitric acids (1:8 v/v). After digestion, the residue was dried at high temperature and 25 drops of diluted H_2SO_4 (1:1 v/v) were added [23]. Finally, the volume of residue was increased to 100.0 mL with deionized water in a measuring flask, 25.0 mL of solution was selected, and the experiment was done according to the suggested procedure.

Standard reference material

A 0.1-g standard sample (MA-1b reference gold ore) was dissolved in a mixture containing nitric, hydrochloric, and hydrofluoric acids (2:4:1 volume ratio) with heating. The obtained solution was diluted and filtered [24]. The final volume of this solution was raised to 100.0 mL, 25.0 mL of the sample solution was taken, and the amount of Cu was determined by the procedure mentioned earlier.

Preparation of electrodes

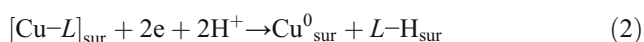
Unmodified carbon paste electrode was composed by mixing of 70 mg of pure graphite powder and 30 μL of silicon oil with a mortar and pestle. For preparation of modified carbon paste electrode (MCPE-CNT), 50 mg pure graphite powder, 5 mg dicyclohexyl-18-crown-6, 15 mg carbon nanotubes, and 30 μL of silicon oil were taken and mixed in a mortar and pestle. A fresh electrode surface was obtained by squeezing out a small amount of paste into the end of a glass tube (ca. 3.0 mm i.d. and 10 cm long), scraping off the excess against a conventional paper, and polishing the electrode on a smooth paper to obtain a shiny appearance. The electrical connection was made with a copper wire.

General procedure

For accumulation step, the MCPE-CNT was immersed in a stirred 25.0 mL of 0.10 mol L⁻¹ acetate buffer solution (pH 5.0) containing 2.0 μg Cu(II) for 200 s. In this step, the Cu(II) ions were accumulated and reduced in -0.8 V. Then, the voltammogram was recorded by potential scanning from 0 to +0.2 V (with 30 mV s⁻¹ scan rate, 4 ms pulse period, and 100 mV pulse amplitude). All the measurements were carried out at room temperature (~23±1 °C). The obtained peak at +0.095 V was used for the voltammetric determination of Cu.

Principle of the method

Copper ions can form complex with 18-crown-6 ethers family [25]. The recommended method based on the entrance of Cu(II) from the pH adjusted solution into the cavity of dicyclohexyl-18-crown-6, whereas the applied potential was -0.8 V. This procedure includes three stages: (1) reduction of accumulated Cu(II) to Cu(0). (2) Thin film formed on the electrode surface in -0.8 V.



where “aq” and “sur” subscripts mean the compound is in solution or at the electrode surface and “L” is dicyclohexyl-18-crown-6.

(3) The differential pulse was applied to electrochemical stripping the Cu(0) back to Cu(II). The resulting oxidation peak forms the analytical signal of copper.



Results and discussion

Electrochemical behavior of copper on the surface of electrodes

The Cu(II) preconcentrate capability of the prepared electrodes was investigated. The related Fig. 1a to e show the differential pulse stripping voltammograms of unmodified carbon paste electrode (UCPE) in 100.0 ng mL⁻¹ Cu(II), CPE-CNT (with carbon nanotubes and without ligand in 100.0 ng mL⁻¹ Cu(II)), MCPE (with ligand and without carbon nanotubes in 100.0 ng mL⁻¹ Cu(II)), MCPE-CNT (with ligand and carbon nanotubes in 100.0 ng mL⁻¹ Cu(II)), and MCPE-CNT (with ligand and carbon nanotube in absence of Cu(II) in accumulation medium) in 0.1 mol L⁻¹ acetate buffer (pH=5) after preconcentration in accumulation medium. In UCPE case, a small peak was obtained at +0.095 V that shows

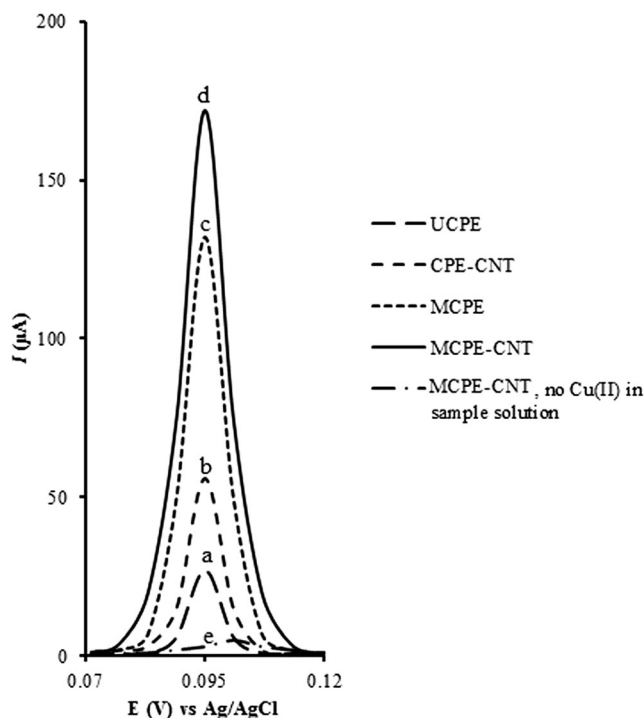


Fig. 1 Differential pulse stripping voltammograms in acetate buffer (pH=5): unmodified carbon paste electrode (UCPE) in 100.0 ng mL⁻¹ Cu(II) (a), CPE-CNT (with carbon nanotubes and without ligand) in 100.0 ng mL⁻¹ Cu(II) (b), MCPE (with ligand and without carbon nanotubes) in 100.0 ng mL⁻¹ Cu(II) (c), MCPE-CNT (with ligand and carbon nanotubes) in 100.0 ng mL⁻¹ Cu(II) (d), and MCPE-CNT (with ligand and carbon nanotubes) in absence of Cu(II) in accumulation medium (e). Other conditions: pH=5, accumulation-reduction time 200 s, amount of modifier 5 mg, amount of CNT 15 mg, scan rate 30 mV s⁻¹, pulse amplitude 100 mV, pulse period 4 ms

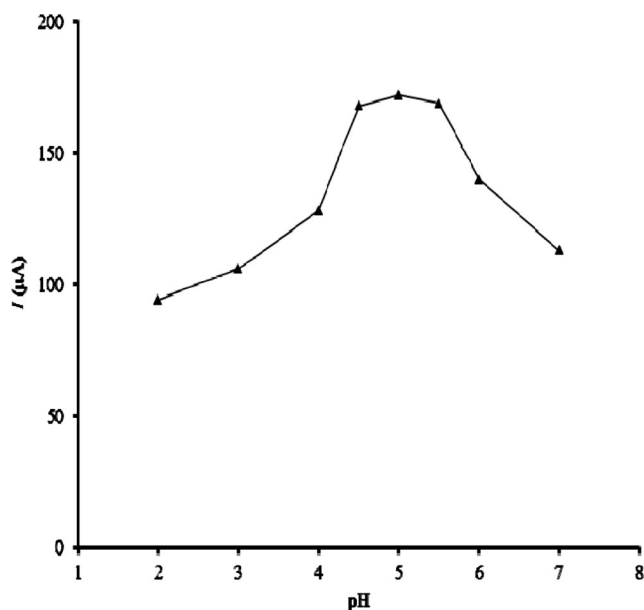


Fig. 2 The effect of pH on the MCPE-CNT response. Other conditions were the same as in Fig. 1 except the pH

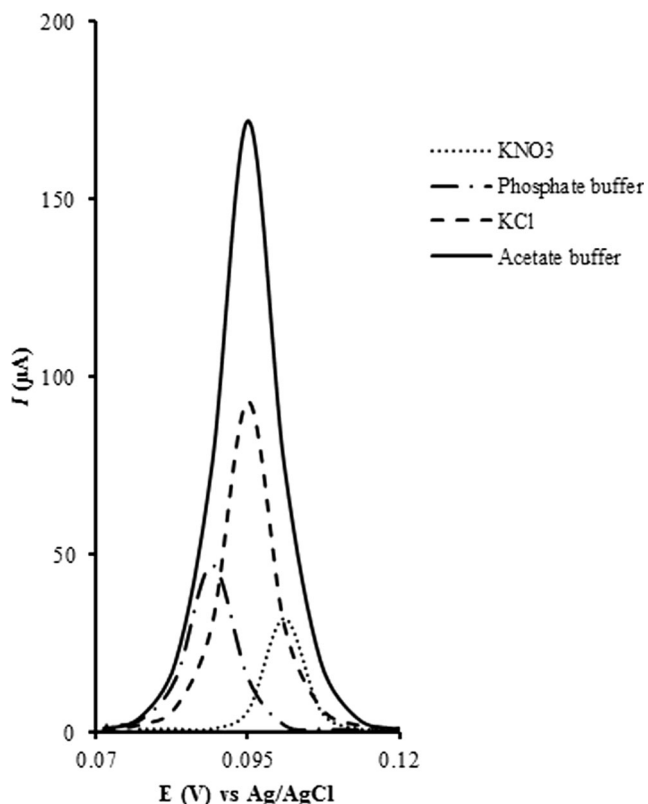


Fig. 3 The effect of supporting electrolyte type on the MCPE-CNT response. Other conditions were the same as in Fig. 1 except the supporting electrolyte type

Cu(II) adsorption process was not significant. Instead, when CNT-CPE was used, a clear stripping peak (about 56 μA) appeared after accumulation in the sample solution containing 100.0 ng mL^{-1} Cu(II). As can be seen, the current intensity of copper at the surface of MCPE (about 132 μA) is several times larger than the UCPE and finally, when MCPE-CNT was used

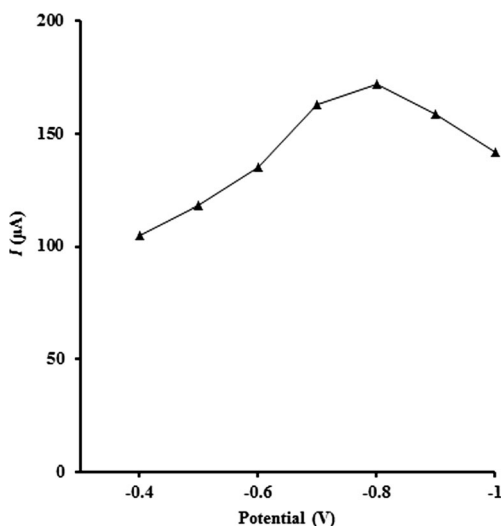


Fig. 4 The effect of reduction potential on the MCPE-CNT response. Other conditions were the same as in Fig. 1

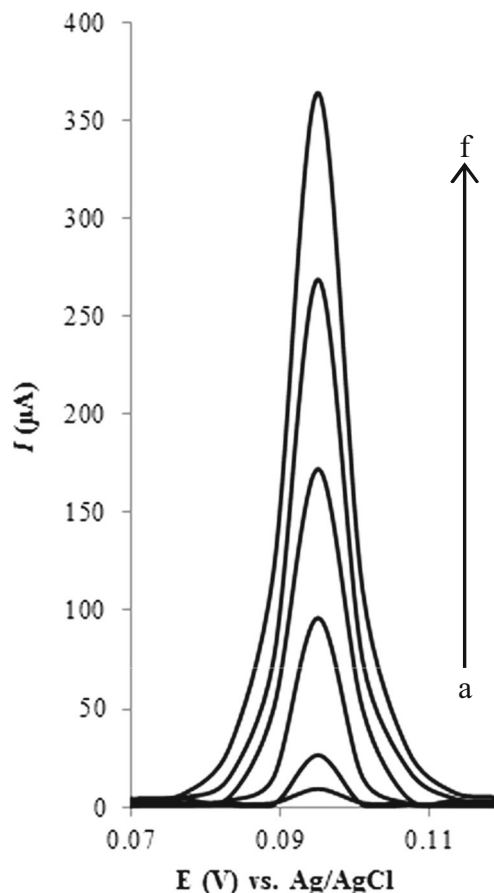


Fig. 5 Differential pulse anodic stripping voltammograms of MCPE-CNT, concentrations (a–f): 4.0, 10.0, 50.0, 100.0, 150.0, and 200.0 ng mL^{-1} of Cu(II)

as working electrode, peak current presented an impressive increase (about 172 μA) after accumulation in the sample solution containing 100.0 ng mL^{-1} Cu(II). Also, while the MCPE-CNT was applied in the absence of analyte ions, only small background current was observed.

Optimization of analytical parameters

To obtain the best performance of the prepared electrode for the electrochemical determination of copper ions, the principal parameters affecting the current intensity such as pH, modifier and carbon nanotubes amounts, accumulation-reduction potential, supporting electrolyte properties, and the accumulation time were studied.

pH effect

The effect of pH on the anodic peak current of MCPE-CNT was investigated between 2.0 and 7.0 (adjusting with nitric acid and sodium hydroxide) in a sample solution containing 100.0 ng mL^{-1} Cu(II). The obtained results (Fig. 2) show that the maximum intensity of peak current

Table 1 Effect of coexisting ions

Foreign ion	Ion/Cu ratio	Recovery %
K ⁺	500	97.9
Ni ²⁺	250	99.2
Al ³⁺	500	100.3
Mg ²⁺	450	99.1
Na ⁺	500	102.5
Mn ²⁺	300	104.3
Ca ²⁺	500	96.1
Pb ²⁺	500	98.2
Cd ²⁺	200	97.1
Hg ²⁺	500	99.1
Zn ²⁺	500	104.2
NH ₄ ⁺	500	97.6
Fe ²⁺	450	101.5
Cl ⁻	500	98.5
F ⁻	500	99.1
NO ₃ ⁻	500	96.1

was obtained at pH 5.0. The current decreasing in more acidic solution could be related to the protonation of dicyclohexyl-18-crown-6 and reduction of its reaction with copper ions. Also, the decrease of current intensity in alkaline medium relevant to reaction of copper with hydroxide ions that reduce the charges of Cu ions and their migration toward the working electrode (MCPE-CNT) surface. Therefore, pH=5.0 was selected as the optimum in the further experiments.

Table 2 Determination of copper in real samples

Sample	Spiked	Found ^a	Recovery (%)
(ng mL ⁻¹)			
Tap water ^b	0.0	N.D.	–
	10.0	9.6±0.26	96.0
Well water ^c	0.0	4.9±0.15	–
	10.0	15.1±0.30	102.0
River water ^d	0.0	10.3±0.24	–
	10.0	20.1±0.34	98.0
(μg g ⁻¹)			
Human hair	0.0	12.5±0.35	–
	10.0	22.2±0.57	97.0

N.D. not detected

^a Mean±Standard deviation (*n*=3)

^b Kerman drinking water, Kerman, Iran

^c Well water, Shahid Bahonar University of Kerman, Kerman, Iran

^d Sarcheshmeh River, Kerman, Iran

Effect of electrode composition

The effect of ligand amount in the electrode construction was studied. Utilization of dicyclohexyl-18-crown-6 as a modifier ligand can greatly increase the sensitivity of the method. The peak intensity increases with the increasing of ligand amount, so that with 5 and 10 % of dicyclohexyl-18-crown-6, relative to the mass of electrode, the peak intensity attained to the maximum and then decreased. Also, the continuous increasing of modifier amount causes the decreasing of peak current, because the excess of dicyclohexyl-18-crown-6 decreases the modified electrode conductivity. So, 5.0 mg of dicyclohexyl-18-crown-6 was chosen as the optimum amount of the modifier.

Also, the effect of carbon nanotubes on the current intensity was studied in the range of 1.0 to 20.0 mg. The results show that in 10.0–15.0 mg of CNT, the peak current was raised to the maximum level and then decreased. So, 15.0 mg of the CNT was applied in the electrode composition.

Effect of supporting electrolyte

To investigate the accumulation medium effect on the modified electrode response, the different supporting electrolytes including phosphate buffer, potassium nitrate, potassium chloride, and acetate buffer (in all cases, pH was adjusted to 5.0) were applied. As can be seen from Fig. 3, the maximum intensity of peak current and sharpness was obtained with acetate buffer. So, the acetate buffer with pH=5 was selected as the best medium for the accumulation of copper ions.

Effect of accumulation-reduction potential

The effect of accumulation-reduction potential was studied on the peak current of Cu between -0.4 and -1.0 V in sample solution containing 100.0 ng mL⁻¹ of copper in acetate buffer (Fig. 4). Then, Cu(0) was analyzed by DPASV with 30 mV s⁻¹ scan rate, 100 mV pulse amplitude, and 4 ms pulse period. With increasing the potential from -0.4 to -0.8 V, the anodic peak current increased and then decreased in more negative potentials. Therefore, -0.8 V was applied as the optimum accumulation-reduction potential for copper determination.

Effect of accumulation time

The effect of accumulation time on the intensity of the peak current was investigated in the range of 10 to 300 s. Based on the obtained data, the intensity of anodic peak current for Cu(II) was found to increase with increasing time up to 200 s because of saturation of the surface with copper ions and remains constant for longer times. So, 200 s was used for all subsequent experiments.

Table 3 Analysis of copper in standard reference material

Sample	Composition	Found ^a	Recovery (%)
MA-1b reference gold ore	Si;24.5,Al;6.11,Fe;4.62,Ca;4.60 K;4.45, Mg;2.56,C;2.44,Na;1.49 S;1.17,Ti;0.38, Ba;0.18,P;0.16 Mn;0.09 % Cr;200.0,Pb;200.0,Rb;160.0,Zr;140.0 Au;17.0,Zn;100.0,Bi;100.0,Ni;90.0 Mo;80.0,Te;40.0,Co;30.0,Y;20.0 W;15.0,Sc;13.0,As;8.0,Ag;3.9,Sb;3.0 Cu;100.0 $\mu\text{g g}^{-1}$	97.6±2.5	97.6

^a Mean±standard deviation ($n=3$)

Performance characteristics

Several standard solutions containing known amounts of copper were prepared in acetate buffer (pH=5.0) and subjected to the optimized DPASV procedure. As can be seen from Fig. 5, the obtained calibration graph for the determination of copper under the optimized conditions showed the linearity in the range of 4.0–200 ng mL^{-1} . Also, the equation of calibration graph was $\mu\text{A}=1.7764C (\text{ng mL}^{-1})+4.0019$ with $R^2=0.9984$. The detection limit (was determined using a $3s_b/\text{slope}$ ratio where s_b is the standard deviation of the mean value of the blank current) and the precision (expressed as the relative standard deviation (R.S.D.) for seven repetitive measurements) were calculated as 1.1 ng mL^{-1} and $\pm 2.3\%$, respectively. This high precision

indicates a good reproducibility of the modified carbon paste electrode possibly due to the strong adsorption affinity for copper ions at the electrode surface.

Interferences study

Several anions and cations were tested to investigate the possible interferences in copper determination with the proposed electrode. The tolerance level was described as the maximum amount of the interfering ions that can produce an error of $\pm 5\%$ on the Cu(II) peak current. The tolerance level of each ion was tested and if interference was observed, the ratio was diminished until it ceased. For this goal, the effect of several ions, at an initial mole ratio of 500-fold (ion/copper), was studied on the recovery of 100.0 ng mL^{-1} of Cu(II) from

Table 4 Comparison of the MCPE-CNT with other reported electrochemical sensors for the preconcentration of copper

Method	Electrode	RSD (%)	Linear range (ng mL^{-1})	DL (ng mL^{-1})	Ref.
Fluorescence	–	–	0–890	2.38	[26]
Fluorescence	–	–	0– 3.8×10^4	559.2 and 311.4	[27]
Fluorescence	GCE ^a	–	0–635.5	–	[28]
SWAdSV ^b	CSPE ^c	9	–	0.4	[29]
LASV ^d	Gold	–	127.1–1271	8.3	[30]
Potentiometry	CPE ^e	5	$6.34\text{--}6.34 \times 10^5$	5.08	[31]
DPCSV ^f	Platinum	3.77 and 5.91	0.53–107	0.159	[32]
DPASV	CPE	–	>100 and >120	1.10 and 1.45	[33]
DPASV	CPE	3.1	5.02–1017	0.64	[34]
DPASV	CPE	–	3.17–101.7	0.70	[35]
DPASV	CPE	3.7	4.77–159	1.97	[36]
DPASV	CPE	2.4	2–120	0.34	[37]
DPASV	Gold	1.06	3–225	1.26	[38]
DPASV	CPE	–	50.8–635.5	12.7	[39]
DPASV	CPE	2.9	4.45–63.5	1.46	[40]
DPASV	CPE	2.3	4.0–200	1.1	This work

^a Glassy carbon electrode

^b Square wave adsorptive stripping voltammetry

^c Carbon screen printed electrode

^d Linear anodic stripping voltammetry

^e Carbon paste electrode

^f Differential pulse cathodic stripping voltammetry

25.0 mL of sample solution. As the results indicate in Table 1, the Cu(II) recoveries were quantitative in the presence of the extreme amounts of interference species and only five ions including Ni(II), Mg(II), Mn(II), Cd(II) and Fe(II) have interferences at the ratios of 250-, 450-, 300-, 200- and 450-fold, respectively; those are not too high. This indicates that the MCPE-CNT electrode is more selective for Cu(II) determination than the tested potential interfering ions. Thus, the combination of the modified electrode and DPASV is suitable for the preconcentration and determination of copper ions from different matrices.

Analytical applications

In order to evaluate the method validity, MCPE-CNT was used for the preconcentration and determination of copper in water samples (tap water, well water, and river water) and human hair. The method reliability was surveyed with the analysis of the samples spiked with the exact amount of copper. The results presented in Table 2 reveal that the recoveries of the spiked samples at the 95 % confidence level are satisfactory.

To verify the method accuracy, this procedure was applied for the determination of copper in a standard reference material, MA-1b reference gold ore. Analytical results are presented in Table 3 that shows the obtained results are in good agreement with the reference values and there are no significant differences between the obtained results (with the recommended method) and the accepted values. Thus, the method is trustworthy for the analysis of a wide range of samples.

Comparison of MCPE-CNT with some reported modified electrodes

In Table 4, some analytical characteristics of the MCPE-CNT were compared with several modified electrodes that were applied for the determination of copper with different methods [26–40]; the MCPE-CNT electrode shows excellent analytical characteristics. In comparison, between the suggested method and 15 previously reported works, only 5 cases have the better detection limits [29, 32, 34, 35, 37], but these 5 references have the worse RSDs. In the five references [28–30, 32, 38], the applied electrodes are expensive, whereas the suggested method uses the cheapest electrode (CPE). Also, the recommended method has the best RSD except in only one instance [38].

Conclusion

In this study, a modified carbon paste electrode with dicyclohexyl-18-crown-6 and multi-walled carbon nanotubes in combination with differential pulse anodic stripping

voltammetry was applied for the determination of trace amounts of copper. The results confirm this technique is suitable for the determination of Cu(II) in different samples without need of any sophisticated apparatus. This prepared sensor has good performance characteristics such as wide dynamic linear range (4.0–200 ng mL⁻¹) and low detection limit (1.1 ng mL⁻¹). Also, the prepared electrode has a high selectivity coefficient for many potentially interfering ions, because a crown ether was applied as a modifier in the electrode construction. Crown ethers can form complex with only ions in which their sizes are the same as the crown cavity. Therefore, the usage of crown ether improves the method selectivity significantly. This modified electrode, the MCPE-CNT, coupled with DPASV was used in water samples, human hair, and standard reference materials and the obtained results are satisfactory. In addition, the intrinsic advantages of the prepared electrochemical sensor are the simple operation, cheapness, fast response, precise results, and direct utilization for the determination of copper in several matrices.

References

1. Tao Y, Gu X, Pan Y, Deng L, Wei Y, Kong Y, Li W (2015) Overoxidation of conducting polymers combined with in situ plated bismuth film: an approach for simultaneous detection of cadmium and lead ions. *J Electrochem Soc* 162:H194–H199
2. Taher MA, Daliri Z, Fazelirad H (2014) Simultaneous extraction and preconcentration of copper, silver and palladium with modified alumina and their determination by electrothermal atomic absorption spectrometry. *Chin Chem Lett* 25:649–654
3. Vedhi C, Selvanathan G, Arumugam P, Manisankar P (2009) Electrochemical sensors of heavy metals using novel polymer-modified glassy carbon electrodes. *Ionics* 15:377–383
4. Zhang T, Li C, Mao B, An Y (2014) Determination of Cd²⁺ by ultrasound-assisted square wave anodic stripping voltammetry with a boron-doped diamond electrode. *Ionics* 21:1761–1769
5. Germiniano TO, Corazza MZ, Segatelli MG, Tarley CRT (2014) Double-imprinted cross-linked poly(Acrylamide-co-Ethylene Glycol Dimethacrylate) as a novel sorbent for the on-line preconcentration and determination of copper(II) by flame atomic absorption spectrometry. *Anal Lett* 48:61–74
6. Chaiyo S, Siangproh W, Apilux A, Chailapakul O (2015) Highly selective and sensitive paper-based colorimetric sensor using thio-sulfate catalytic etching of silver nanoplates for trace determination of copper ions. *Anal Chim Acta* 866:75–83
7. Fazelirad H, Taher MA, Ashkenani H (2014) Use of nanoporous Cu(II) ion imprinted polymer as a new sorbent for preconcentration of Cu(II) in water, biological, and agricultural samples and its determination by electrothermal atomic absorption spectrometry. *J AOAC Int* 97:1159–1166
8. U.S. Environmental Protection Agency Report EPA/625/R-04/108 (2004)
9. Pineau A, Fauconneau B, Marraud A, Lebeau A, Hankard R, Guillard O (2015) Optimisation of direct copper determination in human breast milk without digestion by Zeeman graphite furnace atomic absorption spectrophotometry with two chemical modifiers. *Biol Trace Elem Res* 166:119–122

10. AlOthman Z, Unsal YE, Habila M, Shabaka A, Tuzen M, Soylak M (2015) Determination of copper in food and water by dispersive liquid-liquid microextraction and flame atomic absorption spectrometry. *Anal Lett* 48:1738–1750
11. Ouyang A, Jiang L, Liu Y, Jiang L, Hao Y, He B (2015) Determination of copper and zinc pollutants in *Ludwigia prostrata* Roxb using near-infrared reflectance spectroscopy (NIRS). *Appl Spectrosc* 69:370–376
12. Hien NK, Bao NC, Nhung NTA, Trung NT, Nam PC, Duong T, Kim JS, Quang DT (2015) A highly sensitive fluorescent chemosensor for simultaneous determination of Ag(I), Hg(II), and Cu(II) ions: design, synthesis, characterization and application. *Dyes Pigm* 116:89–96
13. LaFerriere BD, Maiti TC, Amquist IJ, Hoppe EW (2015) A novel assay method for the trace determination of Th and U in copper and lead using inductively coupled plasma mass spectrometry. *Nucl Instrum Methods Phys Res A* 775:93–98
14. Ali TA, Mohamed GG, El-Dessouky MMI, El-Ella SMA, Mohamed RTF (2013) Modified screen-printed electrode for potentiometric determination of copper(II) in water samples. *J Solution Chem* 42:1336–1354
15. Ghaedi M, Naderi S, Montazerzohori M, Sahraei R, Daneshfar A, Taghavi Moghadam N (2012) Modified carbon paste electrodes for Cu(II) determination. *Mater Sci Eng C* 32:2274–2279
16. Gupta VK, Singh LP, Singh R, Upadhyay N, Kaur SP, Sethi B (2012) A novel copper (II) selective sensor based on dimethyl 4, 4' (o-phenylene) bis(3-thioallophanate) in PVC matrix. *J Mol Liq* 174:11–16
17. Koçak B, Er E, Çelikkhan H (2015) Stripping voltammetric analysis of dicofol on graphene-modified glassy carbon electrode. *Ionics* 21:2337–2344
18. Vu H, Nguyen LH, Nguyen T, Nguyen H, Nguyen T, Tran D (2015) Anodic stripping voltammetric determination of Cd²⁺ and Pb²⁺ using interpenetrated MWCNT/P1,5-DAN as an enhanced sensing interface. *Ionics* 21:571–578
19. Fan W, Wang X, Li X, Xue F (2015) Determination of metallothionein in *Daphnia magna* by modified square wave cathodic stripping voltammetry. *Electrochem Commun* 52:17–20
20. Guha K, Mascarenhas R, Thomas T, D'Souza O (2014) Differential pulse anodic stripping voltammetric determination of Hg²⁺ at poly(Eriochrome Black T)-modified carbon paste electrode. *Ionics* 20:849–856
21. Hevia K, Arancibia V, Rojas-Romo C (2015) Levels of copper in sweeteners, sugar, tea, coffee and mate infusions. Determination by adsorptive stripping voltammetry in the presence of α -lipoic acid. *Microchem J* 119:11–16
22. Jahandari S, Taher MA, Fazelirad H (2014) Evaluation of a new multi-walled carbon nanotube paste electrode modified with Alizarin Red S for the determination of tellurium by differential pulse stripping voltammetry. *Int J Environ Anal Chem* 94:930–942
23. Fazelirad H, Taher MA (2014) Preconcentration of ultra-trace amounts of iron and antimony using ion pair solid phase extraction with modified multi-walled carbon nanotubes. *Microchim Acta* 181:655–662
24. Fazelirad H, Taher MA (2013) Ligandless, ion pair-based and ultrasound assisted emulsification solidified floating organic drop microextraction for simultaneous preconcentration of ultra-trace amounts of gold and thallium and determination by GFAAS. *Talanta* 103:375–383
25. Goswami S, Chakrabarty R (2009) Fluorescence sensing of Cu²⁺ within a pseudo 18-crown-6 cavity. *Tetrahedron Lett* 50:5910–5913
26. Tang Y-H, Qu Y, Song Z, He X-P, Xie J, Hua J, Chen G-R (2012) Discovery of a sensitive Cu(II)-cyanide “off-on” sensor based on new C-glycosyl triazolyl bis-amino acid scaffold. *Org Biomol Chem* 10:555–560
27. Shi D-T, Zhang B, Yang Y-X, Guan C-C, He X-P, Li Y-C, Chen G-R, Chen K (2013) Bis-triazolyl indoleamines as unique “off-approach-on” chemosensors for copper and fluorine. *Analyst* 138:2808–2811
28. Zhang Y-J, He X-P, Hu M, Li Z, Shi X-X, Chen G-R (2011) Highly optically selective and electrochemically active chemosensor for copper (II) based on triazole-linked glucosyl anthraquinone. *Dyes Pigm* 88:391–395
29. Faucher S, Cugnet C, Authier L, Lespes G (2014) Determination of total and extractable copper in agricultural soil by using disposable modified-carbon screen-printed electrodes. *Anal Bioanal Chem* 406:1249–1252
30. Dai X, Compton RG (2005) Determination of copper in the presence of various amounts of arsenic with L-cysteine modified gold electrodes. *Electroanalysis* 17:1835–1840
31. Javanbakht M, Badiei A, Ganjali MR, Norouzi P, Hasheminasab A, Abdouss M (2007) Use of organofunctionalized nanoporous silica gel to improve the lifetime of carbon paste electrode for determination of copper(II) ions. *Anal Chim Acta* 601:172–182
32. Attar T, Dennouni-Medjati N, Harek Y, Larabi L (2013) The application of differential pulse cathodic stripping voltammetry in the determination of trace copper in whole blood. *J Sens Instrum* 1:31–38
33. Ashrafi AM, Vytras K (2012) New procedures for voltammetric determination of copper (II) using antimony film-coated carbon paste electrodes. *Electrochim Acta* 73:112–117
34. Janegitz BC, Marcolino-Junior LH, Campana-Filho SP, Faria RC, Fatibello-Filho O (2009) Anodic stripping voltammetric determination of copper(II) using a functionalized carbon nanotubes paste electrode modified with crosslinked chitosan. *Sens Actuators B* 142:260–266
35. Canpolat EC, Sar E, Coskun NY, Cankurtaran H (2007) Determination of trace amounts of copper in tap water samples with a Calix[4]arene modified carbon paste electrode by differential pulse anodic stripping voltammetry. *Electroanalysis* 19:1109–1115
36. Takeuchi RM, Santos AL, Padilha PM, Stradiotto NR (2007) Copper determination in ethanol fuel by differential pulse anodic stripping voltammetry at a solid paraffin-based carbon paste electrode modified with 2-aminothiazole organofunctionalized silica. *Talanta* 71:771–777
37. Ashkenani H, Taher MA (2012) Selective voltammetric determination of Cu(II) based on multiwalled carbon nanotube and nanoporous Cu-ion imprinted polymer. *J Electroanal Chem* 683:80–87
38. Mohadesi A, Taher MA (2007) Voltammetric determination of Cu(II) in natural waters and human hair at a meso-2,3-dimercaptosuccinic acid self-assembled gold electrode. *Talanta* 72:95–100
39. Cesarino I, Marino G, do Rosario Matos J, Cavaleiro ETG (2008) Evaluation of a carbon paste electrode modified with organofunctionalised SBA-15 nanostructured silica in the simultaneous determination of divalent lead, copper and mercury ions. *Talanta* 75:15–21
40. Zhihua W, Xiaole L, Jianming Y, Yaxin Q, Xiaoquan L (2011) Copper(II) determination by using carbon paste electrode modified with molecularly imprinted polymer. *Electrochim Acta* 58:750–756