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Original scientific paper

Preparation and characterization of selective electrode for determination of copper ion(II)

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Abstract
A chemically modified carbon paste electrode with diphenyl carbazide the potentiometric determination of Cu(II) is demonstrated. The electrode exhibits linear response to Cu(II) over a wide concentration range (9.2×10^{-7} - 5.0×10^{-1}) with Nernstian slope of 30±0.15 mV per decade. It has a response time of about 40 s and can be used for a period of two months with good reproducibility. The detection limit of this electrode was 7.0×10^{-7} M. The proposed electrode shows a very good selectivity for Cu(II) over a wide variety of metal ions. This chemically modified carbon paste electrode was successfully used for the determination of Cu(II) in various water samples solution and pharmaceutical formulation.

Keywords
Diphenyl carbazide; Copper; Potentiometric; Method validation

Introduction

A few years ago chemically modified carbon paste electrodes (CMCPEs) were applied to analytical determinations.

Copper is an essential element and is also toxic. Copper is one of the important and essential nutrients for human health as well as the growth of animals and plants [1-7]. Copper is required for normal metabolic processes. Copper combines with certain proteins to produce enzymes that act as catalysts to help a number of body functions. Copper helps provide energy required by biochemical reactions. Although copper is an essential micronutrient and is required by the body in very small amounts, excess copper in the human body can cause stomach and intestinal distress such as nausea, vomiting, diarrhea, and stomach cramps. The lowest level at which these adverse effects occur has not been well defined. Copper is also a commonly occurring element in natural waters.

Several analytical techniques have been monitored for the determination of copper(II) in different matrices. The common methods for the detection of copper (II) and other metals include liquid chromatography [8], electrophoresis [9,10], Electrochemical [11-13], spectrophotometry [14-18], solid-phase extraction coupled with atomic absorption spectroscopy [19], flame atomic absorption spectrometry [20] atomic emission spectroscopy [21], inductively coupled plasma mass spectrometry [22], and flow injection analysis [23]. Copper is an industrially important metal and it is used in coin making, wire making, medicine, alloys, fashioning metal products, transportation industry and thermal conductance. However, even if these methods present high sensitivity and selectivity, they are expensive, time-consuming and cannot be used for in situ analyses. Therefore, there is a growing interest in developing electrochemical methods for the detection of copper ions in different matrices.

The purpose of the present work is to obtain a better selective modified electrode based on diphenyl carbazide (DPHCZ) for Cu(II) ion. It can be blend with graphite and paraffin oil to make a very highly reproducible copper selective electrode. In this work we are introducing a very simple and inexpensive (potentiometric) method for determination of copper(II) in wide concentration range and in presence of variety of metal ions with minimum number of interferences.

Experimental

Reagents

All reagents used were analytically pure grade and doubly distilled water was used throughout. Pure graphite powder (Merck), paraffin oil (Fluka) were used for the preparation of carbon paste electrode. DPHCZ (Merck), Tetrahydrofuran (THF) (Fluka). All other solutions used in interference studies were prepared from analytical grade nitrate salts from analytical grade nitrate salts (all from Merck company).

Apparatus

Potentiometric and pH measurements was carried out using a digital Shott Gerate pH meter (Consort C 830, Belgium) with combined glass pH electrode. A water bath shaker (Grant instruments, Cambridge Ltd, England) was used to control the temperature of the test solutions. A saturated calomel electrode (SEC) was used as the external reference (Mettler, Switzerland). The electrochemical system may be represented as follows:

carbon paste electrode/test solution/saturated calomel electrode .

FT-IR 4100 (Fourier Transform Infrared Spectrometer) Jasco using KBr disk in the range 4000 - 400 cm^{-1}, Nernst glower, deuterium try glycine sulfate (DTGS), 0.1 cm^{-1}.

Preparation of solutions

Solutions were prepared from a stock solution of 0.50 M copper(II), prepared from a sufficient quantity of copper(II) nitrate in triple distilled deionized water (0.01 µs) and titrated with a standard solution of EDTA using Murexide as indicator. The solution was placed in the dark and protected against light. The working solutions were prepared daily by suitable dilution of stock solution potassium nitrate (1 M) solution was prepared and used as supporting electrolyte, to maintain constant ionic strength. All other solutions used in interference studies were prepared by dissolving the appropriate amount of the compounds, and the diluted solutions from these were prepared by subsequent dilutions of the stock solutions.

Preparation of complex (Cu -DPHCZ)

Complex (Cu-DPHCZ) was prepared by mixing equal volumes of 10^{-2} M solution of Cu^{2+} with methanolic solution of DPHCZ with stirring, then we evaporate methanol gradually to obtain a precipitate. IR data (Figure 1) of Cu -DPHCZ is shown in Table 1.

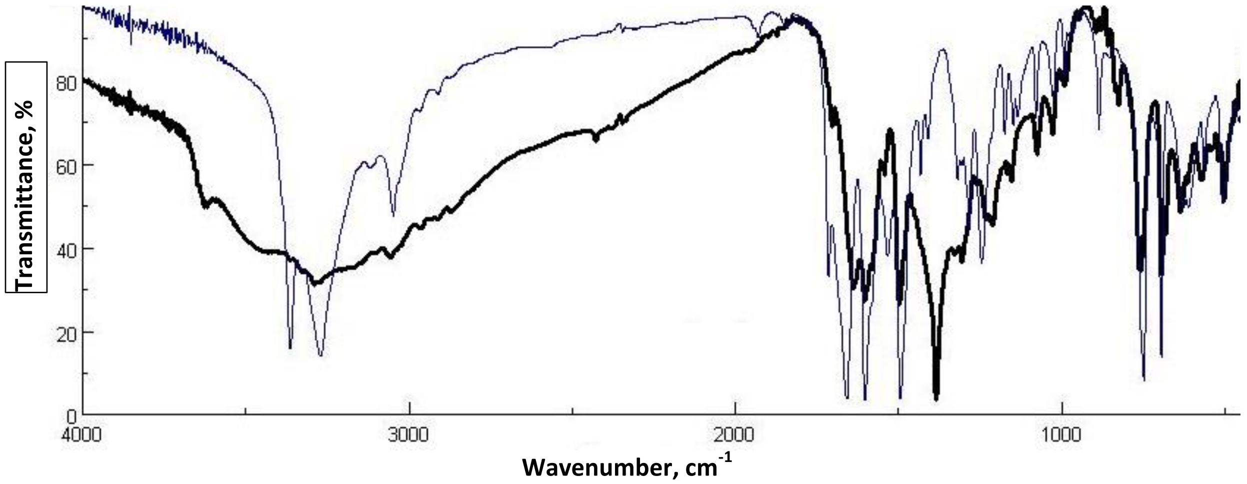

Figure 1. *IR spectrum of DPHCZ (black light spectrum), Cu- DPHCZ (black dark spectrum)*

Table 1*. IR data for DPHCZ and Cu-DPHCZ complex*

	Wavenumber, cm^{-1}	
	DPHCZ	Cu –DPHCZ
N-H	3363-3270	---
C-N	1281	1384
C=O	1666	1637
Aromatic	1500-1600	1500-1600

Preparation of chemically modified carbon paste CMCPE and construction of Cu electrode.

Pure graphite powder (2.375 g) and 0.75 g of Cu-DPHCZ was mixed in a 25 ml beaker and 5–10 ml of THF was added and shaked by sonication for 15–20 min. The mixture was left for a long time to evaporate THF. After complete evaporation of the THF 0.75 g of liquid paraffin was added to the mixture and then mixed well to form a uniform paste. Electrode bodies were made from a disposable 1 ml polyethylene syringes the tip of which had been cut off with a razor blade. These bodies were filled with approximately 0.3 ml of CMCPE. Smooth surfaces were obtained by applying manual pressure to the piston while holding the electrode surface against a smooth solid support. A fresh electrode surface was obtained by squeezing out a small amount of paste, scrapping 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. Electrode potential was measured against the SCE as the reference electrode.

Selectivity of sensors

Potentiometric selectivity coefficient, $K_{A\,B}^{MPM}$, of an ion-selective electrode (ISE) was commonly used as quantitative expression of the ability of the electrode to respond primarily to the analyze ion in the presence of interfering ions. The effect of the presence of some different species on the response of Cu^{2+} electrode was investigated, and the selectivity coefficient, K_{AB}^{MPM}, of the proposed electrode was calculated in the presence of related organic and inorganic substances using matched potential method (MPM) [24-25]. The selectivity coefficient which was measured by matched potential method was calculated according to the following equation:

$$K_{\mathrm{AB}}^{\mathrm{MPM}} = \frac{a'_{\mathrm{A}} - a_{\mathrm{A}}}{a_{\mathrm{B}}} \tag{1}$$

where a'_{A} is the known activity of primary ion, a_{A} is the fixed activity of primary ion, and a_{B} is the activity of interfering ions.

General procedure

The performance of the electrode prepared was investigated by measuring *emf* values of 9.2×10^{-7} - 5×10^{-1} M of Cu^{2+}. The electrode was calibrated by added volumes of 50 mM stock solution of Cu^{2+} successively in 50 ml of water to generate a total concentration ranging from 9.2×10^{-7} - 5×10^{-1} M Cu^{2+}, followed by immersing the Cu^{2+} electrode, together with a calomel reference electrode in the solution. The potential reading was recorded after stabilization, and the e.m.f was plotted as a function of the logarithm of the Cu^{2+} concentration. The concentration graph was used for subsequent determinations of unknown Cu^{2+} concentrations.

Potentiometric determination of Cu

Copper was determined potentionmetrically by the direct and standard addition methods [26-27]. In this method the proposed electrode (Cu-DPHCZ) was immersed into a sample of 15 ml with an unknown concentration of a Cu^{2+} solution, and the equilibrium potential of E_{u} was recorded. Then 1 ml of 50 mM of standard Cu^{2+} was added into the testing solution and the equilibrium potential of E_{s} was obtained. From the potential change, $\Delta E = E_{\mathrm{u}} - E_{\mathrm{s}}$, we could determine the concentration of the testing sample using the equation:

$$c_{\mathrm{x}} = \frac{c_{\mathrm{s}} V_{\mathrm{s}}}{(V_{\mathrm{x}} + V_{\mathrm{s}}) \times 10^{\Delta E/S} - V_{\mathrm{x}}} \tag{2}$$

Where c_{x} and V_{x} are concentration and volume of an unknown sample, c_{s} and V_{s} are concentration and volume of the standard, respectively. S is the slope of the calibration graph (slope of the electrode response), and ΔE / mV is the difference between *e.m.f.* after and before addition of the standard solution.

Results and discussion

Optimization of the amount of modifier in the electrode.

For this purpose seven electrodes were prepared. The amounts of carbon powder and paraffin oil were constant in each electrode. The proportions of modifier in these seven electrodes were, 5.0, 7.5, 10.5, 12.5, 15.0, 17.5, and 20.0 % of weight percentage of ionophore. The resulting Nernstian slopes and correlation coefficients are shown in Table 2. These results show that by increasing the percentages of modifier up to 12.5 % the slopes decrease sharply, but within 15-20 % the slopes are becoming more Nernstian and slopes of the electrode are only slightly changed. Electrodes with less than 15.0 % of modifier show super Nernstian slopes, since in these compositions electrodes behave mostly as a pure carbon paste electrode [28]. By using more than 25.0 % of the modifier non linearity in the in the electrode response was observed. Since electrode with 15 % of ionophore has a good slope and the amount of the ionophore was less than the other Nernstian electrode this percentage was chosen as the optimum amount for the copper electrode.

Table 2. *The paste compositions and the electrode characteristics of copper(II) sensor*

	Composition, % w/w				
Electrodes	**Ionophore**	**Graphite**	**Paraffin**	**Slope, mV decade-^{1}**	**Detection limit, M**
I	5.0	47.50	47.50	52.15	5.39×10^{-5}
II	7.5	46.25	46.25	51.02	8.12×10^{-6}
III	10.5	44.75	44.75	46.22	4.03×10^{-6}
IV	12.5	43.75	43.75	37.91	9.23×10^{-7}
V	**15.0**	**42.50**	**42.50**	**30.15**	**7.00×10^{-7}**
VI	17.5	41.25	41.25	29.94	6.61×10^{-7}
VII	20.0	40.00	40.00	29.57	5.35×10^{-7}

Effect of ionic strength on the response of the electrode

The effect of ionic strength (0.1–0.5 M KNO_3) on the calibration curve of copper electrodes was investigated. The electrode response is slightly changed within the 0.1– 0.5 M KNO_3 electrolyte solution. However, we choose 0.3 M as an optimum value, since in this ionic strength the linear range was wider than for the other concentrations

Response of electrode to various cations

The potential responses of various chemically modified CMEs based on DPHCZ are shown in Figure 2. The copper selective electrode exhibited linear response to the logarithm of the activity of Cu^{2+} within the concentration range of 9.2×10^{-7} - 5×10^{-1} M of $Cu(NO_3)_2$ with Nernstian slope of 30±0.15 mV per decade and correlation coefficient of 0.996.

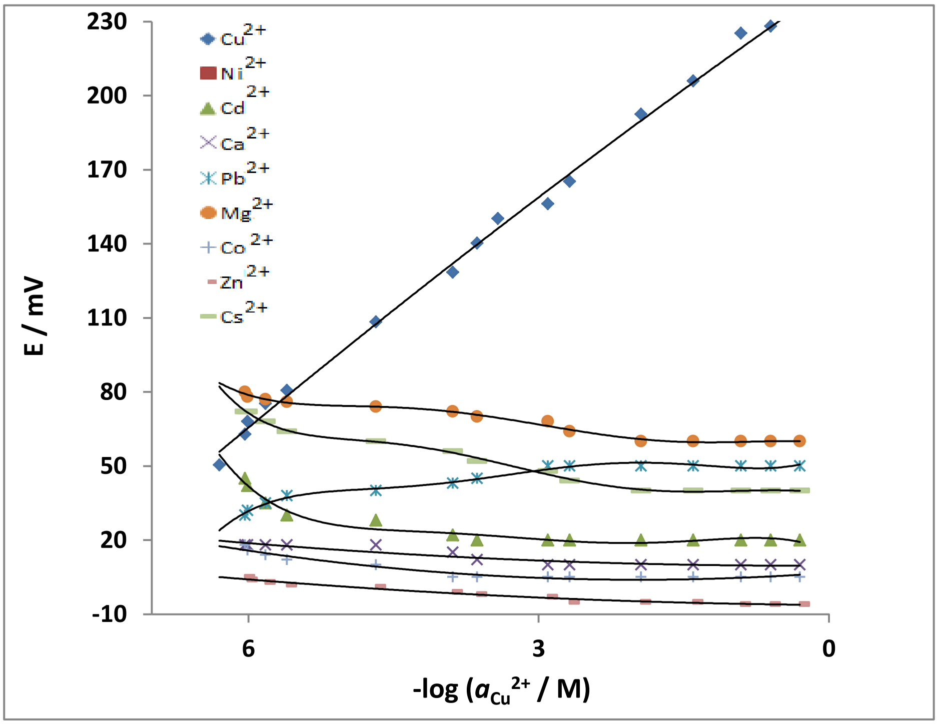

Figure 2*. Schematic diagram of electrode response to various cations*

Optimization of pH

The behavior of the copper electrode in relation to the variation of pH (1–12) was studied. The composition of the electrode and the ionic strength of the solution were kept constant during all experiments. The results showed that the electrode response is more Nernstian at lower pHs (≤ 6). Since at higher pHs (≥ 6) copper will precipitate as copper hydroxide, the electrode has a better characteristic response (pH 4 offered a better slope and a wider linear range than in the other pH values), therefore, we chose pH 4 as an optimum condition for this electrode (Figure 3).

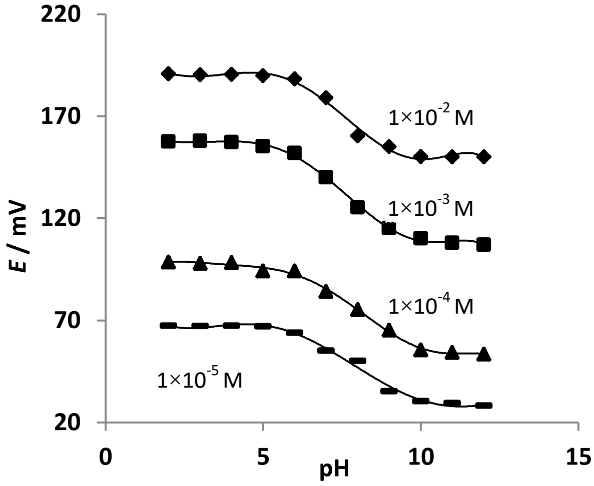

Figure 3. *Effect of the pH on the response of the electrode*

Calibration graphs

Using the optimized composition and conditions described above, the potentiometric response of the electrode was studied based on the Cu concentration in the range of 5.0×10^{-7} - 5.5×10^{-1} M. The calibration curves for the electrodes containing 15 % of ionophore gave an excellent linear response from 9.2×10^{-7} - 5.0×10^{-1} M, as shown in Fig. 4. The results given in Table 3 show the characteristics performance of the electrode.

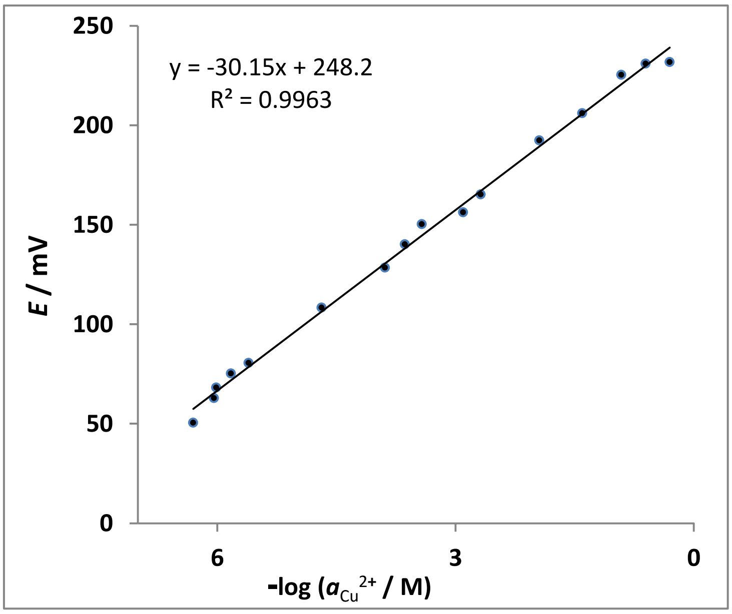

Figure 4. *Calibration graph of Cu electrode*

Table 3. *Response characteristics of electrodes*

Electrode	15 % -ionophore
Plasticizer	paraffin oil
Parameter	
Slope, mV decade^{-1}	30.15
Correlation cofficient	0.996
Linearity range, M	9.2×10^{-7}-5.0×10^{-1}
Lower detection limit, M	7.00×10^{-7}
Response time, s	t ≤40
Working pH range	2-6
Temperature, °C	25
Life time, day	61

Response characteristics of modified and unmodified carbon paste electrodes

The unmodified electrode shows no response under the optimum condition. The response time of the modified electrode is measured according to IUPAC recommendation. The response time in variation of concentration from 1×10^{-5} to 1×10^{-1} M Cu^{+2} is shown in Figure 5; the measured response time was 40 s.

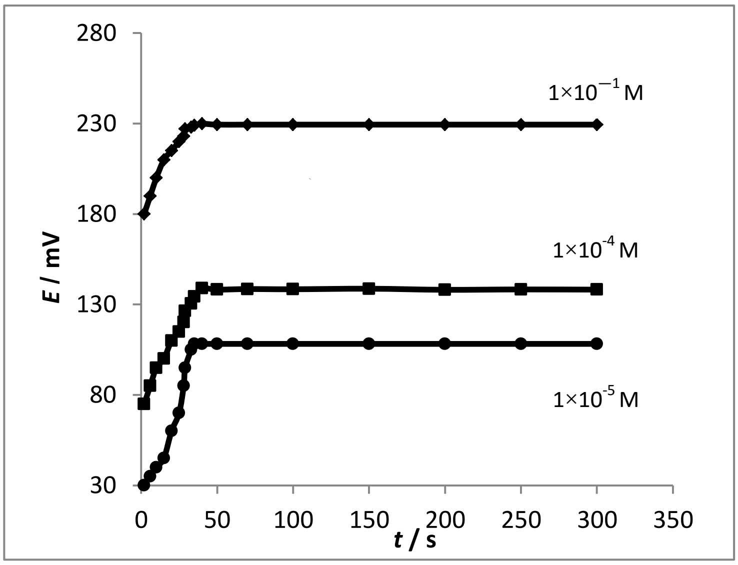

Figure 5. *Response time of electrode*

Lifetime

The electrode lifetime was investigated by performing the calibration curve and the periodic testing of standard solutions (9.0×10^{-7} - 2.5×10^{-1} M) and calculating the response slope. It was observed that the electrode exhibits a good stability in terms of slope in the linear domain of concentration and the electrode can be used continuously for about 61 days without considerable decrease in its slope value.

Selectivity of electrode

The influence of some inorganic cations such as of Li^+, Na^+, K^+, Ca^{2+}, Zn^{2+}, Ba^{2+}, Mn^{2+}, Mg^{2+}, Ni^{2+}, NH^{4+}, Pb^{2+}, Co^{2+}, Fe^{3+}, Al^{3+} and Cr^{+3} on the electrode response was investigated. The selectivity of the electrode was measured by applying the matched potential method (MPM). According to this method, the activity of Cu^{2+} was increased from a_A = 1 mM (reference solution) to a'_A = 1.1 mM, and the changes in potential (Δ*E*) corresponding to this increase were measured. Then a solution of an interfering ion of concentration aB is added to a new 1 mM reference solution until the same potential change (Δ*E*) was recorded. The selectivity factor, K_{AB}^{MPM}, for each interference was calculated using Equation (1). The results are given in the Table 4. Results revealed reasonable selectivity for Cu^{+2} in presence of many related substances. The selectivity coefficient obtained by this method showed that there were no significant interferences from the cations; this reflected a very high selectivity of the investigated electrode towards Cu.

Table 4. *Selectivity coefficients for the Cu-DPHCZ responsive electrode*

Interferent	K_{AB}^{MPM}	Interferent	K_{AB}^{MPM}
Na^{1+}	-	Hg^{2+}	-
K^{1+}	1.12×10^{-7}	Zn^{2+}	1.12×10^{-4}
Ag^{1+}	-	pb^{2+}	9.74×10^{-5}
NH_4^+	-	Cs^{2+}	3.37×10^{-7}
Mg^{2+}	1.01×10^{-7}	Al^{3+}	2.51×10^{-7}
Ca^{2+}	1.17×10^{-5}	Cr^{3+}	1.85×10^{-7}
Ba^{2+}	6.25×10^{-7}	Fe^{3+}	3.35×10^{-6}
Ni^{2+}	6.30×10^{-6}	Cd^{2+}	1.33×10^{-4}
CO^{2+}	1.00×10^{-5}	Mn^{2+}	3.33×10^{-6}

Electrode renewal and its reproducibility

The electrode surface should be renewed when the copper solution is changed from higher to lower concentration to remove residual copper adsorbed on the surface of carbon paste electrode. This process improves reproducibility which was tested by using four similar carbon paste electrodes at the same time to determine 5×10^{-4} M Cu^{2+}. As results (148.1, 147.5, 148.4, 146.9 and 147.5 mV) illustrate all electrodes show similar potential response with a standard deviation of 0.84. To evaluate the reproducibility of *emf* response of the cell assembly alternating measurements were performed in 5×10^{-5} and 5×10^{-2} M of copper solution. The procedure was repeated five times and the results are given in (Table 5).

Table 5. *Alternating measurements in 5×10^{-5}M and 1×10^{-2}M copper solutions*

c / M	E_1 / mV	E_2 / mV	E_3 / mV	E_4 / mV	E_5 / mV	SD, mV	RSD, %
5×10^{-5}	117.9	117.2	117.6	117.5	116.8	0.42	0.36
5×10^{-4}	148.1	147.5	148.4	146.9	147.5	0.58	0.40
5×10^{-3}	178.2	177.3	178.3	176.4	176.8	0.84	0.47
5×10^{-2}	208.4	209.2	210.2	210.9	207.4	1.39	0.67

Validity of the proposed method

The accuracy and precision of the proposed methods were carried out by five determinations at three different concentrations using both direct and standard addition methods. The precision and accuracy of the method expressed as percentage relative standard deviation as precision, and percentage of deviation of the measured concentration (recovery, %) as accuracy. The results obtained are within the acceptance range. Average recovery of 100.80-101.91 %, percentage relative standard deviation, RSD = 1.58-0.44 %. Table 6 shows the values of RSD and R for different concentrations of the Cu^{+2} determined from the calibration curves and by using standard addition methods. The accuracy and precision show that the electrode has a good repeatability and reproducibility. The proposed electrode was found to be selective for the estimation of $Cu^{2+.}$

Table 6. *Accuracy and precision for the determination of Cu^{2+} using the proposed electrode in pure solution*

	Direct mothed				**Standard-addition method**			
Taken amount of Cu, M	**C_{Cu} / M**	**SD, M**	**RSD, %**	**R, %**	**C_{Cu} / M**	**SD, M**	**R, %**	**RSD, %**
2.00×10^{-6}	2.03×10^{-6}	3.21×10^{-8}	1.58	101.91	2.03×10^{-6}	1.92×10^{-8}	101.90	0.94
2.00×10^{-4}	2.01×10^{-4}	2.16×10^{-6}	1.08	100.52	2.01×10^{-4}	1.64×10^{-6}	100.90	0.81
2.00×10^{-2}	2.01×10^{-2}	1.36×10^{-5}	0.68	100.52	2.01×10^{-2}	8.94×10^{-5}	100.80	0.44

Average of five determinations

Determination of copper ions in various water samples

The proposed Cu-electrode was found to work well under laboratory conditions. It was successfully applied to the determination of copper ions in tap water and well water using the direct and standard additions methods. The analysis of samples does not required pretreatment for poteniometric determination using the present electrode.

It has been also used for the potentiometric determination of copper(II) in pharmaceutical preparations (New Bonacare, Daily Vit) by applying two methods. The obtained average recovery, relative standard deviation and confidence limit values are summarized in Tables 7 and 8, which reflect the high accuracy and precision of the electrode

Table 7. *Determination of copper (II) in various water samples*

Sample	**Direct**			**Standard addition**		
	$c_{Cu}{}^{2+}$ / mol L^{-1}	**CL, mol / L^{a}**	**RSD, %**	**$c_{Cu}{}^{2+}$ / mol L-^{1}**	**CL, mol/L**	**RSD, %**
Tap water	1.10×10^{-6}	1.10×10^{-6} $\pm1.43\times10^{-8}$	1.04	9.23×10^{-7}	9.23×10^{-7} $\pm3.13\times10^{-8}$	2.72
Well water	2.11×10^{-5}	2.11×10^{-5} $\pm2.59\times10^{-7}$	0.98	1.99×10^{-5}	1.99×10^{-5} $\pm1.90\times10^{-7}$	0.76
Well water	1.57×10^{-6}	1.57×10^{-6} $\pm1.90\times10^{-8}$	0.96	1.48×10^{-6}	1.48×10^{-6} $\pm1.24\times10^{-8}$	0.67

[a]*Five independent analyses. CL - Confidence Limit; t = 2, for four degree of freedom and 95 % confidence limit).*

Table 8. *Determination of copper (II) in different pharmaceutical formulations.*

Formulation	Label claim	Proposed Electrode			
		Potentiometry			
		Direct		**Standard addition**	
		Detected Cu^{2+}, % ± SD [a]	RSD, %	Detected Cu^{2+}, % ± SD [a]	RSD, %
New Bonacare[b]	60 mg / tablet	100.94±0.83	1.27	99.84± 0.10	0.15
Daily Vit[c]	2 mg / tablet	99.73±0.01	0.50	100.82±0.02	1.02

[a]*Five independent analyses;* [b]*Supplied by aphamia, Syria;* [c]*Supplied by biomedpharma products, Syria.*

Conclusions

The proposed electrode based on Cu-DPHCZ as the electroactive compound can be used as an interesting alternative analytical tool for the determination of copper(II) in pure solutions, pharmaceutical preparations and water samples. The electrode showed a Nernstian slope of 30.0±0.15 mV decade^{-1}, a wide concentration range from 9.2×10^{-7} to 5.0×10^{-1} mol L^{-1}, a low detection limit of 7.00×10^{-7} mol L^{-1} and a short response time (≤ 40 s) over the pH range 2.0-6.0. The proposed potentiometric method offers the advantages of simplicity, accuracy and applicability to turbid and sample solutions

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