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Original Article

Rapid determination of trace level copper in tea infusion samples by solid contact ion selective electrode



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ABSTRACT

A new solid contact copper selective electrode with a poly (vinyl chloride) (PVC) membrane consisting of *o*-xylylenebis(*N,N*-diisobutyldithiocarbamate) as ionophore has been prepared. The main novelties of constructed ion selective electrode concept are the enhanced robustness, cheapness, and fastness due to the use of solid contacts. The electrode exhibits a rapid (< 10 seconds) and near-Nernstian response to Cu²⁺ activity from 10⁻¹ to 10⁻⁶ mol/L at the pH range of 4.0–6.0. No serious interference from common ions was found. The electrode characterizes by high potential stability, reproducibility, and full repeatability. The electrode was used as an indicator electrode in potentiometric titration of Cu(II) ions with EDTA and for the direct assay of tea infusion samples by means of the calibration graph technique. The results compared favorably with those obtained by the atomic absorption spectroscopy (AAS).

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1. Introduction

Tea prepared from dried leaves of the *Camellia sinensis* plant is the most widely consumed nonalcoholic beverage worldwide because of its aroma, taste, smell, and multiple positive health-promoting effects [1,2]. Tea is consumed in the form of infusions worldwide from ancient times as a delectable item or as a natural medicine. Tea infusions are usually prepared by soaking the cured leaves, leaf buds, and internodes into boiling water. The hot water extracts various classes of

organic compounds, certain amounts of major, minor, and trace elements including metals. The chemical components of tea leaves and their infusions have attracted an ever-increasing attention because of their relation to health and disease. For these reasons, determination of heavy metals such as arsenic, chromium, cadmium, lead, copper, etc. in tea and tea infusion samples are important [3–5].

Copper is an essential trace element in biological systems and in living organisms where it serves as a cofactor in at least 30 important enzymes [6]. Despite copper being an essential

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element for humans, it is also toxic at elevated concentrations and is known to cause gastrointestinal catarrh, Wilson disease, hypoglycemia, and dyslexia [7,8].

There are several techniques, which have been used for the determination of copper in solution including flame atomic absorption spectroscopy (FAAS) [9], stripping voltammetry [10,11], inductively coupled plasma-mass spectrometry (ICP-MS) [12], spectrophotometry [13], and chromatography [14]. Most of the mentioned methods have drawbacks such as high cost of equipment and expensive materials, time-consuming, and complicated operation.

Application of ion-selective electrodes (ISEs) continues to be an interesting area of analytical research [15–17]. A number of Cu(II) selective electrodes have been developed using solid membranes of insoluble salts of copper, copper chelates, macro cyclic polyethers, noncyclic neutral ionophores containing dithiocarbamate groups, Schiff bases, calixarenes, sol-gel-coated wire, and some liquid membrane sensors using Cu(II) complexes have also been reported [18–28]. Among these ISEs, the solid-contact ones (SC-ISEs) have attracted extensive attention for the past few years [29,30]. Solid contact electrodes offer several advantages over the conventional electrodes regarding their simple construction, robustness, miniaturization, lower cost of production, and no risk of inner filling solution leakage problem. Furthermore, this type of electrode allows for low detection limit, wide measuring range, and working pH range [31–35].

In this paper, a new solid contact copper selective electrode with a PVC membrane consisting of *o*-xylylenebis(*N,N*-diisobutyldithiocarbamate) as ionophore has been prepared as an alternative copper selective electrode. The potentiometric properties of the electrode was investigated and applied to the assay of tea infusion samples. However, it has been demonstrated that the solid contact improved the analytical parameters of the electrode such as, response time and working pH range.

2. Methods

2.1. Materials

Tetrahydrofuran (THF), high molecular weight poly(vinyl chloride) (PVC), 2-nitrophenyl octyl ether (NPOE), potassium tetrakis (*p*-chlorophenyl) borate (KTpClPB), *o*-xylylenebis(*N,N*-diisobutyldithiocarbamate), and graphite were purchased from Fluka (Buchs, Switzerland). Epoxy (Macroplast Su 2227) and hardener (Desmodur RFE) were purchased from Henkel (Istanbul, Turkey) and Bayer AG (Darmstadt, Germany). All solutions were prepared from analytical-reagent grade salts using distilled deionized water. The chloride or nitrate salts of all cations (from Merck, Darmstadt, Germany) were used in all instances.

2.2. Apparatus and electrochemical measurements

A laboratory-made computer-controlled high-input impedance eight-channel potentiometric system was used for the potential measurement. The data output was recorded by a home-made software program. All the electromotive forces (Emf) were

measured relative to a saturated Ag–AgCl reference electrode (Gamry, Warminster, PA, USA) in solutions stirred with a magnetic stirrer. The pH of the solutions was adjusted by using a glass pH electrode (SI Analytics GmbH, Mainz, Germany) with a Jenway 3040 model Ion Analyzer (Bibby Scientific Limited, Staffordshire, UK). Solutions at required concentrations were homogenized using an Ultrasonic LC30 stirrer (Elma Hans Schmidbauer GmbH & Co. KG Kolpingstr, Singen, Germany).

Potentiometric measurements were carried out with the following cell assembly: SC-ISE | test solution | Ag–AgCl, KCl (saturated). The cell consists of SC-ISE as the indicator electrode, a saturated Ag–AgCl reference electrode, and a magnetic stirrer. The performance of the electrode was investigated by measuring the Emf's of copper nitrate solutions prepared in the concentration range 10^{-1} – 10^{-7} mol/L by serial dilution. All measurements were carried out at room temperature. Reference and indicator electrodes were washed with deionized water and dried with adsorbent tissue before each measurement of the solutions.

A Unicam 929 Model (Analytical Technology Inc., Collegeville, PA, USA) flame atomic absorption spectrophotometer, equipped with an air–acetylene flame burner and a deuterium continuous source background corrector was used for the determination of Cu(II). All operating conditions were as follows: wavelength, 324.8; lamp current (mA) 5, and slit width 0.5 nm.

Elga PureLab Option Q Water Purification System (Elga Process Water, Buckinghamshire, UK) was used for the purification of the water.

2.3. Electrode construction

A solid contact copper selective electrode was constructed as described in our previous works [35,36]. A conductive material was prepared by mixing 50% (w/w) graphite, 35% (w/w) epoxy, and 15% (w/w) hardener in sufficient THF. The mixture was allowed to stand in air until the appropriate viscosity was attained. A shielded copper wire was dipped into this mixture a few times to obtain a uniform solid contact with coating thickness of ~0.2 mm and then allowed to stand overnight in room temperature.

The ion selective membrane contained ionophore: PVC:KTpClPB:NPOE in the ratio of 6.9:57.2:1.6:34.9 (w/w; mg). The membrane solution was prepared by dissolving of the membrane components in 2.0 mL THF. Solid contacts were dipped into the membrane solution at least three times and then coated membranes were allowed to dry in air for at least 1 day. The schematic procedure for the preparation of solid contact electrode is shown in Figure 1. The dried membrane electrodes were soaked in a 1×10^{-2} mol/L $\text{Cu}(\text{NO}_3)_2$ solution for 1 day before use. The prepared electrodes were stored in laboratory conditions, when not in use. Before individual measurement process, the electrodes were reconditioned for at least half an hour in a 1.0×10^{-2} mol/L $\text{Cu}(\text{NO}_3)_2$ solution. Three identical electrodes were prepared and subjected to the same studies.

2.4. Sample preparation and determination

Four different tea samples were bought in a market place. For the preparation of tea infusion sample; extraction was

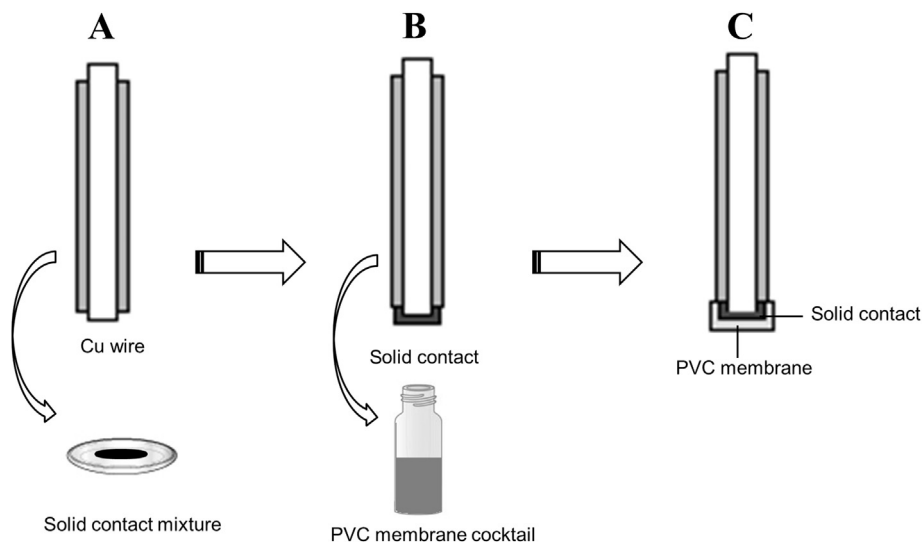


Figure 1 – The schematic procedure for the preparation of solid contact electrode.

performed using 5 g tea with 200 mL distilled boiled water with a 10-minute infusion period. The pH of the all samples was adjusted to 4.5. The pH was adjusted by the addition of 0.1 mol/L nitric acid or sodium hydroxide. The concentration of copper was then determined for each tea sample by prepared ion selective electrode.

3. Results and discussion

Potentiometric properties of solid contact copper selective electrode with a PVC membrane were investigated. Commercially available ionophore *o*-xylylenebis(*N,N*-diisobutyldithiocarbamate) was used as a potential creating membrane component [37]. The critical response characteristics of the

solid contact copper-selective electrode were systematically assessed according to the International Union of Pure and Applied Chemistry (IUPAC) recommendations [38–40].

The potentiometric performance of the electrode was investigated by measuring the Emf's of copper nitrate solutions prepared in the concentration range 10^{-1} – 10^{-7} mol/L by serial dilution. The obtained calibration plot for the electrode is presented in (Figure 2). For the electrolyte activities from 1.0×10^{-6} and 1.0×10^{-1} mol/L, the solid contact copper-selective electrodes exhibit linear responses with a near-Nernstian slope of 31.28 mV/dec ($R^2 = 0.996$). The limit of detection, as calculated from the intersection of two extrapolated segments of the calibration curve, was 4.9×10^{-7} mol/L.

In order to check the effect of pH on the proposed electrode, the potentials of the membrane electrodes were

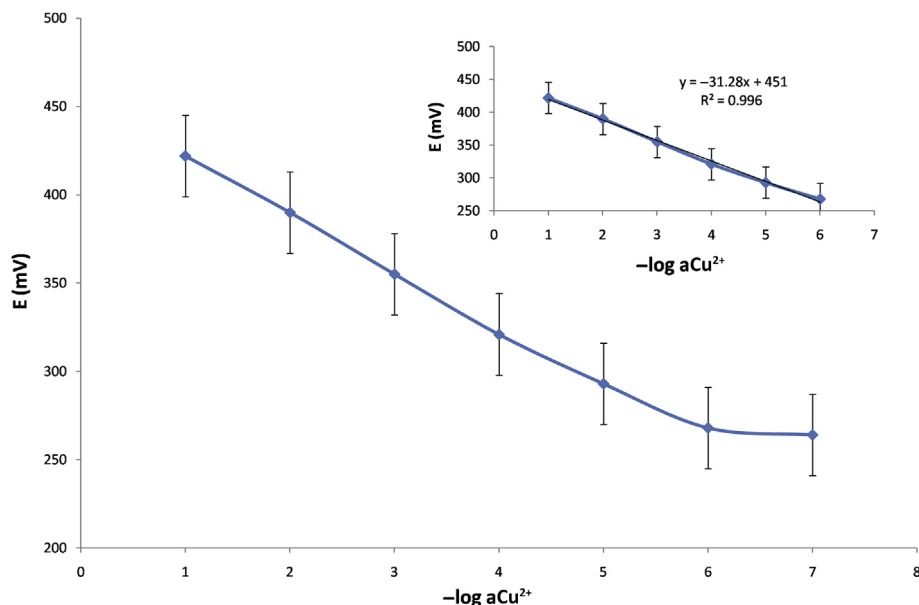


Figure 2 – The potentiometric response and calibration plot of the Cu^{2+} -selective electrode.

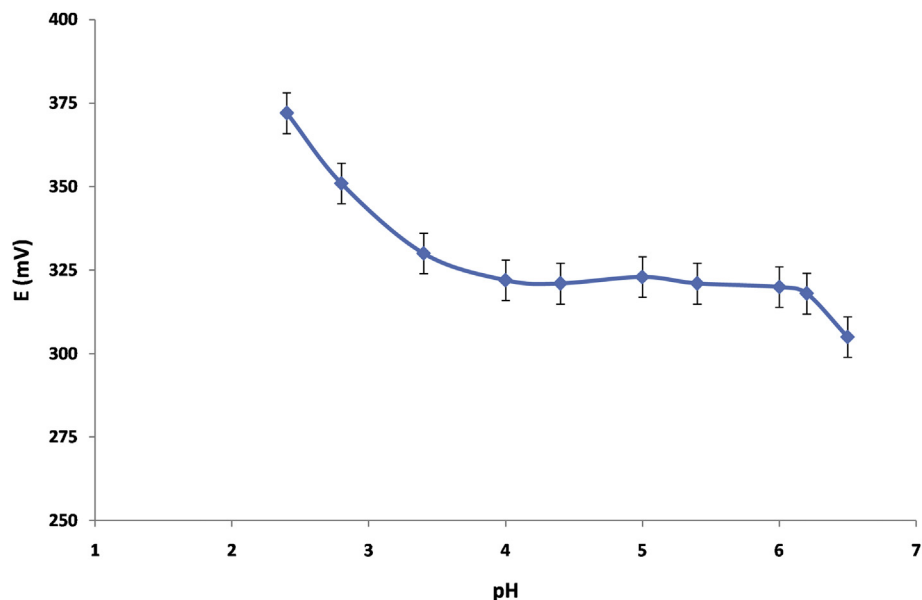


Figure 3 – Effect of the pH of the test solution on the potential response of the electrode.

collected at 1.0×10^{-4} mol/L Cu^{2+} ion solution by varying the pH of the solutions from 2.4 to 6.5. The pH was adjusted by the addition of 0.1 mol/L nitric acid or sodium hydroxide and from the obtained potentials a graph was drawn for potential and pH of the solution (Figure 3). It is revealed from Figure 3 that the potential response for electrodes remains constant over the pH range 4.0–6.0. Therefore, the same was regarded as the working pH range for the electrode.

Dynamic response time is an important factor of an ISE. Response times were determined after the potential of a solution of copper(II) nitrate had become constant, and similar measurements were carried out in another solution of 10-fold lower concentration. This dynamic response is plotted as potential versus time and is shown in Figure 4. Figure 4 depicts the responses of ISEs produced using the same protocol. The sensing behavior of the electrode remained unchanged when

potentials were recorded either from low to high concentrations or vice versa. The response time was defined as the time taken to reach a potential of 90% of the potential difference in two measurements. To measure the response time of the proposed sensor the concentration of the test solution was successively changed from 1.0×10^{-6} mol/L to 1.0×10^{-1} mol/L. The average time required for the electrodes to reach a potential response was < 10 seconds over the full range of concentrations.

Reversibility and reproducibility are also important factors for ion selective electrodes. Figure 4 shows that the potentiometric responses of the three solid contact copper selective electrodes are reversible. Average potential values and standard deviations obtained in 1×10^{-2} , 1×10^{-3} , and 1×10^{-4} mol/L Cu^{2+} solutions are 390.47 ± 1.21 , 355.28 ± 1.85 , and 321.35 ± 2.18 mV ($N = 10$, at 95% confidence level), respectively.

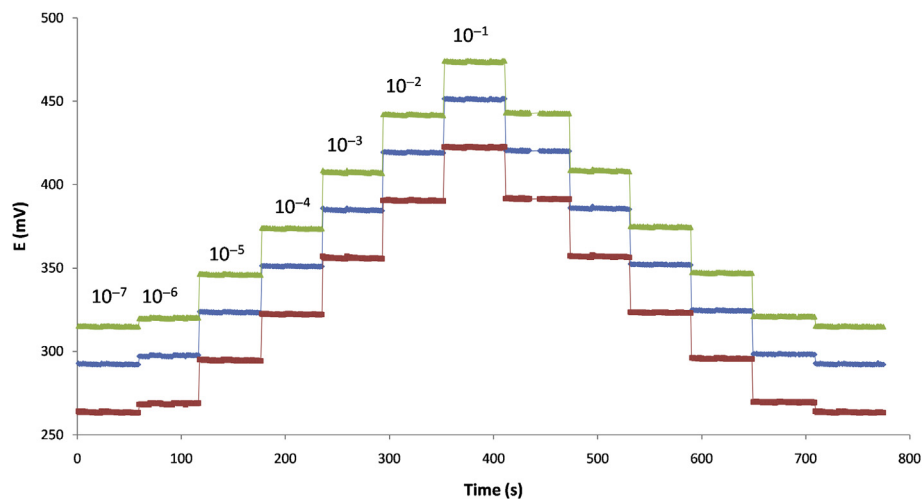


Figure 4 – Reversibility and reproducibility of the constructed copper selective electrodes.

Table 1 – Potentiometric performance characteristics of the solid contact copper selective electrode.

Parameter	Cu ²⁺ -selective PVC membrane electrode	
Membrane composition	6.9% (w/w) ionophore, o-Xylylenebis(N,N-diisobutyldithiocarbamate), 57.2% (w/w) PVC, 34.9% (w/w) NPOE, 1.6% (w/w) KTpClPB	
Slope (mV/decade)	31.3 ± 0.1	
Correlation coefficient (r)	0.996	
Limit of linear range (mol/L)	1 × 10 ⁻¹ –1 × 10 ⁻⁶	
Limit of detection (mol/L)	4.9 × 10 ⁻⁷ mol L ⁻¹	
Response time for 10 ⁻² mol/L (s)	< 10	
Working pH range	3.5–6.0	
Selectivity coefficient K _{Cu²⁺,Aⁿ⁺} ^{pot}	Interferent (A)	K _{Cu²⁺,Aⁿ⁺} ^{pot}
	Co ²⁺	1.58 × 10 ⁻⁴
	Na ⁺	1.94 × 10 ⁻⁵
	K ⁺	3.82 × 10 ⁻³
	Zn ²⁺	5.9 × 10 ⁻⁶
	Ba ²⁺	2.94 × 10 ⁻⁵
	NH ₄ ⁺	8.78 × 10 ⁻⁵
	Ni ²⁺	5.01 × 10 ⁻³
	Cd ²⁺	1.04 × 10 ⁻³
	Ca ²⁺	3.16 × 10 ⁻⁴
	Pb ²⁺	3.16 × 10 ⁻³

A vital characteristic of an ISE is its selectivity to the primary ion over interfering ions. The selectivity determines whether the sensor can be used in practical samples containing a range of cations and anions. The selectivity coefficients were determined via the separate solution method (SSM). The resulting values of the selectivity coefficients are given in Table 1. As can be seen from this table, most of the cations would not affect the selectivity of the suggested sensor. Generally, the selectivity coefficient values in Table 1

show that the prepared solid contact electrode can act as selective toward Cu²⁺ ions satisfactorily.

Potentiometric performance characteristics of the solid contact copper selective membrane electrode are summarized in Table 1. As shown in this table, the performance of the prepared electrode is comparable with the results of reported PVC membrane electrode constructed with o-xylylenebis(N,N-diisobutyldithiocarbamate) as ionophore [37]. In addition, the use of solid contact was found to improve the analytical parameters of the electrode and our electrode surpassed the typical PVC membrane electrode in linear dynamic range and response time.

The lifetime of the copper selective membrane electrode was studied over a 4-month period. During this period the electrode was used weakly and its slopes and detection limits were measured. After 3 months changes were observed in the slope (from 31.28 mV/decade to 30.12 mV/decade of activity) and detection limit (from 4.9 × 10⁻⁷ mol/L to 5.6 × 10⁻⁶ mol/L). The electrode membrane swelled so much it became mechanically weak at the end of its lifetime.

3.1. Analytical applications and recovery studies

The prepared solid contact electrode has been employed as an indicator electrode for the titration of selective Cu(NO₃)₂ solution against an EDTA solution as titrant. A 10-mL solution of 1 × 10⁻³ mol/L Cu²⁺ was titrated against a 1 × 10⁻² mol/L EDTA solution at a constant pH of 4.5. The addition of EDTA causes a decrease in potential as a result of the decrease in free metal ion concentration, i.e., Cu(II) ions due to its complexation with EDTA as shown in Figure 5. The amount of Cu(II) ion in solution can be accurately determined from the resulting neat titration curve providing a sharp equivalence point. The end point corresponds to be 1:1 stoichiometry of the Cu²⁺:EDTA complex.

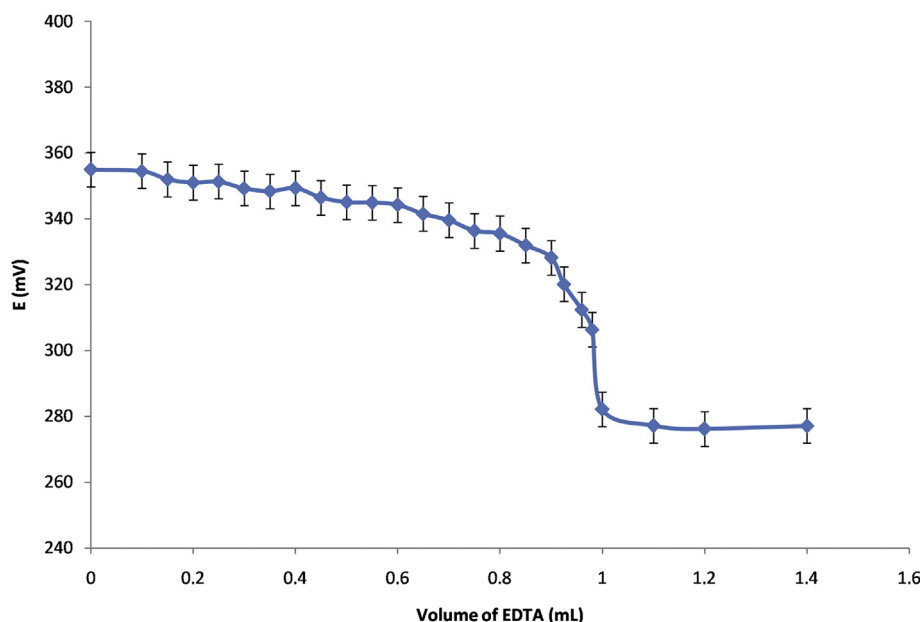


Figure 5 – Potentiometric titration curve of 10 mL of 1 × 10⁻³ M Cu²⁺ solution with 1 × 10⁻² M EDTA at pH 4.5.

Table 2 – Determination of copper in tea infusion sample using solid contact ion selective electrode.

Tea sample	C _{Cu+2} , added (mol/L)	C _{Cu+2} ± SD, found (mol/L) ^a	R ± SD% ^b	AAS	t test ^c
1	0	4.04E–6 ± 9.15E–7		1.98E–6	2.35
	2.00E–06	6.02E–06 ± 7.23E–7	99.66 ± 2.25		
	4.00E–06	7.87E–06 ± 8.35E–7	97.89 ± 1.58		
	6.00E–06	1.00E–05 ± 6.38E–7	99.70 ± 3.45		
2		8.62E–6 ± 2.9E–7		9.05E–5	2.74
	2.00E–06	1.08E–05 ± 3.25E–7	101.88 ± 3.15		
	4.00E–06	1.45E–05 ± 4.46E–7	97.84 ± 3.87		
	6.00E–06	1.87E–05 ± 5.15E–7	91.22 ± 2.57		
3		4.17E–6 ± 1.27E–7		1.39E–5	2.62
	2.00E–06	6.08E–06 ± 2.14E–7	98.54 ± 3.57		
	4.00E–06	9.70E–06 ± 3.32E–7	96.23 ± 2.65		
	6.00E–06	1.47E–05 ± 2.85E–7	93.64 ± 4.45		
4		5.94E–6 ± 7.51E–7		5.65E–6	0.53
	2.00E–06	7.82E–06 ± 6.98E–7	98.49 ± 3.65		
	4.00E–06	1.22E–05 ± 7.47E–7	103.22 ± 2.87		
	6.00E–06	1.90E–05 ± 5.18E–7	104.45 ± 3.17		

^a Average of three replicate measurements ± standard deviation.

^b Average recovery and standard deviation.

^c The theoretical values of t at p = 0.05 is 2.78.

Table 3 – Comparisons of the potentiometric characteristics of the present ISE to the various reported Cu²⁺ ISE.

Ref	Linear range	Slope	pH range	Response time (s)	Lifetime	Detection limit (M)	Interfering ions
Proposed electrode	1.0 × 10 ^{–6} –1.0 × 10 ^{–1}	31.3	4–6	10	3 mo	4.9 × 10 ^{–7}	Cd ²⁺
41	1.2 × 10 ^{–7} –1 × 10 ^{–1}	29.5		9		9.8 × 10 ^{–8}	–
42	1.25 × 10 ^{–6} –3 × 10 ^{–2}	30.3		5		8.99 × 10 ^{–7}	–
43	3 × 10 ^{–7} –1 × 10 ^{–2}	30	3–7.4	< 10	4 mo		–
17	2 × 10 ^{–6} –5 × 10 ^{–3}	28.86	3–8	10	9 wk	6.3 × 10 ^{–7}	Fe ³⁺
44	9.8 × 10 ^{–6} –1 × 10 ^{–1}	30.3	3.1–7.6	6	2 mo		Cd ²⁺

ISE = ion-selective electrodes.

The prepared sensor was also used for the direct assay of tea infusion samples by means of the calibration graph technique and standard addition method. A reference method based on AAS was used for evaluation of the accuracy of the obtained results. The measurements were done in triplicate. Recoveries of copper added to the analyzed tea samples (3 additions to each sample) were calculated. For the statistical treatment of data; Student t test was performed at 95% confidence level. The results obtained were then compiled in Table 2 which showed that potentiometric measurements of Cu²⁺ ions in tea infusion samples are in good agreement with those obtained by AAS. For all of the tea samples the calculated t values at 95% confidence levels are smaller than the critical t value (2.78). Thus, one can conclude that there are no significant differences between the performances of the two methods and the proposed sensor shows its utility in quantification of Cu²⁺ in real samples.

4. Conclusion

We have described the development and fabrication of a copper selective solid-state ion-selective electrode, based on xylylenebis(N,N-diisobutyl)dithiocarbamate, for the selective measurement of copper levels in the tea infusion samples.

The use of a solid contact was found to improve the analytical parameters of the electrode.

Comparison of the proposed electrode with other Cu²⁺ ion selective electrodes is also given in Table 3. The prepared solid contact sensor shows favorable performance characteristics with short response time (< 10 seconds) and low detection limit of 4.9 × 10^{–7} mol/L. When the potentiometric characteristics of the present electrode compared with the other solid-contact copper selective electrodes [17,41–44], the present electrode has better analytical parameters in terms of concentration range and response time. The present electrode is simple and cheap to construct due to the absence of internal solutions. The determination of copper in tea infusion samples indicated that the constructed potentiometric sensor was capable of monitoring copper in real samples, providing a handy alternative for routine analysis. The proposed sensor has the advantages of simplicity and rapidity and it can be successfully employed for the determination of Cu²⁺ in real samples without the need for preconcentration or pretreatment steps in the concentration range from 1 × 10^{–1} mol/L to 1 × 10^{–6} mol/L.

Conflicts of interest

All authors have no conflicts of interest to declare.

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