Ion-Selective Carbon Paste Electrode Based On 2-Amino-N-Benzthioazolyl Benzamide (ABTB) For Determination of Copper (II) By Potentiometric Method

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Abstract

2-Amino-N-benzthioazolyl benzamide (ABTB) was synthesized, characterized and used for the fabrication of a potentiometric sensor for Cu^{2+} metal ions. The electrode exhibits linear response to Cu (II) over a wide concentration range ($4.79\times10^{-8} - 1.85\times10^{-1}$ M) with Nernstian slope of 30 ± 1.5 mV per decade. The electrode can be used in the pH range from 2 to 9. It has a fast response time of about 10 s and can be used for a period of four months with good reproducibility. The detection limit of this electrode was 2.91×10^{-8} 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 electronics waste sample solution.

Keywords: Carbon paste electrode, Cu (II), Potentiometric Method, ABTB, Ion-selective electrodes

1. Introduction

Copper is an essential element that is present in all organisms, but it is toxic at high concentrations. This metal has important industrial uses, even though its toxicity is well recognized. So, the importance of controlling the levels of this pollutant in natural waterways, potable waters, soils, air and industrial wastes has generated much interest in the development of novel sensors for its detection. Ion-selective electrodes (ISEs) designed to respond to a particular ion in solution are an important area in analytical research. Potentiometric measurements using these sensors are a simple, economic, selective, precise and rapid method of analysis, which have found applications in different research fields [1-3]. Recently, several copper (II) ion-selective electrodes have been reported [4-7]. Carbon paste electrode (CPE) was introduced by Adams in 1958 [8]. The well

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is filled with a paste made by mixing powdered graphite with a suitable mulling liquid. By adding modifier materials in paste we can improve the electrode selectivity and sensitivity. The amount of modifier in the paste usually varies between 10 and 30% (w/w), depending on the character of modifying agent and its capability of forming enough active sites in modified paste [9]. Chemically modified carbon paste electrode (CMCPE) preparation is very simple and fast, carbon pastes undoubtedly represent one of the most convenient materials for the preparation of modified electrodes, Their applications in analytical chemistry have been mainly based on selective preconcentration followed by voltammetric determination [10-12] and just a few of these electrodes have been for potentiometric measurements [13-16]. The carbon paste electrodes are easy to construct, and have

increased portability, robustness and economy. Besides, they present a stable electrochemical response that can be renewed by removing an outer layer of the paste and resmoothing the electrode surface. They have lower ohmic resistance than ion-selective electrodes based on polymetric membranes [10, 14, 16].

The present work describes the construction, potentiometric characterization, and analytical application of a carbon paste modified electrode based on ABTB as a potentiometric sensor in copper determination (Fig 1).

The principal analytical parameters of the electrode including linear response range, pH effect, response time, detection limit and selectivity to other ions are evaluated. The electrode is successfully used for metal determination in electronics waste sample solution.

Fig.1. Structure of ABTB used in the construction of the CMCPE

2. Experimental

2.1. Solution preparation

Solutions were prepared from a stock solution of 10^{-3} M copper (II), prepared from a sufficient quantity of copper (II) nitrate in distilled deionized water. The working solutions were prepared daily by suitable dilution of stock solution. Potassium nitrate (1M) solution was prepared and used as supporting electrolyte, to maintain constant ionic strength. All other solutions used

in interference studies were prepared from analytical grade nitrate salts (all from Merck Company). Pure graphite powder (Merck) and paraffin oil (Fluka) was used for the preparation of carbon paste electrode. ABTB as an ionophore was synthesized and purified.

2.2. Synthesis of ABTB

A mixture of isatoic anhydride (1.63 g, 10 mmol), 2-aminobenzthioazole (1.5 g, 10 mmol), *p*-toluenesulfonic acid (0.05 g, 0.25 mmol) and N,N-dimethylacetamide (DMAC,1-2 ml) in a tall beaker was covered with stemless funnel, placed in microwave oven and irradiated with 300W power for 30s (evolution of CO_2 was observed). The reaction mixture was cooled and irradiated again for 90s with interruptions in between. Then, the reaction mixture was allowed to cool to room temperature and poured in cool water (250 ml).

The precipitate formed was filtered and washed with water. Recrystallization from ethanol (95%) gave 2-Amino-N-benzthioazolyl benzamide (ABTB) as white crystals.

IR (KBr): 3342 (broad), 3190, 3063, 2967, 2878, 1645, 1604, 1573, 1522, 1420, 1348, 1276, 1228, 1163, 1020, 916, 881, 858, 746, 684 cm^{-1}

^1H NMR (DMSO-d_6, 300 MHz): δ= 10.01 (sbr, 1H), 7.94 (d, 1H, J=8.10 Hz), 7.44–7.40 (m, 2H), 7.18–7.16 (m,1H), 7.12–7.10(m, 2H), 6.80–6.77 (sbr, 2H), 6.74(d, 1H, J=8.3 Hz), 6.53(t, 1H, J=7.5 Hz) ppm.

^{13}C NMR (DMSO-d_6, 125 MHz): δ= 174.23, 150.20, 147.00, 146.08, 131.02, 126.3, 123.91, 123.20, 121.15, 119.82, 119.1, 116.41, 116.07, 114.4 ppm.

Anal. Calcd. for $C_{14}H_{11}N_3OS$: C, 62.43; H, 4.12, N, 15.60. Found: C, 63.02; H, 4.24, N, 16.01.

2.3. Electrode preparation

The potentiometric carbon paste electrode was prepared by thoroughly hand-mixing of ABTB with pure graphite powder in an agate mortar. Paraffin oil was added and mixed until a uniform paste was obtained. The electrode body was made from a disposable (2.5mm diameter) insulin syringes. The carbon paste was packed into the end of the syringe provided with an unmodified carbon paste-copper wire contact. The electrode surface was pressing against a filter paper to obtain an appropriate packing of the carbon paste and a smooth surface. Unmodified carbon paste electrode was prepared in similar fashion, without addition of the ABTB in graphite powder.

2.4. Apparatus

A digital potentiometer (HIOKI 3256.50) was used for potentiometric measurements. The reference electrode was a double junction saturated Ag/AgCl reference electrode. A Metrohm pH meter (CRISON GLP 22) was used for pH controlling, and a Heidolph type of MR 2000 stirrer was used for stirring the solutions.

2.5. Procedure

The electrodes were immersed directly in a test solution. The pH of this solution was adjusted to 5. The solution was stirred (100 rpm) until the response of the potentiometer became stable (20 min). Then by means of a micropipette (5-100 µl) the solutions of 0.001, 0.01 and 0.1 M Cu $(NO_3)_2$ in 0.3 M KNO_3 (with a pH adjusted to 5) were added to the test solution in different portions. After each addition, the potentiometer was kept in the solution stable potential was indicated, then this potential was reported as a measured potential.

3. Results and discussion

3.1. Response of the electrode to various cations

In preliminary experiments, ABTB was used as a neutral carrier to prepare carbon paste electrodes for wide variety of metal ions, including alkali, alkaline earth, transition and heavy metal ions. The potential obtained for the most sensitive ion-selective electrodes based on ABTB are shown in Fig. 2. The copper selective electrode exhibited linear response to the logarithm of the activity of Cu^{2+} ions within the concentration range of $4.79 \times 10^{-8} - 1.85 \times 10^{-1}$ M of Cu $(NO_3)_2$ with Nernstian slope of 30 ± 1.5 (mV) per decade at 25°C and correlation coefficient of 0.995.
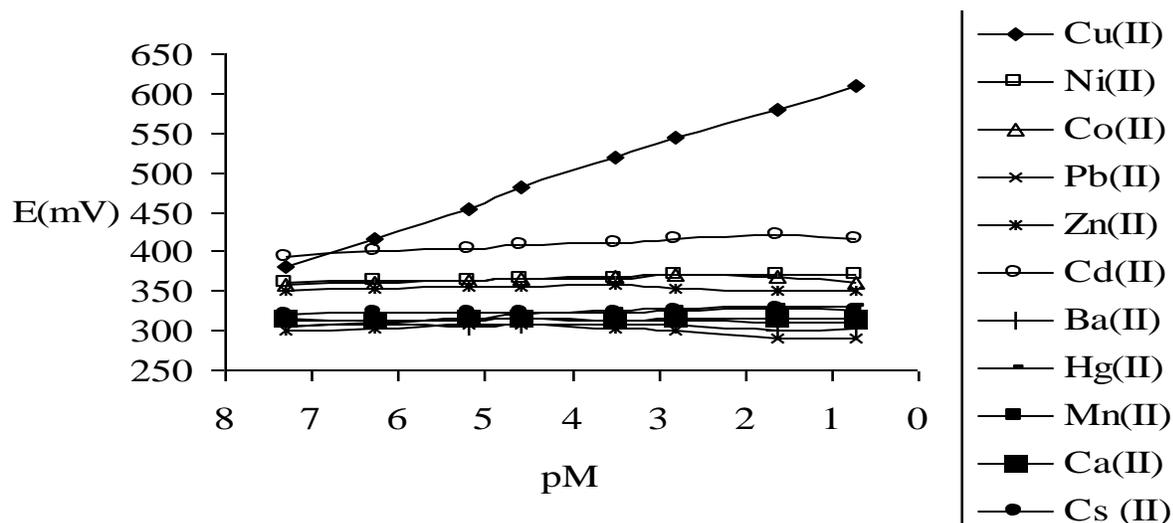
Fig. 2. Schematic diagram of electrode response to various cations

3. 2. Influence of the electrode composition

It is known that the potentiometric sensitivity and linearity for a given ion depend significantly on its amount in the carbon paste electrode composition [16]. Thus, the influence of the percent of ABTB in the carbon paste composition was investigated and the results are summarized in Table 1. For this purpose, eight electrodes were prepared, in which the amounts of paraffin oil was constant. These results show that the electrode (No.7) with 35% paraffin oil, 45% graphite and 20% ABTB has a good Nernstian slope.

Table 1. Optimization of the amount of modifier in the electrode

Number	Paraffin	ABTB	Graphite	Slope	R^2
1	35%	0%	65%	2±1	0.993
2	35%	2%	63%	3±2	0.989
3	35%	7%	58%	4±2	0.996
4	35%	10%	55%	18±2	0.997
5	35%	15%	50%	20±2	0.992
6	35%	18%	47%	26±1	0.998
7	35%	20%	45%	30±1.5	0.995
8	35%	25%	40%	22±2	0.992

3. 3. Effect of ionic strength on the response of electrode

The effect of ionic strength (0.1 – 0.9 M KNO_3) on the calibration curve of copper electrodes was investigated. The electrode response is slightly changed within the 0.1 – 0.9 M KNO_3 electrolyte solution. However, we choose added 0.3 M as an optimum value, since in this ionic strength the linear range was wider than for the other concentrations.

3. 4. Calibration curve and statistical data

The potential response of the selected electrode No. 7 with the composition described in Table 1,at varying concentration of Cu (II) ions displays a linear response to the concentration of Cu^{2+} ions in the range of 4.79 ($\pm$0.8) $\times10^{-8}$ to 1.85 ($\pm$0.6)$\times 10^{-1}$ M (Fig. 3). The slope of calibration graph was 30$\pm$1.5 mV per decade of activity of Cu^{2+} ions. The detection limit of the sensor, as determined from the intersection of the two extrapolated segments of the calibration graph was 2.91 ($\pm$0.5) $\times10^{-8}$ M. The standard deviation of 10 replicate measurements was about $\pm$0.3 m V.
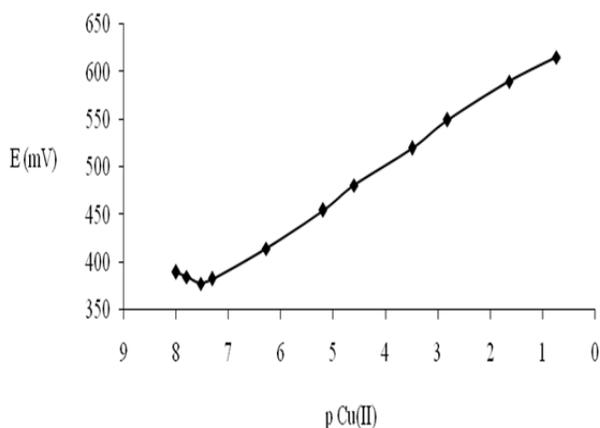
Fig. 3. Calibration curve for the proposed Cu^{2+} ion-selective electrode.

3. 5. Optimization of pH

In order to investigate the pH effect on the potential response of the electrode, the potentials were measured for a fixed concentration of Cu^{2+} solution (1.0 $\times$ 10^{-3} M) having different pH values. The pH varied from 2.0 to 9.0 by the addition of HNO_3 or NaOH. The potential variation as a function of pH is plotted in Fig. 4. The composition of the electrode and the ionic strength of the solution were kept constant during all experiments. The results showed the potential of electrode is constant between pH (2.0-9.0). Thus the

electrode works satisfactorily in the pH range 4.0- 6.0, as no interference from H^+ or OH^- is observed in the range.
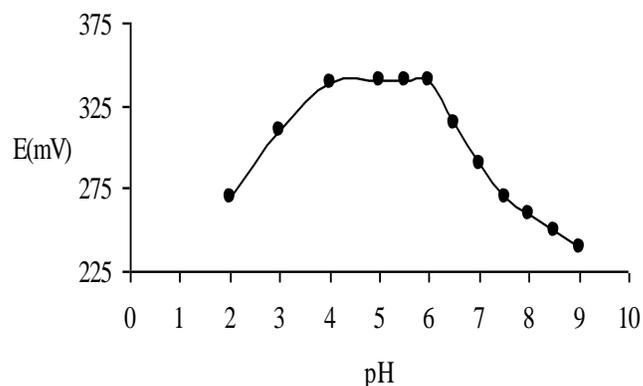
Fig. 4. Schematic diagram of pH effect to potential response electrode.

3. 6. Response and life time

The response time of the modified proposed electrode is measured according to **IUPAC** recommendation. In this work, the response time in variation of concentration from 1×10^{-6} to 1×10^{-2}M Cu^{2+} is measured. The measured response time was 10(s). The optimum conditioning time for the carbon paste electrode in a 1.0×10^{-3} M Cu $(NO_3)_2$ was 24 h, after which it generates stable potentials in contact with Cu^{2+} solutions and the useful lifetime of the sensor is 4 months, during which the potential slope is reproducible to within $\pm$1 mV per concentration decade.

3. 7. Selectivity and interference

In order to investigate the selectivity of the carbon paste electrode, its response was examined for various ions by matched potential method (MPM) as recommended by Gadzekpo and Christian [17]. The selectivity coefficient

(K_{ij}^{Pot}) is given by the expression $K_{ij}^{Pot} = a_i^{I} - a_i /a_j$ and is determined by measuring the change in potential upon increasing by a definite amount the primary ion activity from an initial value of a_i to a_i^{I} and a_j represents the activity of interfering ion added to same reference solution of activity a_i which brings about same potential change. Since the selectivity coefficients for monovalent, bivalent and trivalent ions are considerably lesser than unity, the electrode

was selective to Cu^{2+} ions over these interfering ions, as shown in Table 2. This table shows that all fourteen cations would not affect the selectivity of the present copper electrode, and compare to previously reported copper electrodes have a very small value of selectivity coefficient in most cases, and in wider linear range, Nernstian slope of the proposed electrode is somewhat similar or even better, to the recently published papers in some cases.

Table 2. Selectivity coefficient for various interfering cations and analytical properties for modified carbon paste copper selective electrodes.

Interference (j)	$K_{Cu,j}$		
	A	B	C
Pb^{2+}	3.40×10^{-2}	2.30×10^{-5}	2.10×10^{-6}
Co^{2+}	4.30×10^{-2}	3.50×10^{-5}	6.00×10^{-6}
Ni^{2+}	4.80×10^{-2}	2.80×10^{-5}	3.50×10^{-5}
Cr^{2+}	-	-	4.20×10^{-5}
Zn^{2+}	2.90×10^{-2}	2.90×10^{-5}	1.65×10^{-6}
Fe^{3+}	8.40×10^{-3}	-	4.50×10^{-4}
Ba^{2+}	5.50×10^{-3}	-	5.50×10^{-5}
Mn^{2+}	1.80×10^{-2}	-	4.35×10^{-5}
Sr^{2+}	7.00×10^{-3}	2.70×10^{-6}	4.50×10^{-6}
Al^{3+}	-	-	9.50×10^{-5}
Na^{+}	1.50×10^{-2}	-	5.50×10^{-4}
K^{+}	1.10×10^{-2}	-	4.00×10^{-5}
Ag^{+}	1.20×10^{-2}	7.30×10^{-6}	7.10×10^{-6}
Tl^{+}	-	9.10×10^{-6}	6.50×10^{-5}
Slope (mV/ decade)	29.3	29.6	30 ± 1.5
Linear range (M)	$1.0 \times 10^{-1} - 2.0 \times 10^{-6}$	$1.0 \times 10^{-2} - 5.0 \times 10^{-8}$	$1.85 \times 10^{-1} - 4.79 \times 10^{-8}$

A [18], B [19], C (Present work)

3. 8. Practical application

For testing the proposed copper selective electrode in practical application, the electrode was used for the determination of copper of an electronic industrial waste solution. An atomic

absorption spectrophotometer was used to compare the reference value and the copper electrode response to industrial waste solution Table 3.

Table 3. Determination of copper in an industrial waste solution

	1	2	3
Atomic absorption (AAS)	1.34×10^{-3} M	1.29×10^{-3} M	1.39×10^{-3} M
Carbon paste electrode	1.39×10^{-3} M	1.33×10^{-3} M	1.36×10^{-3} M
Error %	+3.73	+3.10	-2.15

The sensitivity and stability offered by this simple electrode configuration are high enough to allow accurate determination of low levels of copper. The selectivity coefficient data for copper relative to most of the interfering ions are negligibly small. In conclusion, the developed 2-Amino-N-benzthioazolyl benzamide (ABTB) modified carbon paste electrode described in this work offers a reliable, sensitive, and selective tool for the quantitative determination of copper in some important matrices.

4. Conclusions

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