

## Determination of Microgram Amounts of Copper in Real Samples Using New Modified Carbon Paste Electrode

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A new chemically modified carbon paste electrode (CMCPE) based on copper-Cefazoline, Cu(II)-CFZ, ion-associate has been developed. The electrode exhibits a Nernstian slope of 29.44 mV per decade for Cu(II) ion over a concentration range of  $4.01 \times 10^{-6}$ - $7.52 \times 10^{-3}$  mol L<sup>-1</sup>. The electrode has low limit of detection,  $6.28 \times 10^{-7}$  mol L<sup>-1</sup>, fast response time of  $\leq 10$  s, highly selective, thermally stable and its potential response is pH independent in the pH range 1.6-5.8. This modified electrode was successfully used in determination of copper (II) in different water samples, milk powder, brass powder, soft drink and tea.

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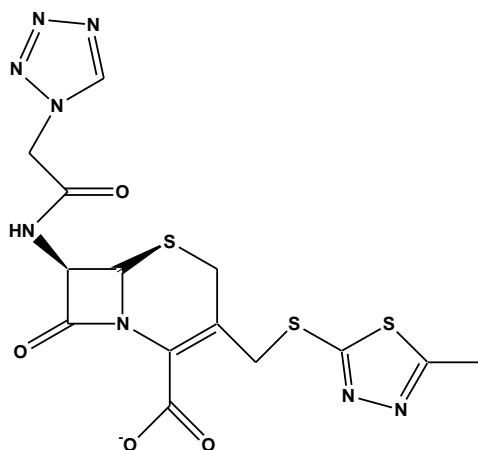
**Keywords:** Carbon paste electrode; Copper (II); Ion-associate; Potentiometry, Cefazoline

### 1. INTRODUCTION

Chemically modified carbon paste electrodes (CMCPEs) are well known as potentiometric sensors for determination of various species [1-3]. Carbon paste electrodes (CPEs) combine a carbon powder with a pasting liquid (an organic binder), modifying the conventional electrode surface is necessary to improve the analytical performance of the electrode towards specific application in electroanalysis [4]. The operation mechanism of such chemically modified carbon paste electrodes (CMCPEs) depends on the properties of the modifier materials used to impart selectivity and sensitivity towards the target species [5]. CMCPEs possess advantages of much lower ohmic resistance [6,7], very stable response and easy renewal of its surface.

Although copper is an essential element for human body, but it is toxic at high concentration levels. Cu(II) shortage can cause anemia but its increase causes Wilson disease (WD) [8]. The increased accumulation of copper (II) in the environment from numerous industrial sources, poses a danger to public health [9]. Several analytical methods have been used for determination of copper

including spectrophotometry [10,11], high performance liquid chromatography [12], liquid-liquid microextraction [13,14], atomic absorption spectrometry [15,16], and inductively coupled plasma/mass spectrometry [17,18]. Several Cu(II) sensors have been developed based on benzothiazol derivative [19], hydroxybenzylidene thiosemicarbazide [20], Schiff base [21], salens [22], porphyrins [23], Phenyl-2-(2-hydroxyphenylhydrazo)butane-1,3-dione [24], chelating ionophores [25] and copper complex [26]. The ion-selective electrodes reported for the determination of Cu(II) in literature exhibit poor selectivity, narrow concentration range, non-Nernstian response, long response time and poor reproducibility [27-34]. Thus, trials in this field are done to find new electroactive species for development of new Cu(II) electrodes. In this work copper-Cefazoline, Cu(II)-CFZ, ion-associate has been prepared, incorporated in CMCPE and examined as an ion-recognition site in potentiometric sensor for Cu(II) ions. Cefazolin ((6R,7R)-3-[[[(5-methyl-1,3,4-thiadiazol-2-yl)thio]methyl]-8-oxo-7-[(1H-tetrazol-1-ylacetyl)amino]-5-thia-1-azabicyclo[4.2.0]oct-2-ene-2-carboxylic acid (Fig.1) is antibacterial drug for infection of skin, lung, bone, joint, stomach, blood, heart valve, and urinary tract. It was found that cefazoline (CFZ) forms highly insoluble ion-associate with Cu(II), thus potentiometric CMCPE based on this ion-associate has been prepared. Calibration curves are plotted in the concentration range  $1.0 \times 10^{-8}$ - $1.0 \times 10^{-1}$  mol L<sup>-1</sup> Cu(II). Essential analytical parameters are established, carbon paste composition, slope characteristics, detection limit, response time, selectivity, and dependence of the electrode potential on the pH of the solution. The electrode was applied for the determination of copper in different types of real samples. Also, the electrode was used as indicator electrode for potentiometric titration of Cu(II) ions using EDTA.



**Figure 1.** Structure of Cefazoline drug.

## 2. EXPERIMENTAL

### 2.1. Reagents and Materials

Sodium tetratphenylborate (NaTPB), sodium tetrakis (1-imidazolyl)borate (NaTIMB), cetyltrimethylammonium bromide (CTAB), dioctyl phthalate (DOP), dibutyl-butyl phosphonate (DBBP), tricresyl phosphate (TCP), dioctyladipate (DOA), dibutylphthalate (DBP) and oleic acid were

purchased from Aldrich chemical company. Graphite powder,  $\text{KNO}_3$ ,  $\text{NaNO}_3$ ,  $\text{HNO}_3$ ,  $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ ,  $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ,  $\text{Ba}(\text{NO}_3)_2$ ,  $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ ,  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ,  $\text{NiCl}_2$ ,  $\text{NaCl}$ ,  $\text{Pb}(\text{NO}_3)_2$ ,  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ,  $\text{NH}_4\text{NO}_3$ ,  $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ , disodium salt of ethylenediaminetetraacetic acid ( $\text{Na}_2\text{EDTA}$ ), were purchased from El-Nasr pharmaceutical Chemicals. Copper nitrate trihydrate  $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$  (95%) was purchased from Oxford laboratory products-Mumbai-India 95-103%.

## 2.2. Solutions

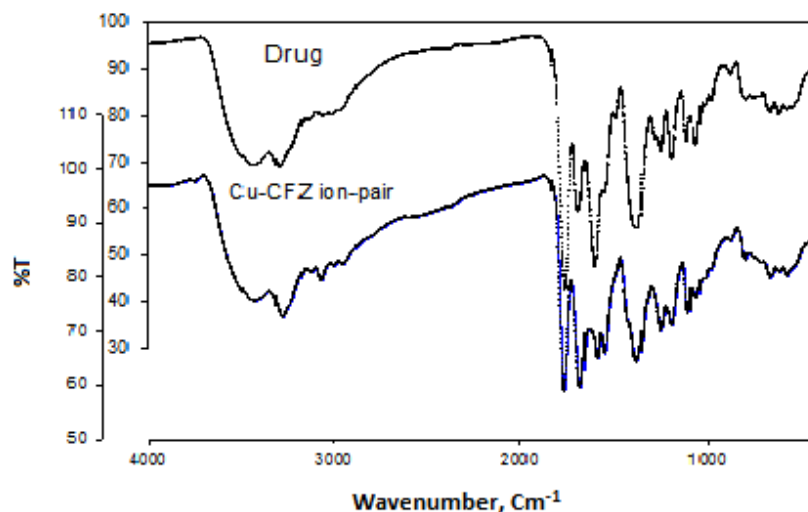
Deionized water was used for all preparations and throughout all experiments. Stock solution ( $0.1 \text{ mol L}^{-1}$ ) of Copper nitrate trihydrate solution was prepared by dissolving 2.415 g  $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$  in 100 mL deionized water, and two drops of 0.1 M nitric acid was added for reservation to prevent hydrolysis and standardized by complexometric titration [35]. It was kept in glass bottles in refrigerator. Solutions of lower concentrations were prepared by dilution before the measurements. Stock solution ( $1.0 \times 10^{-2} \text{ mol L}^{-1}$ ) of EDTA was prepared and then lower concentrations ( $1.0 \times 10^{-3}$ ,  $1.0 \times 10^{-4} \text{ mol L}^{-1}$ ) were prepared by dilution.

## 2.3. Apparatus

For potential measurements JENWAY 3010 digital pH/mV meter was used. A SENTEK R1/2MM Ag/AgCl electrode was used as reference electrode. Millipore Elix S (Automatic Sanitization Module) (ASM) was used for obtaining the deionized water. Elemental microanalyses were performed in Micro-analytical center, FTIR-460 plus JASCO 4000-400  $\text{cm}^{-1}$  KBr pellets was used for IR spectra. Perkin-Elmer Optima 2000 ICP instrument was used for the atomic emission spectrometry measurements.

## 2.4. Preparation of copper-cefazoline ion-associate (Cu(II)-CFZ)

A solution of  $\text{Cu}(\text{NO}_3)_2$  containing 1.0 mmol in 10 mL deionized water was added to a solution of sodium cefazoline containing 2.0 mmol in 10 mL deionized water, where a pale green precipitate was obtained. The precipitate is filtered off, washed with deionized water and air dried. The ion-associate is characterized by FTIR and elemental analysis. The data of elemental analysis are found to be: %C 33.81(theoretical 34.55), %H 3.9 (theoretical 2.87) and %N 22.9 (theoretical 23.03), which is in a good agreement with the theoretical values. The IR spectrum of cefazoline drug is characterized by a peak at  $1603 \text{ cm}^{-1}$  assigned for the asymmetric carboxylate group which is shifted to lower wave number ( $1592 \text{ cm}^{-1}$ ) in the IR spectrum of Cu(II)-CFZ and another one at  $1391 \text{ cm}^{-1}$  assigned for the symmetric carboxylate group which is decreased to  $1375 \text{ cm}^{-1}$  in the spectrum of the ion-associate. This is evidence for the formation of the ion-associate through the interaction of carboxylate group of the cefazoline drug with the copper ion, Fig. 2.



**Figure 2.** IR spectra of Cefazoline drug and Cu(II)-CFZ ion-associate.

### 2.5. Preparation of modified carbon paste electrodes

A Teflon holder body of 12.0 cm length with a hole at one end (7.0 mm diameter, 3.5 mm deep) for the carbon paste filling served as the electrode body. A stainless steel bar passing the center of the holder is used to serve the electrical communication. This bar is moving downward by rotation action to push the paste down when regeneration of the electrode surface is desirable. The modified paste is prepared by adding the suitable weight of the ion-associate and high purity graphite with acetone. This combination is homogenized, left at room temperature till the acetone is vanished and then the requested amount of plasticizer is added and mixed strongly with agate pestle in agate mortar. The paste is filled in the hole of the electrode body. The carbon paste was smoothed onto a paper and used immediately for potentiometric determination without soaking. All EMF measurements were carried out with the following cell assembly:

Ag//AgCl, KCl (3 mol L<sup>-1</sup>) // test solution //filling graphite modified paste // carbon paste electrode

### 2.6. Effect of interfering ions

The effect of various inorganic cations on the electrode response was investigated graphically by plotting the calibration curves for all ions tested and comparing them to the calibration curve of Cu(II) ion. The selectivity coefficient values were determined by applying the matched potential method (MPM) [36-38] that depends neither on the Nicolsky-Eisenman equation nor on any of its modifications. This method was recommended in 2002 by IUPAC [38] as a method that gives analytically relevant practical selectivity coefficient values.

### 2.7. Potentiometric Determination

The standard addition method was applied, in which a known incremental change is made through the addition of standard solution to the sample. This was achieved by adding known volumes of a standard Cu(II) solution to 50 mL water containing different amounts of the Cu(II) samples including, milk powder, brass powder, Tea and different types of water samples. The change in mV reading was recorded for each increment and used to calculate the concentration of the Cu(II) in sample solution using the following equation [39]:

$$C_x = C_s \left( \frac{V_s}{V_x + V_s} \right) \left( 10^{n(\Delta E/S)} - \frac{V_x}{V_s + V_x} \right)^{-1}$$

Where,  $C_x$  is the concentration to be determined,  $V_x$  is the volume of the original sample solution,  $V_s$  and  $C_s$  are the volume and concentration of the standard solution added to the sample to be analyzed, respectively,  $\Delta E$  is the change in potential after addition of certain volume of standard solution, and  $S$  is the slope of the calibration graph.

### 2.8. Sample Analysis

For analysis of milk samples, 2.0 g milk powder was ashed at 400°C in a crucible for 3 h and then 2 mL of conc.  $\text{HNO}_3$  was added and the mixture was heated to dissolve residue. The resulting solution was diluted with deionized water in a 25 mL volumetric flask [22]. The Cu(II) content in the resulting solution was determined potentiometrically using the Cu(II)-CFZ and by atomic absorption spectrometry (AAS).

For analysis of brass powder, 1.0 g of the sample was dissolved in minimally conc.  $\text{HNO}_3$  and the solution was transferred to 100 mL volumetric flask and diluted to the mark with deionized water [25]. Lower concentrations were prepared by successive dilution. The content of copper in each of the resulting solutions was measured by direct potentiometry using the present Cu(II)-CFZ and by AAS.

Different water samples were analyzed namely tap water from Cairo university Lab., mineral water, sea water and wastewater from copper smelter production unit. A 250 mL samples was acidified with  $\text{HNO}_3$  acid to dissociate the metal-complexes then heated to eliminate the organic matter and then transferred after cooling to 100 mL volumetric flask. Deionized water was added to the mark then the pH was adjusted to 2.5-4.0 using concentrated  $\text{HNO}_3$  acid. The amount of copper was measured by the proposed copper selective electrode and by (AAS).

For analysis of tea, 1.0 g of dry tea sample (dried at 110°C) was placed in 50 mL beaker, followed by the addition of nitric and perchloric acid for sample digestion. The procedure developed by Ganjali et al [40] was followed for sample solution preparation.

For analysis of soft drinks, the samples were digested using 69% of nitric acid to remove organic material and to convert the metals present into soluble forms. Concentrated nitric acid (69%), 10 mL, was added to 25 mL of the sample. The mixture was evaporated on a hot plate in a fume cupboard until the brown fumes decreased leaving white fumes. A 50 mL of distilled water was added and this was concentrated by evaporation on a hot plate to 25 mL. Subsequently, additional 25 mL of distilled water was added to make up to 50 mL [41].

For analysis of copper in electroplating bath of the banknote plates, 100 mL of the plating solution was transferred to 250 mL beaker, and then the pH of the solution was measured. Due to the high acidity of this solution ( $\text{pH} < 1.0$ ), the pH was adjusted to 2.5-4.0 by adding ammonium hydroxide (17%) solution. A 2.5 mL of this solution was transferred to 50 mL measuring flask and the volume was complete to the mark with deionized water. Lower concentrations were prepared in a similar manner.

### 3. RESULTS AND DISCUSSION

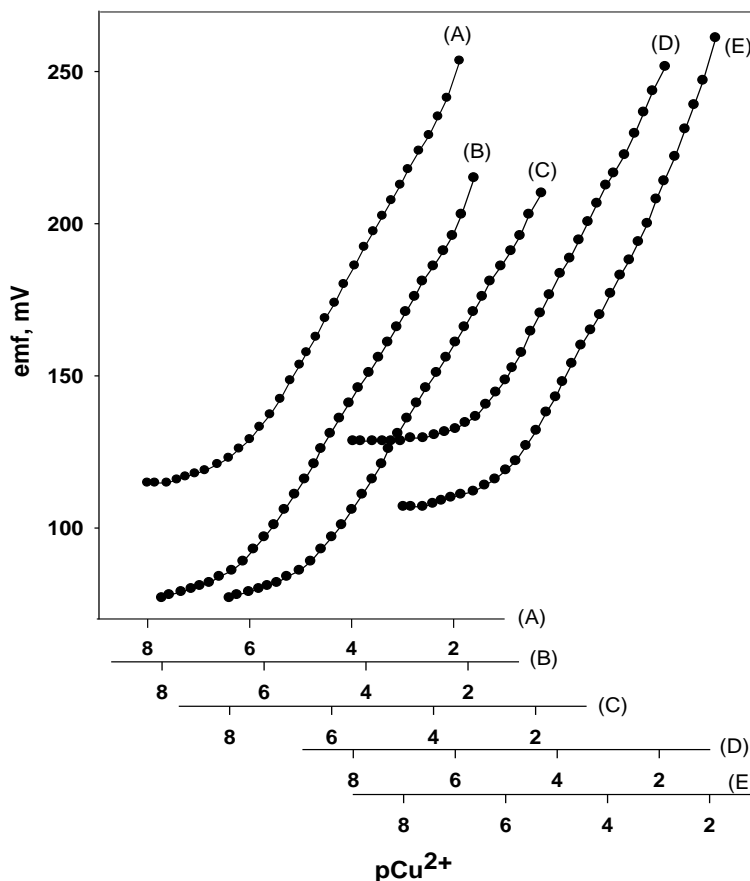
#### 3.1. Effect of Composition

The sensitivity and selectivity depend significantly on the carbon paste composition and the nature of the modifier, Cu(II)-CFZ. Thus, the influence of the Cu(II)-CFZ amount in the carbon paste was studied. The potential response of all potentiometric carbon paste electrodes as a function of the Cu(II) activity was investigated in the concentration range  $1.0 \times 10^{-8}$  to  $1.0 \times 10^{-1}$  mol L<sup>-1</sup>. As can be seen from table 1, the slope of the calibration curves of the electrodes modified with Cu(II)-CFZ (1-5%) increased from 27.39 to 32.13 mV/concentration decade, Fig. 3.

**Table 1.** Composition and slope of calibration curves for copper (II) CMCPEs.

% composition						Slope (mV/decade)	Limit of detection (mol L <sup>-1</sup> )	Linear range (mol L <sup>-1</sup> )
No.	Plasticizer		Reagent	Graphite	Additive			
	%	Name						
1	45	DOA	1	54	-	27.39	$6.28 \times 10^{-7}$	$1.01 \times 10^{-6}$ - $2.11 \times 10^{-3}$
2	45*		2	53	-	29.44	$6.28 \times 10^{-7}$	$4.01 \times 10^{-6}$ - $7.52 \times 10^{-3}$
3	47		3	50	-	30.90	$6.28 \times 10^{-7}$	$1.95 \times 10^{-6}$ - $2.11 \times 10^{-3}$
4	45		4	51	-	31.82	$3.00 \times 10^{-6}$	$6.32 \times 10^{-6}$ - $3.32 \times 10^{-3}$
5	44		5	51	-	32.13	$1.01 \times 10^{-6}$	$2.54 \times 10^{-6}$ - $2.11 \times 10^{-3}$
6	46		2	52	-	29.29	$9.99 \times 10^{-7}$	$1.95 \times 10^{-6}$ - $7.52 \times 10^{-3}$
7	43		2	55	-	28.50	$9.95 \times 10^{-6}$	$2.54 \times 10^{-6}$ - $7.52 \times 10^{-3}$
8	45	TCP	2	53	-	29.29	$9.99 \times 10^{-7}$	$2.54 \times 10^{-6}$ - $7.52 \times 10^{-3}$
9	45	DBP	2	53	-	33.35	$9.99 \times 10^{-7}$	$4.01 \times 10^{-6}$ - $7.52 \times 10^{-3}$
10	45	DBBP	2	53	-	21.31	$4.50 \times 10^{-6}$	$4.01 \times 10^{-6}$ - $6.09 \times 10^{-4}$
11	45	DOP	2	53	-	31.01	$6.28 \times 10^{-7}$	$2.54 \times 10^{-6}$ - $3.32 \times 10^{-3}$
12	44		2	54	-	30.26	$9.99 \times 10^{-7}$	$2.54 \times 10^{-6}$ - $2.11 \times 10^{-3}$
13	44		2	53	1.0 NaTPB	31.52	$2.54 \times 10^{-6}$	$2.54 \times 10^{-6}$ - $1.29 \times 10^{-3}$
14	44		2	53	1.0 CTAB	37.76	$7.09 \times 10^{-5}$	$1.78 \times 10^{-4}$ - $1.78 \times 10^{-2}$
15	44		2	53	1.0 NaTImB	30.99	$1.01 \times 10^{-6}$	$2.54 \times 10^{-6}$ - $1.78 \times 10^{-2}$

\*Optimum composition chosen



**Figure 3.** Potential response of Cu(II)-CFZ CMCP electrode of different composition, (A) 1%, (B) 2%, (C) 3%, (D) 4% and (E) 5% ion-associate.

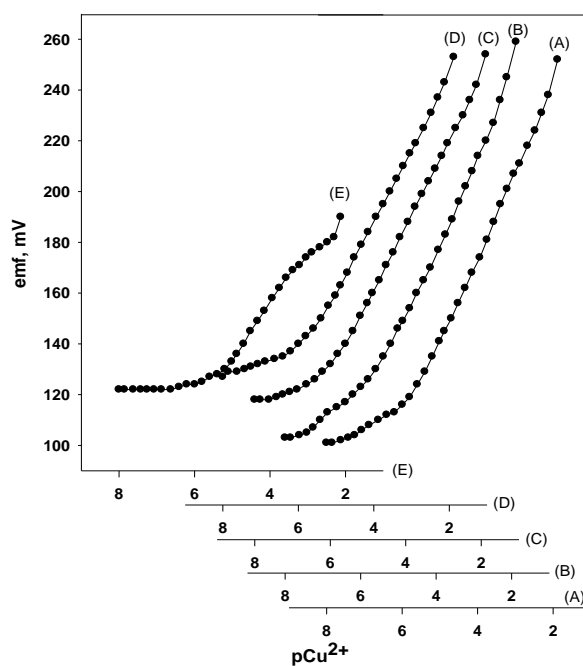
The electrode modified with 2% Cu(II)-CFZ and plasticized with DOA 45% is the best composition as it gives Nernstian slope, 29.44 mV, and it has lower detection limit  $6.28 \times 10^{-7}$  mol L<sup>-1</sup> and wider concentration range  $4.01 \times 10^{-6}$ - $7.52 \times 10^{-3}$  mol L<sup>-1</sup> than the other compositions examined. Also the change in the amounts of graphite and plasticizer was examined. The results indicated that by decreasing the amount of graphite the electrode response is almost constant, but the detection limit increased (electrode No. 6). On the other hand, increasing the amount of graphite decreased the slope to 27.4 mV/decade with large increase in the detection limit,  $6.28 \times 10^{-7}$  mol L<sup>-1</sup> (electrode No. 1). The response of the present ion-selective electrode has been attributed to an exchange process of Cu(II) ions between the analyzed aqueous solution and the mediator. The equilibrium of the system is achieved when the electrochemical potential of Cu(II) ions in the two phases are equal and the Cu(II) ions in the aqueous phase do not influence the activity of the ions in the organic phase [42].

### 3.2. Effect of Plasticizer and Additive

The plasticizer to be used in the paste phase should exhibit high lipophilicity, high molecular weight and low tendency for exudation from the paste matrix. Since the nature of the plasticizer influences the dielectric constant of the paste phase and the mobility of the ionophore molecules, it is

expected to play a key role in determining the characteristics of the electrode. The influence of solvent mediator (plasticizer) type on the characteristics of the Cu(II) chemically modified carbon paste electrode, Cu(II)-CFZ, was investigated using six solvents with different polarities TCP, DOP, DBP, DOA, DBBP and Oleic acid. The data given in table 1 showed that the paste incorporating DBBP ( $\epsilon = 4.6$ ) (No.10) as solvent mediator had the worst response towards copper ions, in which the slope was 21.31 mV and the detection limit was  $4.5 \times 10^{-6}$  mol L<sup>-1</sup>. DBP ( $\epsilon = 6.4$ ) and DOP ( $\epsilon = 5.1$ ) based electrodes (Nos. 9, and 11) gave near-Nernstian responses of slopes 33.35 and 31.01 mV over the concentration range  $4.01 \times 10^{-6}$ - $7.52 \times 10^{-3}$  and  $2.54 \times 10^{-6}$ - $3.32 \times 10^{-3}$  mol L<sup>-1</sup>, respectively, and detection limits of  $9.99 \times 10^{-7}$  and  $6.28 \times 10^{-7}$  mol L<sup>-1</sup> respectively. Electrodes No. 2, and 8 containing DOA ( $\epsilon = 3.9$ ), TCP ( $\epsilon = 6.9$ ) as plasticizers showed Nernstian slope of 29.44, 29.29 mV over a concentration range of  $4.01 \times 10^{-6}$ - $7.52 \times 10^{-3}$ , and  $2.54 \times 10^{-6}$ - $7.52 \times 10^{-3}$  mol L<sup>-1</sup> with a detection limit of  $6.28 \times 10^{-7}$ , and  $9.99 \times 10^{-7}$  mol L<sup>-1</sup>, respectively. The Cu(II)-CFZ with DOA as solvent mediator produced the best response as shown in Fig.4, this is likely due to high lipophilicity, relatively high molecular weight and low dielectric constant of this plasticizer which enables solvation and mobility of ion-associate through the paste.

It is known that lipophilic negatively charged additives improve the potentiometric behavior of certain cation-selective electrodes by reducing the ohmic resistance and improving the response behavior and selectivity [43, 44]. Thus, the effect of some additives like NaTPB, NaTIMB and CTAB was studied, Table 1. On contrary with what reported in literature, it was found that all additives tested did not improve the performance characteristics of the electrode (slope, linear range, and detection limit).

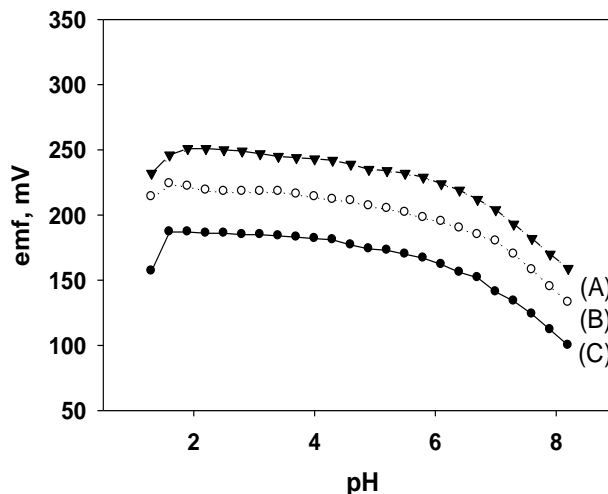


**Figure 4.** Effect of plasticizers on the response of Cu(II)-CFZ CMCPE using 2% ion-associate, 53% graphite and 45.0%DBP (A), 45.0% DOP (B), 45.0% DOA (C), 45.0% TCP (D) or 45.0% DBBP (E).



### 3.3. Effect of pH

The effect of pH on the response of Cu(II)-CFZ electrode was examined with a series of Cu(II) sample solutions,  $1.0 \times 10^{-4}$ - $1.0 \times 10^{-2}$  mol L<sup>-1</sup>. The pH was adjusted by adding small volumes of 0.1-1.0 mol L<sup>-1</sup> of HNO<sub>3</sub> or NaOH to the test solutions and the variation of potential was followed. The potential readings of the electrodes are nearly constant between pH 1.6 and 5.8, Fig. 5. At pH > 6.0 the emf values of the sensors sharply decrease due to precipitation of Cu(OH)<sub>2</sub> and/or formation of hydroxy copper complexes.



**Figure 5.** Effect of pH on the response of Cu(II)-CFZ CMCPE using  $1 \times 10^{-3}$  (A),  $1 \times 10^{-4}$  (B) and  $1 \times 10^{-5}$  (C) mol L<sup>-1</sup> of copper solution.

### 3.4. Effect of temperature

Ion-selective electrodes response is usually affected by the temperature of the test solution. The thermal stability of the sensor was examined by construction of calibration curves at various copper solution temperatures, covering the range 30-60 °C. The performance characteristics of the sensor at different test solution temperature are given in table 2. The results indicate that the slopes of the calibration graphs were still in the Nernstian range at temperatures 30-50 °C while at 60 °C the slope was supper Nernstian of 36.87 mV/decade. The linear concentration ranges of the electrodes are almost unchanged with increasing the temperature of the test solution.

**Table 2.** Performance characteristics of Cu(II)-CFZ CMCPE at different test solution temperatures.

Temperature (°C)	Slope (mV/decade)	Linear range (mol L <sup>-1</sup> )
30	30.37	$1.01 \times 10^{-6}$ - $3.32 \times 10^{-3}$
40	32.15	$1.01 \times 10^{-6}$ - $3.32 \times 10^{-3}$
50	34.07	$2.54 \times 10^{-6}$ - $1.29 \times 10^{-3}$
60	36.87	$4.01 \times 10^{-6}$ - $1.29 \times 10^{-3}$

3.5. Determination of the thermal coefficient of the electrodes

In order to examine the applicability of the sensor over a temperature range thermal coefficient value was calculated. The lower the coefficient value the higher the thermal stability of the electrode.

To calculate the thermal coefficient of the cell  $(dE^\circ/dt)_{cell}$ , the standard cell potentials,  $E^\circ_{cell}$ , were determined at different temperatures from the respective calibration plots as the intercept of these plots at  $pCu(II) = 0$ . Knowing that  $E^\circ_{cell}$  is related to  $(dE^\circ/dt)$  by the equation [45]:

$$E^\circ_{cell} = E^\circ_{25^\circ C} + (dE^\circ/dt) (t - 25)$$

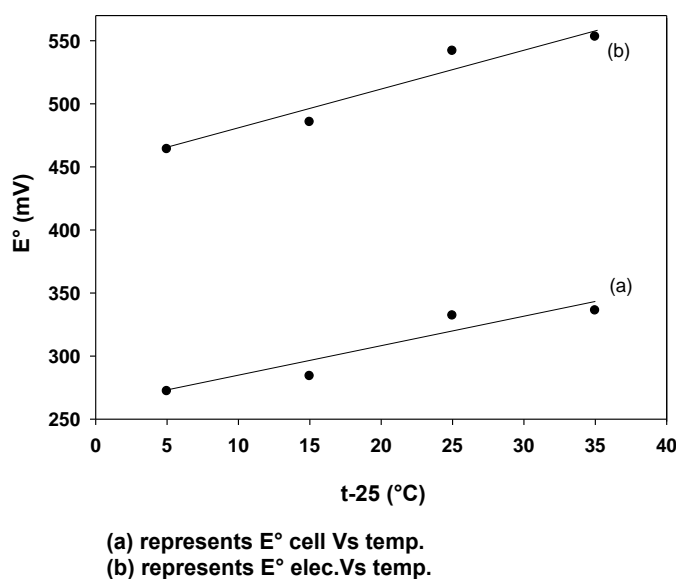
Plot of  $E^\circ_{cell}$  versus  $(t-25)$  produced a straight line with a slope taken as the thermal coefficient of the cell. The values of the standard potentials of electrodes ( $E^\circ_{elec.}$ ) were calculated after the subtraction of the standard electrodes potential of the silver/silver chloride electrode at different temperatures. The standard potential of the Ag/AgCl electrode as a function of temperature were calculated from the following equation [46] (where  $t$  is temperature in  $^\circ C$ ):

$$E^\circ(V) = 0.23695 - 4.8564 \times 10^{-4} t - 3.4205 \times 10^{-6} t^2 - 5.869 \times 10^{-9} t^3$$

for  $0 < t < 95^\circ C$

The calculated values of  $E^\circ_{Ag/AgCl}$  (mV) are 219.1, 211.6, 203.3, and 194.2 at temperatures 30, 40, 50, and 60  $^\circ C$ , respectively.

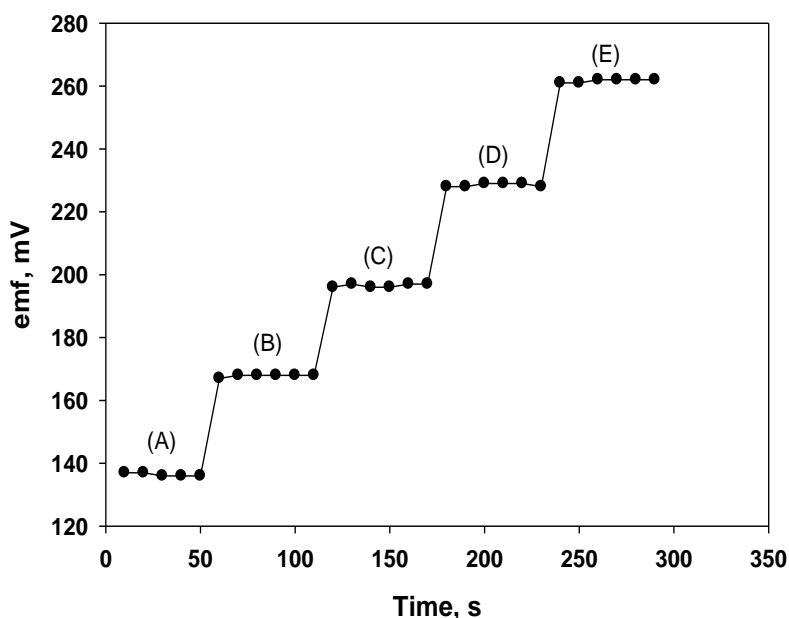
Plots of ( $E^\circ_{elec.}$ ) versus  $(t-25)$  for each electrode gave a straight line, Fig. 6. The slope of the line was taken as the thermal coefficient of the electrode. The values of  $(dE^\circ/dt)_{cell}$ , and  $(dE^\circ/dt)_{elec.}$  were  $2.345 \times 10^{-3}$ , and  $1.3045 \times 10^{-3}$  V/ $^\circ C$ , respectively, which reveal the high thermal stability of the studied electrodes within the investigated temperature range and show no deviation from the theoretical Nernstian behavior.



**Figure 6.** Variation of the standard potential of the cell (a) and the standard electrode potential of Cu(II)-CFZ CMCPE (b) with changes of the test solution temperature.

### 3.6. Response Time

The present Cu(II)-selective electrodes generate stable and reproducible potentials at relatively short response times. Fig. 7 represents potential-time plot. The average time required for the electrode, based on 2% Cu(II)-CFZ, and DOA as plasticizer, to reach a stable potential response within  $\pm 1$  mV of the final equilibrium value after successive immersion in a series of Cu(II) solutions, each having a tenfold difference in concentrations, was 10 s for concentrations  $1.0 \times 10^{-5}$  to  $1.0 \times 10^{-1}$  mol L<sup>-1</sup>, Fig. 7. The fast response time is most probably due to the fast exchange kinetics of the complexation formation and/or decomplexation of copper ion at the test solution-paste interface.



**Figure 7.** Dynamic response time of the Cu(II)-CFZ CMCPE for the stepwise addition of Cu(II) concentration: (A)  $1.0 \times 10^{-1}$ , (B)  $1.0 \times 10^{-2}$ , (C)  $1.0 \times 10^{-3}$ , (D)  $1.0 \times 10^{-4}$  and (E)  $1.0 \times 10^{-5}$  mol L<sup>-1</sup>.

### 3.7. Life Span

The behavior of carbon paste electrodes and their changes with time is not being quoted very often. It may be noticeable for some special mixtures made of more volatile binders (e.g., organic esters [31, 32] which may desiccate within a few weeks. Other mixtures don't live more than 24 hours. The performance characteristics of our electrode based on 2% Cu(II)-CFZ, 45% DOA as plasticizer was investigated. Two methods have been used in the present investigation, In the first method, the electrode was hanged in air without renewing the surface, where the electrode response is measured every 2-5 days, while in the second method, the electrode was soaked in  $10^{-3}$  mol L<sup>-1</sup> Cu(II) solution and the electrode response is measured periodically. The results indicate that the electrode lives for at least 20 days without renewing the surface when soaked in air and 17 days when soaked in  $10^{-3}$  mol L<sup>-1</sup> Cu(II), Table 3.

**Table 3.** Life span of Cu(II)-CFZ CMCPE hanged in air and soaked in  $10^{-3}$  mol L<sup>-1</sup> Cu(II) solution.

Hanged in air		Soaked in $10^{-3}$ mol L <sup>-1</sup> Cu(II) solution	
Time (day)	Slope (mV)	Time (day)	Slope (mV)
1	29.64	1	29.64
2	28.68	2	29.29
5	28.58	5	29.1
9	28.55	11	28.01
14	27.65	13	26.09
15	27.19	14	25.8
20	26.07	17	23.47
25	21.75	18	21.17
28	19.85	19	19.83

### 3.8. Selectivity of Cu(II)-CFZ

Selectivity is the most important character as it determines the extent of utility of any sensor in real sample measurements. It gives the response of ion-selective sensor for the primary ion in the presence of other ions in solution. The selectivity coefficients of Cu(II)-CFZ CMCPE towards many inorganic cations were evaluated by the matched potential method [36-38]. In this method, selectivity coefficient  $K_{Cu,J}^{MPM}$  is given by:

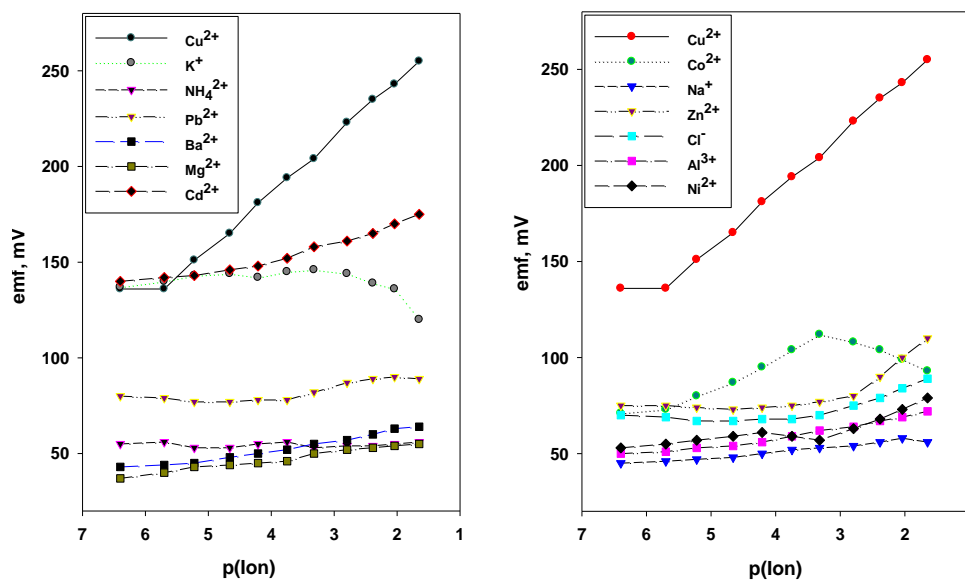
$$K_{Cu,J}^{MPM} = \frac{\Delta a_{pCu^{2+}}}{a_B} = \frac{a'_{pCu^{2+}} - a_{pCu^{2+}}}{a_B}$$

**Table 4.** Selectivity coefficients of various interfering ions for Cu(II)-CFZ CMCPE.

Interfering ion	$K_{Cu(II),J}^{MPM}$
Zn <sup>2+</sup>	$1.438 \times 10^{-3}$
K <sup>+</sup>	$2.743 \times 10^{-4}$
Na <sup>+</sup>	$9.350 \times 10^{-4}$
Mg <sup>2+</sup>	$1.454 \times 10^{-3}$
Co <sup>2+</sup>	$8.995 \times 10^{-4}$
Ni <sup>2+</sup>	$1.349 \times 10^{-3}$
Pb <sup>2+</sup>	$4.132 \times 10^{-3}$
NH <sub>4</sub> <sup>+</sup>	$1.986 \times 10^{-3}$
Cd <sup>2+</sup>	$9.420 \times 10^{-3}$
Ba <sup>2+</sup>	$1.403 \times 10^{-3}$
Al <sup>3+</sup>	$7.592 \times 10^{-3}$
Cl <sup>-</sup>	$7.999 \times 10^{-4}$

The selectivity coefficient is determined by measuring the change in potential upon increasing the concentration by a definite amount of the primary ion activity (pCu(II)) from an initial value of  $a_{pCu^{2+}}$  to  $a'_{pCu^{2+}}$  and  $a_B$  represents the activity of the interfering ion added to the same reference solution

of activity  $a_{\text{pCu}^{2+}}$  which brings about the same change in potential. The activity of Cu(II) as reference solution was taken as  $10^{-5} \text{ mol L}^{-1}$  in this study. The  $K_{\text{Cu},J}^{\text{MPM}}$  values (Table 4) are within the range of  $10^{-3}$ – $10^{-4}$ . This indicates that all ions tested causes negligible interference on the functioning of the proposed copper electrode. The potential response of the electrode at varying concentrations of these ions is shown in Fig. 8. It is clear from the figures that the slopes of the calibration graphs of all cations tested is non significant. Thus, the investigated sensor has high selectivity to Cu(II) ion over all cations examined.



**Figure 8.** Calibration graphs of Cu(II)-CFZ CMPCE for different ions.

### 3.9. Analytical Applications

The utility of the Cu(II)-CFZ electrode was further investigated to determine copper concentration in different samples and as an indicator electrode in titrimetric determination of Cu(II) ions.

#### 3.9.1. Potentiometric determination of copper in real samples

The Cu(II)-CFZ electrode was used successfully for determination of Cu(II) ions in different environmental samples including mineral and tap water, wastewater, tea, Soft drinks and milk powder. Determination of Cu(II) in the previously mentioned samples was performed using the standard addition method. The assay method for Cu(II) ions over the concentration range  $0.372$ – $3.492 \mu\text{g mL}^{-1}$  was achieved using three batches (three determinations each) for the statistical treatment of the results. Water samples of very low concentration of Cu(II) (below the detection limit of the electrode) were spiked by adding aliquots of standard solution of Cu(II) to the samples. It is clear from the results, given in table 5, that there is good agreement between the results of the proposed sensor and those obtained from AAS method. The recovery ranges are between 97.35 and 101.7%.

**Table 5.** Determination of copper in tea, soft water, milk powder and different types of water samples potentiometrically using the proposed Cu(II)-CFZ CMCPE and by AAS.

Sample	Found	Added ( $\mu\text{g/mL}$ )	Total ( $\mu\text{g/mL}$ )	Found <sup>(a)</sup>	Recovery %	RDS%
	AAS method ( $\mu\text{g/mL}$ )			Potentiometrically ( $\mu\text{g/mL}$ )		
Tap water	0.952	–	0.952	0.953	100.1	3.43
	–	2.413	3.365	3.309	98.33	0.32
Wastewater	0.012	0.360	0.372	0.370	99.46	0.41
Mineral water	–	2.438	2.438	2.473	101.4	0.18
Milk Powder	3.492	–	3.492	3.400	97.35	1.48
Soft drink	–	2.438	2.438	2.479	101.7	0.13
Tea	0.372	2.438	2.810	2.759	98.18	2.04

(a): Average of three measurements

RSD: relative Standard deviation

### 3.9.2. Direct potentiometry

For analysis of pure copper solution, brass powder and sea water samples, the content of copper in each was measured by direct potentiometry using the present Cu(II)-CFZ CMCPE and by AAS. As it is seen in table 6, the results obtained by direct potentiometric method are in good agreement with those obtained by atomic absorption method.

**Table 6.** Assessment of copper content in brass, copper solution used in electroplating cells in Banknote Printing House of the Central bank of Egypt and Sea Water by using AAS and Cu(II)-CFZ CMCPE.

Sample	Copper concentration ( $\mu\text{g/mL}$ )		Recovery%	RSD%
	AAS method	Potentiometric method <sup>(a)</sup>		
Copper electroplating solution <sup>(1)</sup>	4.49	4.44	98.88	4.22
	29.9	30.9	103.3	4.08
	374	373	99.73	3.60
Brass <sup>(2)</sup>	1.84	1.83	99.45	4.14
	46.1	46.6	101.1	4.50
	92.1	92.8	100.8	3.88
Sea water <sup>(3)</sup>	3.68	3.71	100.8	1.19
	36.8	37.2	101.1	2.55

<sup>(1)</sup>: This solution is used in Banknote printing plate preparation

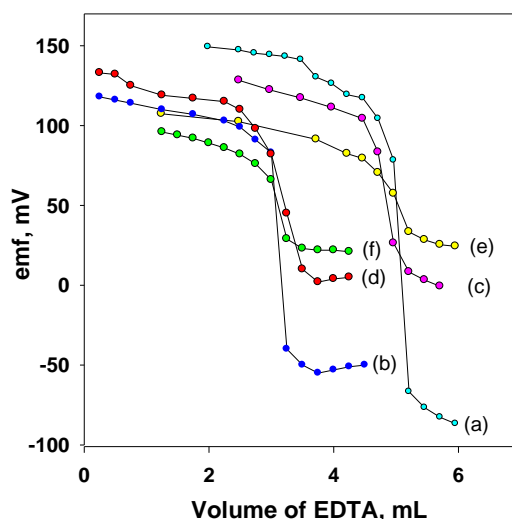
<sup>(2)</sup>: Composition: copper (>60%), zinc (~35%), tin (<6%), lead (<8%), aluminum (<4%), iron (<4%), manganese (<4%), silicon (<4%), and arsenic (<1%).

<sup>(3)</sup>: Water collected from Naama Bay

(a): Average value of three determinations

3.9.3. Potentiometric titrations

The newly proposed CMCP sensor was successfully used as an indicator electrode in the potentiometric titration of copper solution with EDTA. Cu(II) solution of concentrations ranging from 1.27 mg to 8.0 µg were titrated potentiometrically against  $1.0 \times 10^{-4}$ - $1.0 \times 10^{-2}$  mol L<sup>-1</sup> EDTA solutions using the Cu(II)-CFZ as indicator electrode, Fig. 9. The minimum quantification limit applying the potentiometric titration was practically determined by carrying out the titration at different level of Cu(II), Table 7. Recovery values was  $\geq 94.43\%$  at 64 µg Cu(II). Lower concentrations showed low recovery values, 92.3 and 87.5% at 13.0 and 8.0 µg, respectively. The titration curves have jumps that are high enough to be used as indication to the end points of the titrations, Fig. 10.

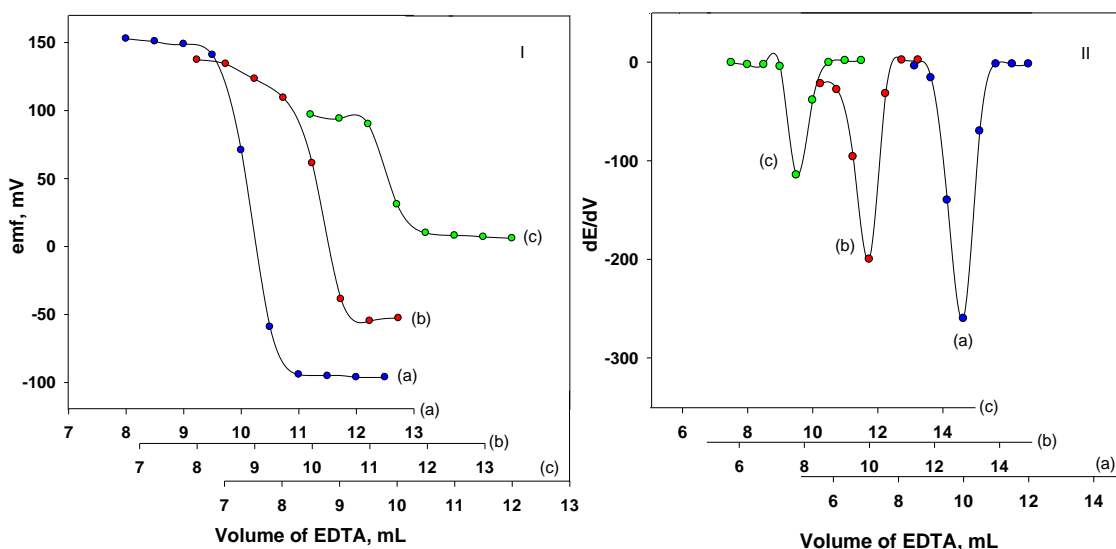


**Figure 9.** Potentiometric titration curves for different amounts of Cu(II), (a) 1.27 mg and (b) 0.794 mg, against  $10^{-2}$  mol L<sup>-1</sup> EDTA, (c) 127 µg and (d) 79.0 µg against  $10^{-3}$  mol L<sup>-1</sup> EDTA and (e) 13.0 µg and (f) 8.0 µg against  $10^{-4}$  mol L<sup>-1</sup> EDTA.

**Table 7.** Determination of copper in pure solutions applying potentiometric titrations.

Taken Mg	Found Mg	Recovery <sup>(a)</sup> %	RSD%
6.350	6.414	101.0	0.72
1.270	1.290	101.6	1.04
0.794	0.787	99.11	0.56
0.635	0.639	100.6	0.71
0.127	0.124	97.63	0.31
0.079	0.078	98.73	1.72
0.064	0.063	94.43	0.94
0.013	0.012	92.30	2.47
0.008	0.007	87.50	1.15

(a): Average value of three determinations



**Figure 10.** Conventional (I) and first derivative (II) potentiometric titration curves for Cu(II), (a) 6.35 mg, (b) 0.635 mg, (c) 64.0  $\mu\text{g}$  of against  $10^{-2}$ ,  $10^{-3}$  and  $10^{-4}$  mol L $^{-1}$  EDTA, respectively.

#### 4. CONCLUSION

The proposed chemically modified carbon paste electrode based on copper cefazoline, Cu(II)-CFZ, ion-associate as electroactive phase can be used in the development of copper ion-selective electrode. The electrode having the composition of 2% Cu(II)-CFZ, 53.0% graphite, and 45.0% DOA responds to Cu(II) ions in a Nernstian behavior with slope of 29.44 mV/decade with limit of detection of  $6.28 \times 10^{-7}$  mol L $^{-1}$ . The electrode is characterized by a relatively fast response, reasonable long-term stability and responsive potential stability. Most of metal ions do not affect the selectivity of the copper electrode. The electrode was applied to direct determination of Cu(II) ions in water samples, milk powder, brass powder, soft drink and tea and as indicator electrode in potentiometric titration. By comparing the response characteristics of the developed Cu(II)-CFZ electrode with some of the reported Cu(II) electrodes, it was found that the present electrode has fast response time ( $\leq 10$  sec) than the electrode developed by Abbaspour and Moosavi (45 sec) [2], Mittal et al. (30 sec) [47] and Singh and Bhatnagar ( $<30$ ) [48]. Also the present electrode has comparable application range to that developed by Gissera et al. ( $9.66 \times 10^{-6}$  -  $1.0 \times 10^{-2}$ ) [49].

The detection limit of the present electrode is much lower than the electrodes reported by Singh and Bhatnagar ( $4.7 \times 10^{-6}$  mol L $^{-1}$ ) [48], Isa et al. ( $2.5 \times 10^{-6}$  mol L $^{-1}$ ) [50], Abbaspour and kamyabi ( $1.0 \times 10^{-6}$  mol L $^{-1}$ ) [51] and Gissera et al. ( $2.5 \times 10^{-6}$  mol L $^{-1}$ ) [49], while it has comparable detection limit to those electrodes developed by Mittal et al. ( $4.0 \times 10^{-7}$  mol L $^{-1}$ ) [47], Gholivand and Nozari ( $6.0 \times 10^{-7}$  mol L $^{-1}$ ) [52] and Mashhadizadeh et al. ( $3.2 \times 10^{-7}$  mol L $^{-1}$ ) [53].



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