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Studies on Electrochemical Behaviour of Copper(II)-Dithiocarbamate Complexes at DME: Applications to Environmental and Biological Samples

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Catalytic hydrogen current method has been explained for the sensitive and selective detection of copper(II) using ammonium 4-phenylpiperazine-1-dithiocarbamate (Amm 4-PP-DTC) and ammonium 4-benzylpiperidine-1-dithiocarbamate (Amm 4-BP-DTC) in different environmental and biological matrices. It was mainly depends on the interaction of copper(II) with 4-Amm 4-PP-DTC and Amm 4-BP-DTC in background electrolyte (NH_4Cl-NH_4OH) medium at pH 6.6. The pronounced parabolic shaped peaks were observed at -0.31V and -0.48 V *vs*. SCE, respectively due to the catalytic hydrogen currents produced from the dithiocarbamate-metal complexes. Then after, catalytic hydrogen currents were recorded using D.C polarography. pH effect, background electrolyte (NH_4Cl-NH_4OH) effect and dithiocarbamates and copper(II) ion effects were optimized in this study. The present developed method was fruitfully applied to analyze copper(II) in various sample of environmental and biological importance. The recovery percentages obtained from this study were found to be 95-99 % and comparable with AAS method.

Keywords: Polarography, Copper(II), Ammonium 4-arylpiperazine-1-dithiocarbamate, Atomic absorption spectroscopy.

INTRODUCTION

Most of the vegetables, grains and meat is rich in copper naturally [1,2]. Ever since, copper has a significant role in maintaining various biological mechanisms, it is highly essential to determine the concentration of copper in different foods [3-5]. Mainly long term exposure to copper from water and soil sources causes the adverse effects including tachychardia, haemoturia, hyper tension, gastro-intestinal bleeding and vomiting's [5]. After accumulation of copper in the liver and some areas of brains leads to Wilson's disease [6]. Copper deficiency associated with a clinical disorder such as a defective reproductive performance, anemia, heart stroke and gastro-intestinal issues are due to the dietary deficiency [7]. On the other hand, copper has wide industrial applications to manufacture superconducting tubes, wires, paints, water pipes and roofing material, *etc*. [8]. Rao and Rao [9,10] designed a novel method to determine the micro amounts of copper in the presence of oxime using *n*-butanol and cyclohexanone. Rekha *et al.* [11] reported the determination of copper in biological samples, plants and pharmaceutical preparations using polarography. An adsorptive catalytic wave method was developed for the analysis of copper in 1,10-phenanthroline and HCl-thioglycollic acid medium with LOD's of 0.03 μg mL^{-1} [12]. Yan and co-workers [13] proposed a method by chelating copper with different ligands (thiosemicarbazone associated with acetonyl acetone, benzaldehyde, salicylaldehyde) in *N*,*N*-dimethylformamide. An adsorptive polarographic methodology was proposed for the detection of micro levels of copper in human hairs [14]. The sensitive determination of copper in the presence of sulphuric acid and thiourea was reported by Biernat and Syzmaszek [15]. Copper(II) behaviour in amino butanoate solution was discussed and observed that the two electron reversible reduction peaks were recorded at two different pH ranges (1.2-4.2 and 6.1-11.9). Based on this method, copper(II) was detected with the LOD's of 0.6 ppm [16]. Acetate and benzinoxime buffers were used for the determination of copper(II) in alloys of aluminium [17].

Dry ash method for the analysis of copper(II) in ammonium chloride-anhydrous sodium sulphite buffer medium using polarography was developed. In this method, copper(II) was detected in various cheese samples obtained from Dutch with very low detection limits [18]. Palaniappan and Revathi [19] designed a novel polarographic method to analyze copper(II) by indirect method. This method was based on the formation of stable complex with salicylaldehyde thiosemicarbazone [19]. In the presence of antipyrine-sodium perchlorate medium, polarographic method coupled to catalytic current was developed for the detection of copper(II) [20]. The voltammetric studies were carried out to develop a sensitive method for the detection of copper(II) with xanthates at DME using D.C. polarography in different samples of environmental importance [21]. Huang and Du [12] have developed a polarographic method for the determination of copper(II) using adsorptive catalytic waves in HCl-thioglycollic acid-1,10-phenanthroline medium, which provided a good space to achieve very low detection limits in real water systems. A novel polarographic technique was explained based on the interaction of ethyl orange and ascorbic acid as a function of catalytic activity. Based on this principle, trace and ultra-trace amounts of copper(II) was detected in human finger nails [22].

In this study, two novel dithiocarbamates namely, ammonium 4-phenylpiperazine-1-dithiocarbamate (Amm 4-PP-DTC) and ammonium 4-benzylpiperidine-1-dithiocarbamate (Amm 4-BP-DTC) were used to develop a sensitive and selective catalytic hydrogen currents technique using D.C. polarography for copper(II) detection. In this method, pronounced catalytic hydrogen currents with peak potential at -0.31 and -0.48 V *vs.* SCE with Amm 4-PP-DTC and Amm 4-BP-DTC, respectively were found in NH_4Cl-NH_4OH medium. The diffusion current wave for copper(II) with $E_{1/2}$ was recorded at -0.51 V *vs.* SCE.

EXPERIMENTAL

Analytical grade reagents and doubly distilled deionized water were used in this study. All chemicals such as ammonia solution, carbon disulphide, phenyl piperazine, ammonium chloride and 4-benzyl piperidine were supplied from S.D. Fine chemicals, Mumbai, India. Standard solution of copper(II) (1 μg mL^{-1}) was prepared by weighing 3.928 g L^{-1} of $CuSO_4 \cdot 2H_2O$ and dissolved in doubly distilled deionized water and made up to the mark in 1 L volumetric flask. The synthesis procedure for Amm 4-PP-DTC and Amm 4-BP-DTC was reported in the earlier studies [23-30]. Amm 4-PP-DTC (0.01 M) was prepared by weighing 2.55 g of Amm 4-PP-DTC and dissolved in 100 mL doubly distilled deionized water. Amm 4-PP-DTC (0.01 M) was prepared by weighing 2.67 g of Amm 4-BP-DTC and dissolved in 100 mL doubly distilled deionized water. Stock solutions of Amm 4-PP-DTC, Amm 4-BP-DTC and NH_4Cl-NH_4OH were prepared by appropriate dilutions in 250 mL volumetric flasks and refrigerated at 4 °C.

D.C. Polarography models CL-357 and CL-25 (Elico Private Ltd, India) were used to record current-voltage curves. The comparison study was performed using Shimadzu AA 6300 spectrometer.

General procedure: Fixed volumes of background electrolyte (NH_4Cl-NH_4OH), ligands (Amm 4-PP-DTCand Amm 4-BP-DTC) and followed by the metal solution were added into the 100 mL beaker. The pH of the solution was adjusted using 0.1 M HCl or NaOH and transferred into the polarographic cell. Then after, the solution was degassed using 99.9 % pure nitrogen gas for 15 min to remove the dissolved oxygen. Finally, the polarograms were recorded with D.C. polarography.

RESULTS AND DISCUSSION

Different optimized experimental conditions were established to analyze copper(II). The recorded polarograms were depicted in Fig. 1.

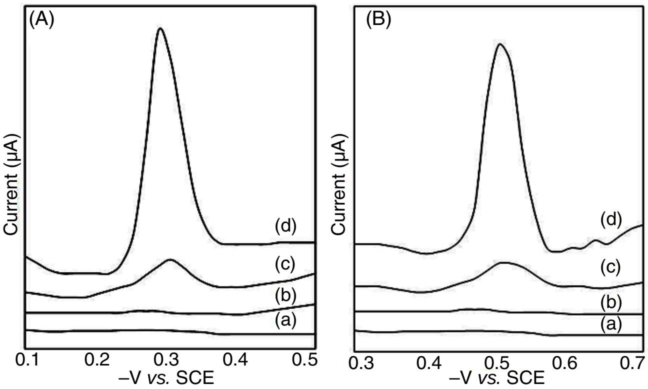

Fig. 1. The recorded polarograms for copper(II) with (A) Amm 4-PP-DTC (a) 0.4 M NH_4Cl, pH ~ 6.6 (b) a+ 2.0 mM Amm 4-PP-DTC (c) a+ 3.0 ppm copper(II) (d) b+ 3.0 ppm copper(II) (B) Amm 4-BP-DTC (a) 0.4 M NH_4Cl, pH~6.6 (b) a+ 3.6 mM Amm 4-BP-DTC(c) a+ 3.0 ppm copper(II) (d) b+3.0 ppm copper(II) in NH_4Cl-NH_4OH medium

Method optimization: The effect of pH was studied at fixed concentration of copper(II), background electrolyte and ligands (Amm 4-PP-DTC and Amm 4-BP-DTC) as 3.0 ppm, 0.4 M and (3.0 mM and 4.0 mM), respectively, varying the pH from 5.0 to 10.0. Interestingly, it was observed that the height of catalytic hydrogen currents increased gradually with increase in pH until it reach 6.6. Beyond the pH 6.6, the height of catalytic hydrogen currents started decreasing. The maximum current height with Amm 4-PP-DTC and Amm 4-BP-DTC were achieved at pH 6.6. Therefore, the pH 6.6 was selected as optimum for further studies as illustrated in Fig. 2A. With the increase in pH, a slight shift in the peak towards positive potential was observed. The effect of background electrolyte (NH_4Cl-NH_4OH) on the catalytic hydrogen currents height was studied in the range of 0.1 to 0.8 M by fixing the other parameter constant as mentioned in the pH effect. The resulted polarograms were well defined at 0.4 M NH_4Cl-NH_4OH with Amm 4-PP-DTC and Amm 4-BP-DTC. Further increase in the concentration, the catalytic hydrogen current height decreased, therefore the optimum concentration of 0.4 M was chosen for all the studies as shown in Fig. 2B.

The effect of ligand (Amm 4-PP-DTC and Amm 4-BP-DTC) concentration was varied ranging from 0.5-6.0 mM by keeping all other parameters unchanged as explained in the above discussion.

The obtained experimental results indicated that the catalytic hydrogen current height have changed linearly with the ligand concentration up to 3.0 mM for Amm 4-PP-DTC and 4.0 mM for Amm 4-BP-DTC. With further increase in dithiocarbamate concentration the catalytic hydrogen current height was unaffected and confirmed the formation of stable copper(II)-dithiocarbamate complexes. Therefore, 3.0 mM and 4.0 mM concentrations were fixed for further quantitative studies. The plot of {[dithiocarbamate]/ip} *vs.* {dithiocarbamate} is a straight line as shown in Fig. 2D, which clearly indicates that the reaction occurring on the surface of the electrode (DME) is an adsorption phenomenon. The effect of mercury column height was varied and the polarogramsfor copper(II) (2.0 ppm) were recorded. It was observed that the $i_c/\sqrt{h}$ decreased with the increase in the mercury column height, which is indicative of catalytic hydrogen currents. The effect of gelatin

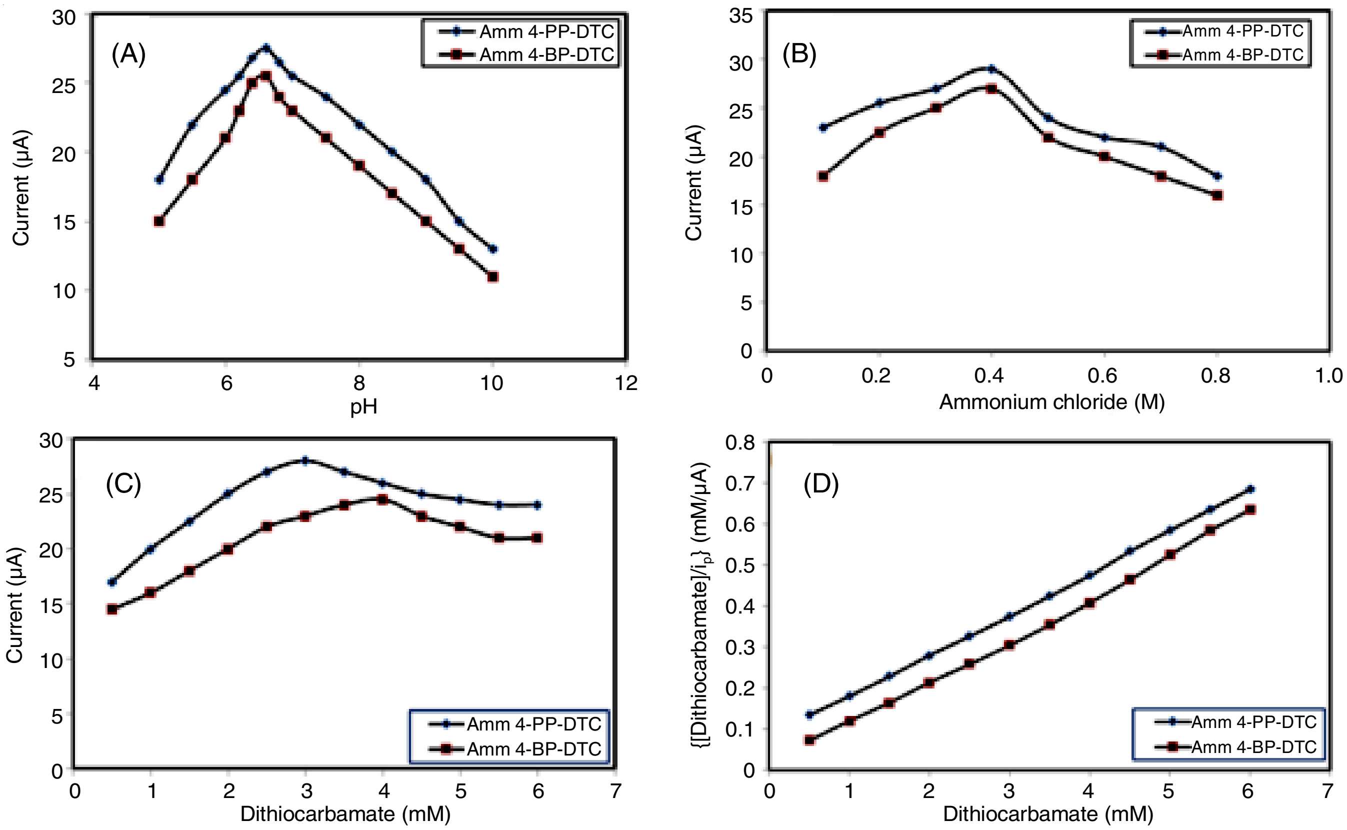

Fig. 2. Effect of (A) pH (B) NH_4Cl-NH_4OH (C) dithiocarbamate and (D) Langmuir adsorption isotherm plot for copper(II)-dithiocarbamate systems

and Triton X-100 were studied in the concentration range of 0.005 to 0.01 % and 0.002 to 0.004 %, respectively. The sharp decrease on the height of catalytic hydrogen currents after addition of 0.005 % gelatin was observed. However, further increase in the concentration of surface-active material made the 2 % variation on the height of the catalytic hydrogen currents. In the case of Triton X-100, suppression of catalytic hydrogen currents were less when compared to gelatin. In the both cases, the peak potentials has been shifted to more positive with the increase in concentration of surface-active materials.

The effect of temperature on the copper(II)-Amm 4-PP-DTC and Amm 4-BP-DTC systems were measured from 15 to 45 °C. The height of the catalytic hydrogen current increased with the increase in temperature, however the co-efficient of temperature (i_c) decreased. It was found that above 30 °C the catalytic hydrogen currents height is unaffected by the temperature. At optimum experimental conditions, concentration of copper(II) was studied by varying 0.05 to 6.0 ppm. The catalytic hydrogen currents height increased linearly with the increase in copper(II) concentration from 0.05 to 6.0 ppm. Fig. 3 represents the effect of excipients on the catalytic hydrogen currents height produced from the copper(II)-dithiocarbamate complexes. In this case the excipients such as neutral salts monovalent cations and divalent cations were employed. The

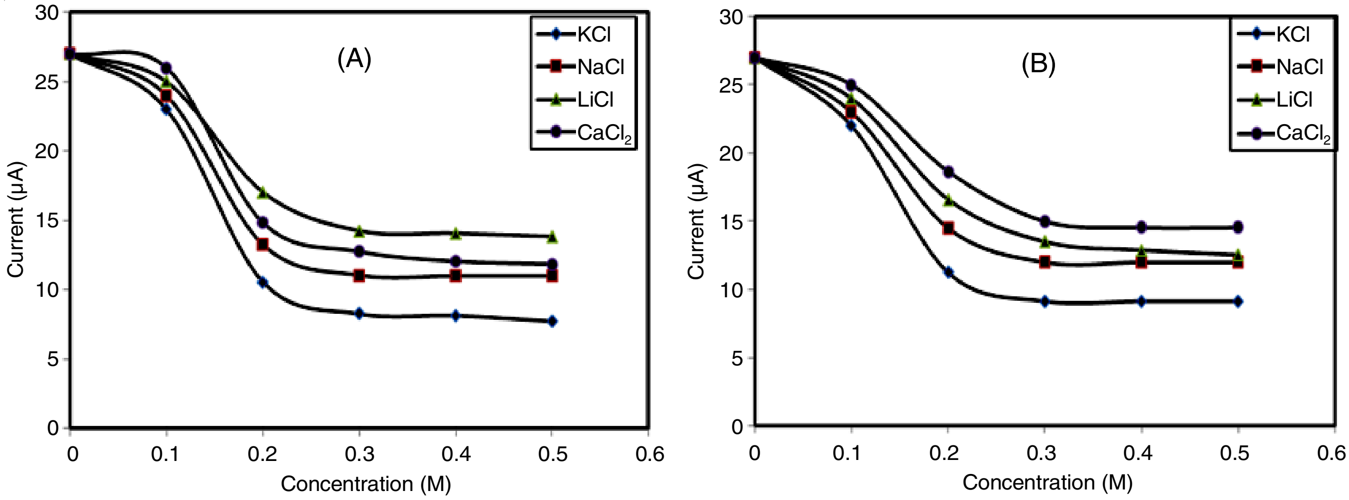

Fig. 3. Effect of indifferent ions on copper(II) complexes of (A) Amm 4-PP-DTC and (B) Amm 4-BP-DTC

obtained experimental results suggests that the replacement of monovalent cations with divalent cations can affect the catalytic hydrogen current height. Fig. 3 clearly states that increase in calcium chloride concentration do affect the catalytic hydrogen current height when compared to the monovalent chloride ions.

Analytical applications: The established catalytic hydrogen currents method was adopted for the detection of copper(II) indifferent environmental, vegetable and biological samples to examined the accuracy and precision. In this study, 1 L each of the water samples collected from industrial estate and surrounding places of Amararaja batteries (Tirupati town, Chittoor district) were heated at 80 °C for 90 min and preconcentrated to 100 mL. The obtained analytical data was represented in Tables 1 and 2.

Vegetable samples (3.5 g each) collected from the local market was dried for 48 h at room temperature and then after, dry ash method was adopted to prepare the samples. The residue was diluted with doubly distilled deionized water in a 50 mL volumetric flask and used for further analysis. The obtained analytical data was shown in Tables 3 and 4.

Milk samples were collected from the local dairy farm. To the different crucibles, each milk sample was added drop wise and heated at 450 °C for 60 min to eliminate moisture and further evaporated until the solution turns in to black ash. Then after, the ash was collected and dissolved in 3 mL of concentrated HNO_3 and evaporated to dryness. The finally obtained residue was further dissolved in 3 mL of dilute HNO_3 and filtered. To this filtrate, doubly distilled deionized water was used to dilute in 25 mL beaker. This clear aliquot solution was used for further studies. The obtained results were shown in Table-5.

Conclusion

The present catalytic hydrogen current method is facile, rapid and cost effective for the detection of copper(II) in different environmental, vegetables and biological samples. The newly synthesized dithiocarbamates made the method more

TABLE-1
DETECTION OF COPPER(II) WITH Amm 4-PP-DTC FROM DRINKING WATER SAMPLES

Sample	Copper(II) added (ppm)	Present method (D.C. Polarography)		AAS method	
		Copper(II) found (ppm)	Recovery (%) ± RSD[b]	Copper(II) found (ppm)	Recovery (%) ± RSD[b]
Industrial estate	0.2	0.246	99.10 ± 2.54	0.248	99.55 ± 2.55
	0.4	0.482	99.05 ± 2.53	0.488	99.40 ± 2.56
	0.6	0.712	99.16 ± 2.51	0.718	99.66 ± 2.61
	0.8	0.962	100.00 ± 2.92	0.962	100.00 ± 2.94
	1.0	1.056	98.10 ± 2.33	1.100	100.00 ± 2.92
Amaraja batteries	0.2	0.238	98.05 ± 2.35	0.236	99.50 ± 2.44
	0.4	0.457	99.25 ± 2.48	0.457	99.70 ± 2.75
	0.6	0.712	99.37 ± 2.54	0.702	99.64 ± 2.63
	0.8	0.967	99.15 ± 2.46	0.965	99.14 ± 2.55
	1.0	1.099	98.05 ± 2.31	1.107	99.00 ± 2.44

For each run, 5 mL of the concentrated sample was used, n = Six individual determinations ± RSD.

TABLE-2
DETECTION OF COPPER(II) WITH Amm 4-BP-DTC FROM DRINKING WATER SAMPLES

Sample	Copper(II) added (ppm)	Present method (D.C. Polarography)		AAS method	
		Copper(II) found (ppm)	Recovery (%) ± RSD[b]	Copper(II) found (ppm)	Recovery (%) ± RSD[b]
Industrial estate	0.2	0.295	98.55 ± 2.37	0.299	99.00 ± 2.50
	0.4	0.542	98.50 ± 2.35	0.548	99.10 ± 2.56
	0.6	0.675	98.31 ± 2.32	0.677	99.16 ± 2.53
	0.8	0.815	95.10 ± 2.06	0.832	97.50 ± 2.27
	1.0	1.076	96.05 ± 2.15	1.095	98.00 ± 2.30
Amaraja batteries	0.2	0.260	97.00 ± 2.26	0.268	98.10 ± 2.27
	0.4	0.524	99.10 ± 2.55	0.530	99.50 ± 2.55
	0.6	0.655	99.05 ± 2.53	0.653	99.55 ± 2.50
	0.8	0.836	99.08 ± 2.52	0.830	99.47 ± 2.51
	1.0	1.087	96.15 ± 2.19	1.110	98.00 ± 2.37

For each run, 5 mL of the concentrated sample was used, n = Six individual determinations ± RSD.

TABLE-3
DETECTION OF COPPER(II) WITH Amm 4-PP-DTC IN VEGETABLES SAMPLES

Sample scientific/Local name	Copper(II) added (ppm)	Present method (D.C. Polarography)		AAS method	
		Copper(II) found (ppm)	Recovery (%) ± RSD[b]	Copper(II) found (ppm)	Recovery (%) ± RSD[b]
Abelmoschusesculentus/Ladies finger	1.0	1.045	98.15 ± 2.26	1.046	98.45 ± 2.34
Lycopersiconesculentum/Tomato	1.0	1.127	98.95 ± 2.79	1.035	99.35 ± 2.60
Coceiniagrandis/Little gourd	1.0	1.970	99.70 ± 2.67	1.099	99.90 ± 2.86

For each run, 5 mL of the concentrated sample was used, n = Six individual determinations ± RSD.

TABLE-4
DETECTION OF COPPER(II) WITH Amm 4-BP-DTC IN VEGETABLE SAMPLES

Sample scientific/Local name	Copper(II) added (ppm)	Present method (D.C. Polarography)		AAS method	
		Copper(II) found (ppm)	Recovery (%) ± RSD^b	Copper(II) found (ppm)	Recovery (%) ± RSD^b
Abelmoschusesculentus/Ladies finger	1.0	1.126	97.75 ± 2.10	1.134	98.15 ± 2.26
Lycopersiconesculentum/Tomato	1.0	1.055	98.30 ± 2.28	1.068	98.86 ± 2.35
Coceiniagrandis/Little gourd	1.0	1.084	99.25 ± 2.56	1.088	99.80 ± 2.71

For each run, 5 mL of the concentrated sample was used, n = Six individual determinations ± RSD.

TABLE-5
DETECTION OF COPPER(II) WITH Amm 4-BP-DTC AND AMM 4-PP-DTC IN COW MILK

Cow milk	Copper(II) added (ppm)	Copper(II) found in samples (ppm)			
		Present method (D.C. Polarography)		AAS method	
		Amm 4-PP-DTC	Amm 4-BP-DTC	Amm 4-PP-DTC	Amm 4-BP-DTC
1	1.0	1.89 ± 1.502	1.86 ± 1.419	1.85 ± 1.502	1.91 ± 2.385
2	1.0	1.47 ± 1.722	1.45 ± 1.425	1.44 ± 1.715	1.49 ± 1.586
3	1.0	1.73 ± 1.419	1.75 ± 1.402	1.77 ± 1.517	1.79 ± 1.732
4	1.0	2.26 ± 1.375	2.27 ± 1.562	2.28 ± 1.917	2.30 ± 1.599
5	1.0	2.24 ± 1.610	2.25 ± 1.426	2.26 ± 1.515	2.28 ± 1.501
6	1.0	2.01 ± 1.448	2.04 ± 1.504	2.03 ± 1.257	2.06 ± 1.513
7	1.0	1.92 ± 1.611	1.94 ± 1.484	1.96 ± 1.257	1.99 ± 1.964
8	1.0	1.72 ± 1.498	1.75 ± 2.385	1.77 ± 1.732	1.79 ± 1.742
9	1.0	1.60 ± 1.419	1.62 ± 1.517	1.64 ± 1.257	1.67 ± 1.414
10	1.0	1.81 ± 1.402	1.83 ± 1.627	1.87 ± 1.498	1.89 ± 1.906

For each run, 1 mL of the concentrated sample was used, n = Six individual determinations ± RSD.

sensitive and selective. The presence of dithiocarbamate in a medium containing NH_4Cl-NH_4OH background electrolyte and copper(II) give rise to a catalytic hydrogen currents, positive to the copper(II) reduction wave. The results obtained from the optimized parameters suggested the distinctive property of catalytic reactions on the surface of DME. The height of the catalytic hydrogen current decreased slightly with the increase in gelatin and Triton X-100 concentration which suggested that the adsorption is involved in the mechanism of the catalytic currents. The surfactants decrease the free surface area of the electrode and thereforedecreases the height of the catalytic hydrogen currents. The adsorption phenomenon was further supported from the study of indifferent electrolyte effect where the catalytic current decreased more with increasing ionic strength of Ca^{2+} than in the presence of K^+ or Na^+ or Li^+ indicating Brdicka type of catalytic currents.

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