Analytical CHEMISTRY
An Indian Journal

Trade Science Inc.

Full Paper

Determination of copper(II) in water, vegetables and alloy samples with polarography at DME using piperidine dithiocarbamate by catalytic hydrogen currents

N.Venkatasubba Naidu*, S.Kanchi, T.Niranjan, K.Saraswathi
Department of Chemistry, S.V.University, Tirupati-517 502, A.P., (INDIA)
E-mail : nvsn69@gmail.com
Received: 25th August, 2010 ; Accepted: 4th September, 2010

ABSTRACT

Facile, rapid and sensitive catalytic hydrogen polarographic method for the determination of Cu(II) with Piperidine dithiocarbamate (pip-DTC) in various water, vegetables and alloys was described in the present paper. The method was based on the catalytic hydrogen wave of pip-DTC-Cu(II) complex in the presence of NH_4Cl-NH_4OH medium at pH 6.6 and produce a catalytic hydrogen wave at -0.35 V vs SCE. Optimum parameters such as effect of pH, NH_4Cl-NH_4OH, Amm Pip- DTC, metal ion concentration and excipient effect on peak height were investigated to enhance the sensitivity of the present method. The proposed method was applied for the determination of Cu(II) in various water, vegetables and alloys and the results obtained were compared with the differential pulse polarography in terms of detection limits.   © 2011 Trade Science Inc. - INDIA

INTRODUCTION

Copper is one of the several metal ions that play an important role in the biological systems[1]. It plays a key role during cell respiration, in the blood of invertebrate animals and in the formation of haemocyanin[2], an important respiratory protein, found in the lymph of most animals belonging to phyla Mollusca and Arthropoda. From the stand point of human health, its role in three physiological functions is of prime importance. Copper is involved in haemopioesis, maintenance of vascular and skeletal integrity besides the structure and function of the central nervous system.

Copper occurs naturally in most vegetables, meat and grains. The study of copper in food items is of great concern, since it plays a definitive role in the intrinsic mechanisms regulating vital biological processes[3-5]. Over exposure to copper causes metallic taste, ptyalism, nausea, vomiting, epigastric burning and diarrhea. Heavy doses of copper causes a series of systematic toxic effects such as haemolysis, hepatic neurosis, gastrointestinal bleeding, oliguria azotemia, haemoglobinuria, haematuria, proteinuria, hyper tension, tachychardia, convulsions and coma. When a congenital deficiency is the haemostatic mechanism for copper exists, the metal accumulates in the liver, discrete areas of the brain, the cornea of the eye and other tissues causing Wilson's disease[6]. A wide variety of clinical disorders have been associated with a dietary deficiency of copper which respond to copper therapy. They include anemia, de-

Full Paper

pressed growth, neo-natal ataxia, impaired reproductive performance, heart failure and gastro-intestinal disturbances[7].

Apart from biological utility of copper, it also finds application in industries[8]. It is used in the electrical industry and fine wires, commutor bars and high conductivity tubes. It is also used in pipe making, roof sheeting and bronze paint and insecticides. In addition to this, it is a pollutant in the environment resulting from the industrial discharge in the form of particulate or soluble copper waste from electroplating, chemical and textile industries. As a pollutant, copper is of particular concern, because of the high degree of toxicity to aquatic organisms. In view of this determination of copper is indispensable.

The polarographic determination of copper in micro amounts via the solvent extraction into n-butanol or cyclohexanone in the presence of oxime was reported by Rao and Rao[9,10]. Polarographic certification analysis of standard samples of copper-based alloys was done by Vatamin et al.[11]. The polarogram of Cu(II) in HCl-thioglycollic acid, 1,10-phenanthroline exhibited an adsorptive catalytic wave which was applied for trace amounts of copper in waste and natural waters. The detection limit was 0.03 μg/ml[12]. Complexes of Cu(II) with thiosemicarbazones of benzaldehyde, salicylaldehyde, biacetyl, benzyl, acetyl acetone, acetonyl acetone in DMF were examined by polarography[13]. Determination of micro amounts of copper in human hair has been proposed by the polarographic adsorptive complex wave. This method was applied in the analysis of copper in human hair and the analytical result was evaluated[14]. The polarographic waves of copper (II) in the presence of sulphuric acid and thiourea were reported by Biernat and Syzmaszek[15].

The polarographic behavior of Cu(II) in 2-amino butanoate solutions at ionic strength, 0.4 were studied. Reversible 2-electron reduction waves were obtained at pH 1.2-4.2 and 6.1-11.9 for the Cu system. The lower limit for the determination of the metal was 0.6 ppm[16]. Copper was detected in aluminium alloys by Lei[17] using sodium acetate buffer and benzoin oxime. Copper in Dutch rennet cheeses are determined polarographically by dry ashing of a sample and polarographed in chloride-ammonia background electrolyte and anhydrous sodium sulphite[18]. Palaniappan
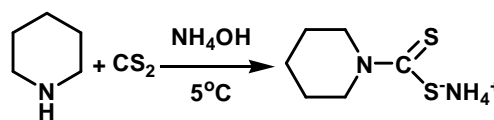
Scheme 1 : Synthesis of Ammonium piperidine dithiocarbamate (Amm pip-DTC)

and Revathi[19] developed an indirect polarographic method for the determination of Cu(II) based on the highly stable complex formation of Cu(II)-Salicyladehyde thio semicarbazone. A catalytic polarographic method for the determination of microgram quantities of Cu(II) was developed based on the catalytic currents of copper in the presence of antipyrine in sodium perchlorate medium[20]. Voltammetric studies was developed for the investigation of Cu(II) in various environmental samples with xanthates at DME by employing D.C. Polarography[21].

The polarogram of Cu(II) in HCl- thioglycollic acid-1, 10 phenanthroline exhibits an adsorptive catalytic waves which is applied to determine trace amounts of copper in waste and natural water[22]. An indirect kinetic method[23] was established for the determination of trace copper in human hair and finger nails based on catalytic function to the reaction between ethyl orange and ascorbic acid. The polarographic peak is observed at -0.30 V Vs SCE.

In the present polarogaphic work on Copper(II) determination with dithiocarbamates using Ammonium Piperidine dithiocarbamate (Amm pip-DTC) in ammonium chloride-ammonium hydroxide medium is examined and found that it gives a pronounced catalytic hydrogen wave with peak potential at -0.35 V Vs SCE.. Cu (II) diffusion current wave with $E_{1/2}$ is at -0.51 V Vs SCE in NH_4Cl-NH_4OH medium. Typical current-voltage curves of Cu (II)-dithiocarbamate system obtained in NH_4Cl-NH_4OH medium. The method is simple, sensitive, selective and rapid for the analysis of traces and ultra-traces of copper(II) in various water, vegetables and alloys.

EXPERIMENTAL

Materials and apparatus

All the experiments were performed at 25°C using freshly prepared solutions. Double distilled mercury and double distilled water were used. The dissolved oxy-
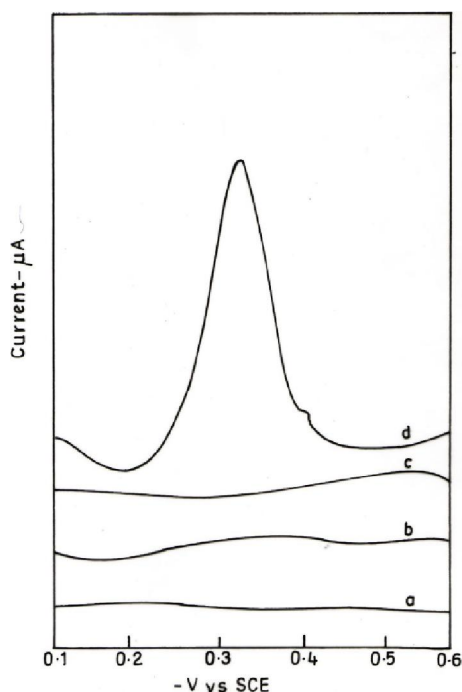
Figure 1 : Polarographic curve of copper (II) in NH₄Cl-NH₄OH medium in the presence of Amm pip-DTC. (a) 0.3 M NH₄Cl, pH ~6.6, (b) a + 2.0 mM Amm pip-DTC, (c) a + 1.0 ppm Cu(II) (d) b + 1.0 ppm Cu(II)

gen in the solutions was removed by passing pure nitrogen gas for 10 -15 minutes. Standard metal ion solution is prepared taking 3.928 g/l of $CuSO_4$ to get 1 µg/ml and adding few ml of acid corresponding to the anions of the salts to suppress the hydrolysis. Ammonium Chloride (1M) (S.D Fine Chemicals, India) is prepared by weighing 53.49 g of ammonium chloride (AnalaR) and dissolved in 1000 ml of doubly distilled deionised water.

5% ammonium hydroxide and 1% HCl (S.D Fine Chemicals, India) for pH adjustments are prepared from AnalaR samples. Potassium iodate(S.D Fine Chemicals, India) and sodium sulphite(S.D Fine Chemicals, India) are also prepared in doubly distilled deionised water using AnalaR samples. Triton X-100 is prepared in W/V basis. 0.2 g of Triton X-100 is weighed and dissolved in 100 ml doubly distilled deionised water in a standard flask. Gelatin (Difco laboratories, USA) is prepared by weighing accurately 0.125 g and dissolved in 25 ml of doubly distilled deionised water.

Synthesis of ammonium piperidine dithiocarbamate (Amm pip-DTC)

Carbon disulphide (80 g) (S.D Fine Chemicals,

India) was slowly added to a solution of piperidine (85 g) (S.D Fine Chemicals, India) in 25 ml of deionised doubly distilled water at 5°C with constant stirring, followed by 40 g of ammonium hydroxide dissolved in 20 ml of doubly distilled deionised water. The product was warmed to room temperature and washed repeatedly 2-3 times with purified acetone. The reaction product was purified by recrystallization in acetone[5]. The purified compound has a melting point of 196-199°C at 740 mm pressure as shown in scheme 1.

Experimental procedure

A measured volume of the supporting electrolyte and ligand are added to the required aliquots of the electroactive species, maintaining the optimum pH and the solution is made upto 25 ml in standard flask with double distilled deionised water and then transferred to the polarographic cell. The dissolved oxygen is expelled by bubbling pure nitrogen through the test solution for 10-15 minutes. Polarogram of the solution is recorded using d.c. recording polarograph as shown in figure 1.

RESULTS AND DISCUSSION

Effect of pH

Effect of pH on solution containing 1.0 ppm of copper in 0.3 M ammonium chloride for Amm pip-DTC (2.0 mM) was studied, varying the pH from 5.0 to 10.0 adjusting with ammonium hydroxide. With increasing pH the height of the catalytic wave increased and after attaining a maximum peak current of pH 6.6, the wave height decreased with further increase in pH. The maximum wave height of the polarogram was selected as optimum pH which was maintained in all other studies. The results were presented in figure 2. The peak potential of the catalytic wave shifted towards positive potential with increase in pH.

Effect of supporting electrolyte concentration

The effect of ammonium chloride in the range of 0.1 to 0.8 M on the nature of current-voltage curves at DME for Cu(II)-dithiocarbamate complex have been studied, keeping the copper ion concentration at 1.0 ppm. The Amm pip-DTC concentration was 2.0 mM for Amm pip-DTC.

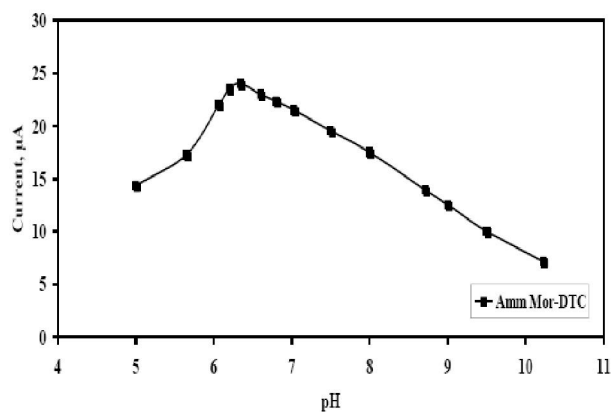The polarogram was well defined in NH₄Cl of 0.3

Full Paper

Figure 2 : Effect of pH on Cu(II)-amm pip-DTC complex system
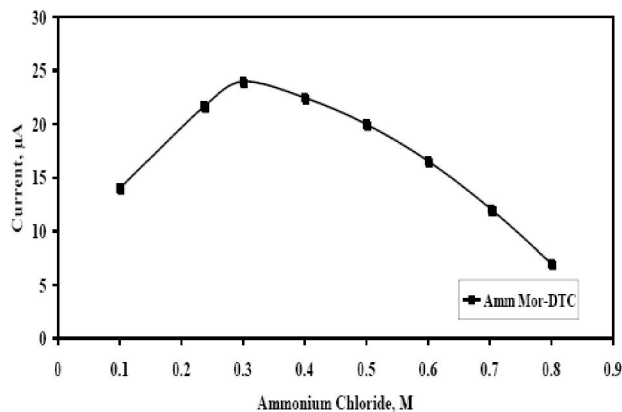

Figure 3 : Effect of supporting electrolyte on Cu(II)-amm pip-DTC complex system
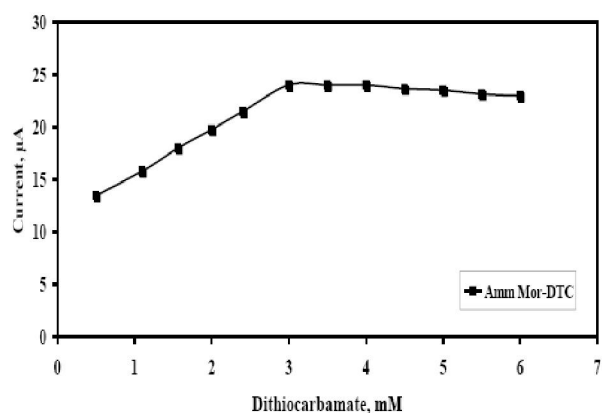

Figure 4 : Effect of reagent concentration on Cu(II)-amm pip-DTC complex system
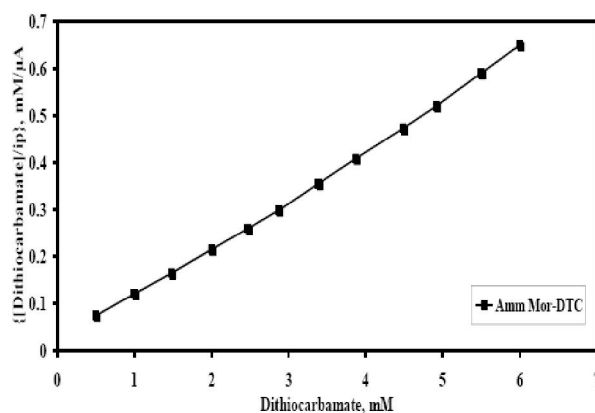
Figure 5 : Langmuir adsoption isotherm plot of Cu(II)-amm pip-DTC complex system
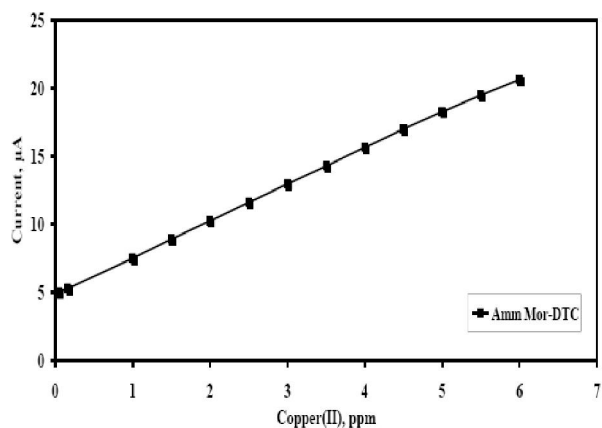
Figure 6 : Effect of copper(II) on peak current
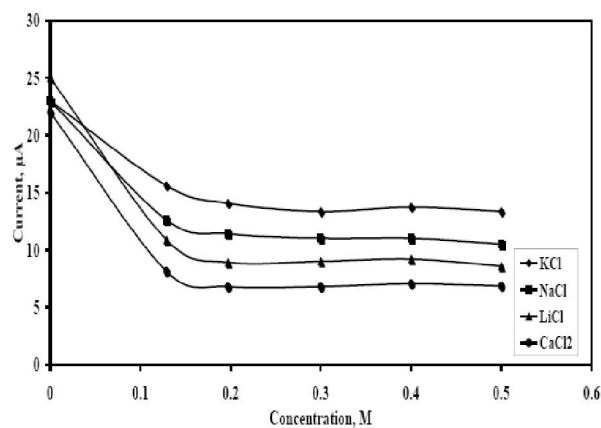
Figure 7 : Effect of indifferent ions on amm pip-DTC-Cu(II) complex

M for Amm pip-DTC and the wave height was increased up to 0.3 M NH_4Cl for Amm pip-DTC. The peak height was decreased beyond this concentration and therefore the optimum concentration was maintained for further studies as shown in figure 3. The peak potential of the catalytic wave shifts towards positive potentials with increase in ammonium chloride concentration throughout the concentration range of NH_4Cl studied.

Effect of reagent concentration

Solutions containing 1.0 ppm of copper ion, 0.3 M

TABLE 1 : Effect of mercury pressure on Cu(II)-Amm pip-DTC complex

System	Amm pip-DTC
Cu(II), ppm	1.0
NH$_4$Cl, M	0.3
Dithiocarbamate, mM	2.0
pH	6.6

S. No	Height of the mercury column, cm	Amm Pip-DTC Current, μA	Ic/√h
1	21	27.00	6.142
2	26	26.50	4.257
3	31	26.00	3.548
4	36	25.00	2.596

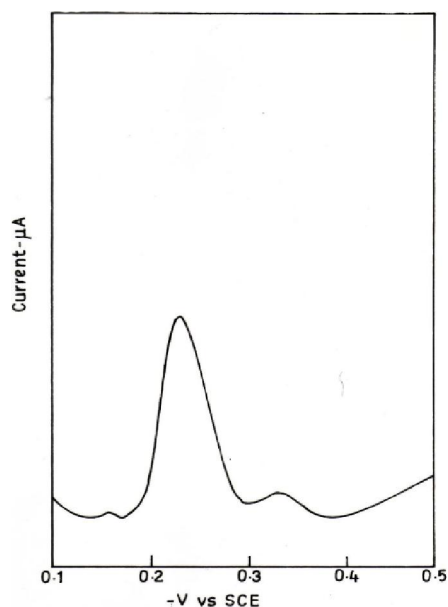**Figure 8 : Differential pulse polarographic curve of copper (II) in NH$_4$Cl-NH$_4$OH medium in the presence of amm pip-DTC. Current range : 100 μA, scanrate : 6 mV/S, pulse amplitude : 50 mV, droptime : 1 Sec, copper(II) : 0.001 ppm**

ammonium chloride for Amm pip-DTC was taken and the dithiocarbamate concentration was varied from 0.5 to 6.0 mM maintaining the pH of the solution at 6.6 in case of Amm pip-DTC. The peak current does not vary linearly with concentration of ligand which was a typical characteristic nature of catalytic wave and obtained was shown in figure 4. From the results it was observed that the wave height increased linearly with dithiocarbamate concentration up to 2.0 mM for Amm pip-DTC. With further increase in Amm pip-DTC concentration the wave height in independent of concentration and shows that the complex was stable. Therefore, 2.0 mM

TABLE 2 : Effect of maximum suppressors on Cu(II)-amm pip-DTC complex

System	Amm pip-DTC
Cu(II), ppm	1.0
NH$_4$Cl, M	0.3
Dithiocarbamate, mM	2.0
pH	6.6

S.No	Maximum suppressor, %	Current, μA Amm Pip-DTC
	A. Gelatin	
1	0.000	27.00
2	0.005	16.00
3	0.010	15.00
	B. Triton X-100	
1	0.000	27.00
2	0.005	25.20
3	0.010	25.00

TABLE 3 : Effect of indifferent cations on Cu(II)-amm pip-DTC complex

System	Amm pip-DTC
Cu(II), ppm	1.0
NH$_4$Cl, M	0.3
Dithiocarbamate, mM	2.0
pH	6.6

S. No	Salt, M	Current, μA			
		KCl	NaCl	LiCl	CaCl$_2$
		Amm Pip-DTC			
1	0.1	23.00	20.00	25.00	22.00
2	0.2	9.53	17.62	17.03	14.83
3	0.3	8.26	11.05	14.42	11.05
4	0.4	8.14	11.00	14.07	9.59
5	0.5	7.73	11.00	13.84	9.36

concentration was fixed for quantitative studies. Plot of {[dithiocarbamate]/i$_p$} Vs {dithiocarbamate} was straight line (Figure 5) and confirms that adsorption phenomenon was involved in the electrode reaction process.

Effect of mercury pressure

The height of the mercury column was varied and the polarogram of copper (1.0 ppm) in quantitative experimental conditions are noted. It was found that the catalytic current as well as ic/√h decreased with the height of the mercury column indicating that the current was

Full Paper

TABLE 4 : Determination of Cu(II) with amm pip-DTC in water samples around Tirupati, Chittoor District, A.P., INDIA. (I) Industrial Estate; (II) Amararaja Batteries

System	Amm pip-DTC	System	Amm pip-DTC
Cu(II), ppm	1.0	Dithiocarbamate, mM	2.0
NH_4Cl, M	0.3	pH	6.6

Sample[a]		Catalytic hydrogen current method(DC)				DPP method	
		Amm pip-DTC				Amm pip-DTC	
	Cu(II) added, ppm	Cu(II) found, ppm	Recovery(%)±R.S.D[b]	t-test*	f-test**	Cu (II) found, ppm	Recovery(%)±R.S.D[b]
I	0.2	0.248	99.00±2.54	1.18	0.23	0.249	99.50±2.55
	0.4	0.480	99.00±2.55	1.06	0.12	0.488	99.50±2.54
	0.6	0.715	99.16±2.51	1.21	0.36	0.718	99.66±2.61
	0.8	0.960	100.00±2.96	1.15	0.20	0.960	100.00±2.96
	1.0	1.060	98.00±2.31	2.16	0.66	1.100	100.00±2.96
II	0.2	0.236	98.00±2.30	1.57	0.50	0.238	99.00±2.42
	0.4	0.457	99.25±2.48	1.09	0.16	0.459	99.75±2.73
	0.6	0.706	99.33±2.52	1.00	0.09	0.708	99.66±2.61
	0.8	0.964	99.25±2.48	1.15	0.20	0.963	99.12±2.50
	1.0	1.090	98.00±2.31	1.30	0.41	1.100	99.00±2.42

[a]5 ml of the concentrated sample is used, [b]Relative Standard Deviation(n=6). *1% level of significance, **5% level of significance

TABLE 5 : Determination of Cu(II) with amm pip-DTC in vegetable samples around Tirupati, Chittoor District, A.P.INDIA

System	Amm pip-DTC	System	Amm pip-DTC
Cu(II), ppm	1.0	Dithiocarbamate, mM	2.0
NH_4Cl, M	0.3	pH	6.6

Sample[a] scientific/ local name	Cu(II) added, ppm	Catalytic hydrogen current method(DC)				DPP method	
		Amm pip-DTC				Amm pip-DTC	
		Cu(II) found, ppm	Recovery(%)±R.S.D[b]	t-test*	f-test**	Cu(II) found, ppm	Recovery(%)±R.S.D[b]
Abelmoschus esculentus/Ladies finger	1.0	1.041	98.10±2.28	1.22	0.39	1.044	98.40±2.33
Lycopersicon esculentum/ Tomato	1.0	1.129	98.90±2.75	1.60	0.65	1.033	99.30±2.60
Coceinia grandis/ Little gourd	1.0	1.97	99.70±2.69	1.15	0.22	1.099	99.90±2.81

[a]5 ml of the concentrated sample is used, [b]Relative Standard Deviation(n=6). *1% level of significance. **5% level of significance

catalytic in nature. The experimental observations are recorded in TABLE 1.

Effect of maximum suppressor

The effect of surface active substances, gelatin in the range 0.005 to 0.01% and Triton X-100, 0.002 to 0.004 % on the catalytic wave height of Cu(II)-Amm pip-DTC system for the determination of copper(II) in various environmental samples.

The catalytic wave decreases sharply up to 0.005% gelatin concentration and with further increase in concentration of the surface active material, the wave height was decreased by only about 2%. The peak potential shifted towards positive potentials and the catalytic peak became round shaped.

The suppression of the catalytic wave is found with 0.002 to 0.005 % Triton X-100 and was small compared to gelatin. The peak potential shifted towards positive potentials in this case also. The observations are presented in TABLE 2.

Effect of temperature

The current-voltage curves of Cu(II)-Amm pip-DTC system was recorded at various temperatures i.e. 15 to 45°C. It was found that with increase in temperature the wave height increased and temperature coeffi-

TABLE 6 : Determination of Cu(II) in brass (Certified amount of Cu(%)= 67.4

System	Amm pip-DTC
Cu(II), ppm	1.0
NH$_4$Cl, M	0.3
Dithiocarbamate, mM	2.0
pH	6.6

*Sample/Dithiocarbamate	Cu(II) in the sample, ppm	
	Catalytic hydrogen current method(DC)	DPP method
Amm Pip-DTC	67.3	67.4

cient value decreased gradually. The current, i$_c$ became completely temperature independent above 30°C.

Effect of copper(II) ion concentration on peak current

At fixed concentration of Amm pip-DTC and ammonium chloride adjusting pH to their optimum values, the metal ion concentration was varied between 0.05 to 6.0 ppm and the proportionality of the peak current was studied. The result obtained was given in figure 6. The peak current increased linearly with copper concentration in the range 0.05 to 6.0 ppm and the calibration plot was shown in figure 6. The method suggests that the determination of micro amounts of copper was possible in unknown samples. It is observed that there was no change in the shape of the wave throughout the copper concentration range studied.

Effect of indifferent cations

The effect of neutral salts and replacement of monovalent cations with divalent cations leads to the changes both in the height and the potential of the catalytic wave. Three alkali chlorides, potassium, sodium and lithium and bivalent cation, calcium are used. With increase in concentration of chloride the wave height decreased continuously and the decrease of wave height in calcium chloride is more compared to monovalent chlorides as indicated in the TABLE 3 and figure 7. The peak potential was shifted towards less negative potentials with all cations.

Applications of the catalytic method to real samples

The catalytic polarographic method for the estimation of Cu(II) using Amm pip-DTC as reagents was ex-tended to the analysis of water, vegetables and alloys.

Water samples

One litre of the water samples collected from Industrial estate and Amararaja batteries (Tirupati town, Chittoor Dt.) was preconcentrated to 100 ml.

Vegetable samples

3.5 g of vegetable samples were collected from local sources and digested by dry ash method. The mass was made up to 100 ml with double distilled water.

Alloy samples

Standard sample of Brass is brought into solution by standard procedures.

Aliquots of the above sample solutions are taken and quantitative experimental conditions are maintained and the solutions are polarographed. Standard addition method was used in case of analysis of Cu(II) in drinking water, vegetables and alloys. The results obtained by this method are further supported by differential pulse polarography and its curve was shown in figure 8. The developed method was compared with the DPP method in terms of Student's 't'-test and Variance ratio 'f'-test as shown in TABLES 4 to 6. The analytical data summarized in TABLE 4 to 6 suggest that the percentage of Cu(II) recovery from drinking water, vegetable and alloy ranges from 95.00 to 100.00 % with R.S.D(%)= 2.15 which was facile, more reliable and sensitive.

The present method for copper(II) in the presence of Amm pip-DTC in NH$_4$Cl-NH$_4$OH medium is found to be sensitive, selective, specific and rapid and may be successfully applied for the analysis of copper various samples of environmental importance.

CONCLUSIONS

It is evident from TABLE 4 to 6 that the proposed method is simple, sensitive, rapid and reproducible. More over the method do not involve elaborate clean up procedures as it requires by the other methods. The obtained results were in good agreement with differential pulse polarographic method. Hence, the method described here serves as good additional technique for the estimation of Cu(II) in various water, vegetables and alloys.

Full Paper

REFERENCES

[1] S.P.Ananda, O.Donald; 'Trace Elements in Human Health and Diseases', **1**, **(1976)**.

[2] G.L.Eichhorn; 'Inorganic Bio-Chemistry', Elsevier Scientific Publishing Company (New York), **(1975)**.

[3] R.A.Romeno, J.A.Navarro, B.Rodriguez, R.Garlica, O.E.Parra, T.Grandillo; Trace.Elem.Med., **7**, 176 **(1970)**.

[4] J.Shen, S.Chen, C.Zhang; Shanghai Yixue, **14**, 603 **(1991)**.

[5] P.A.Waldravens; Clin.Chem., **26**, 185 **(1980)**.

[6] I.H.Scheinberg, I.Sternleib; Pharmacot.Rev., **12**, 204 **(1933)**.

[7] E.J.Underwood; 'Trace Elements in Human and Animal nutrition', 4th Ed., (Academic Press, New York), **(1979)**.

[8] L.M.Purnima, M.S.Vijay; Analyst, **116**, 1981 **(1991)**.

[9] P.M.Rao, S.B.Rao; Indian J.Chem., **9**, 1014 **(1971)**.

[10] Idem; Ibid, **11**, 1160 **(1973)**.

[11] L.Vataman, C.Zhang, J.A.Navarro; Analyst, **124**, 1073 **(1987)**.

[12] Z.Huang, X.Du; Huanjing Huaxue, **7**, 72 **(1988)**; Chem.Abstr., **109**, 236563 **(1988)**.

[13] Yan, Guiyou, Xia, Jiaoyun, Wang, Yan; Yijin Fenxi, **19(3)**, 37 (Ch) **(1989)**.

[14] Z.Zhengaqi, Z.S.Zong, C.Zhaopeng, L.Xiaoli; Fenxi Shiyanshi, **11**, 21 **(1976)**.

[15] J.Biernat, A.Syzmaszek; Bull.Acad.Pol.Sci.Ser.Sci. Chim., **24**, 133 **(1976)**.

[16] B.Johansson, S.Wendsjo; J.Electroanal.Chem.Inter-facial Electrochem., **167**, 165 **(1984)**.

[17] S.Lei; Fenxi Shiyanshi, **7**, 32 **(1988)**.

[18] Z.Zhao, Y.Wang; Huaxue Xuebao, **41**, 761 **(1983)**.

[19] R.Palaniappan, V.Revathi; J.Indian Coun.Chem., **4**, 1 **(1988)**.

[20] K.Saraswathi, N.V.S.Naidu, K.Meena Kumari, K.Padmaja; Chem.Environ.Res., **8(3 & 4)**, 271 **(1999)**.

[21] K.Saraswathi, N.V.S.Naidu, K.Purushotham Naidu, N.Krishnaiah; Analytical Chemistry: An Indian Journal, **7(5)**, 279 **(2008)**.

[22] Z.Huang, X.Du; Huanjing, Huaxue, **7**, 72 **(1988)**.

[23] Wang, Shuhao, Du., Ling Yuro, Zhang., Aimei, Liu., Daojie; Anal.Lett., **31(10)**, 1757 **(1998)**.