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Voltammetric determination of copper at chemically modified electrodes based on crown ethers

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Abstract The feasibility of fabricating copper-sensitive chemically modified electrodes (CMEs) for trace analysis in aqueous and in 40% (v/v) ethanol-water media was investigated. Carbon paste electrodes modified with crown ethers were constructed by mixing the crown ethers into a graphite powder-paraffin oil matrix. The electrodes so formed were able to bind Cu(II) ions chemically and gave better voltammetric responses than the unmodified ones. The crown ethers studied and compared were 15-crown-5, benzo-15-crown-5 and dibenzo-18-crown-6. With a 3% benzo-15-crown-5 CME, Cu(II) could be quantified at sub-ppm levels by differential pulse voltammetry with a detection limit of 0.05 ppm. By differential pulse anodic stripping voltammetry Cu(II) could be quantified over the range 1 to 100 ppb. Interference from metal ions like Ni(II), Co(II), Mn(II), Fe(II), etc. have also been studied. The method was successfully applied to artificial as well as commercial samples of alcoholic beverages.

Introduction

Chemically modified electrodes (CMEs) have been used to accumulate analytes selectively and to protect them from interference by other ions. CMEs consisting of a mixture of carbon paste and modifying reagent have been widely used, since they can be prepared easily and have a stable electrode response [1]. Dimethylglyoxime has been employed for nickel determination [2], dithiocarbamates [3], diquinoyl-8-disulfide [4], alizarin red S [5] for copper, 1,11-bis(8-quinoyloxy)-3,6,9-trioxaundecane [6] for mercury, N-p-chlorophenyl cinnamohydroxamic acid [7] and 1,10-phenanthroline [8] for cobalt determination.

Crown ethers have been used as modifiers for determination of lead [9] and mercury [10, 11]. They have been known to form complexes with a host of cations [12] in-

cluding alkali, alkaline earth metal ions, NH_4^+ , lanthanides and transition metal ions. However, complexations with transition metal ions have been rarely studied. The major thrust has so far been confined to the complexation of alkali metal ions, with oxygen containing crown ethers and of transition metal ions with aza / thia crown ethers. However, some authors have reported that oxygen containing crown ethers do form complexes with transition metal ions, albeit weak ones [13], and have been used in preparation of ion selective electrodes [14]. Similar results were obtained by us from conductometric experiments in ethanol-water mixtures.

In this paper we describe the use of crown ethers (15-crown-5, benzo-15-crown-5 and dibenzo-18-crown-6) as modifiers in carbon paste electrodes for quantification of copper by differential pulse voltammetry (DPV) and differential pulse anodic stripping voltammetry (DPASV). Here, the advantages of weak complexation and a suitably applied reduction potential were used to obtain enhanced voltammetric signals for trace analysis and to prevent interference, respectively. A 40% (v/v) ethanol-water mixture was chosen from the application point of view, as it resembles the composition of some common alcoholic beverages like rum, whiskey, vodka, gin, etc. Copper and other metallic impurities happen to enter into these beverages during the manufacturing and storage processes or in case of adulteration. The standard method [15] for quantification at such low levels is AAS. Here, an attempt has been made to provide an alternative method for analysis that is equally fast and reliable but at a lesser cost.

Experimental

Apparatus. The voltammetric system used for the studies was EG & G Princeton Applied Research 264A potentiostat with model 303A electrode assembly and X-Y chart recorder RE0089.

The autotitrator used for Karl Fischer titration and for standardization of acids and metal salt solutions was the Mettler Toledo DL53 model. The probes used were double pin Pt electrode (DM-142), glass electrode (DG-111-SC) and conductometric sensor (Inlab-717), respectively.

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A GBC 906AA atomic absorption spectrophotometer with air-acetylene flame was used to analyse real samples of alcoholic beverages for comparison.

Chemicals. Double-distilled, deionised water was used for preparation of all solutions. Triple-distilled ethanol (over molecular sieves), containing less than 0.2% water (as determined by Karl Fischer titration), was used to prepare ethanol-water mixtures. Both the solvents were stored in sealed containers to prevent atmospheric contamination. Appropriate volumes of ethanol and water were mixed to give 40% (v/v) solvent mixture.

The crown ethers, 15-crown-5 (15-C-5) Fluka, benzo-15-crown-5 (B-15-C-5) Aldrich and dibenzo-18-crown-6 (DB-18-C-6) Aldrich were used as received. Copper perchlorate was prepared by the standard method described elsewhere [16]. All other chemicals were of reagent grade.

Stock solutions of the metal salts and acids were prepared and standardised by titration against EDTA and sodium carbonate, respectively, on a DL53 autotitrator.

Electrodes. Crown ether coated graphite powders were prepared by dissolving a weighed amount of crown ether in absolute ethanol, adding the required amount of graphite powder and stirring the slurry thus formed until all the ethanol had evaporated. A completely dry powder was obtained by keeping the mixture at 40°C in a vacuum oven under a pressure of 7.5×10^{-3} Pa. Modified carbon pastes were prepared by thorough mixing of coated graphite powder and paraffin oil in a mortar. Plain (unmodified) carbon paste was prepared in similar fashion, but no crown ether was added. The modified pastes contained 3% of crown ether, 57% of graphite and 40% of paraffin by weight.

The pastes were taken in a 2 mL glass syringe whose tip had an internal diameter of about 1 mm. The syringe was filled with about 1 g of the paste. Electrical contact to the paste was established by means of a thin copper wire, by-passing the piston. Smooth surfaces were obtained by applying manual pressure to the piston while holding the electrode surface against a smooth glass plate. Fresh electrode surfaces were obtained by squeezing out a small amount of paste, scraping off the excess and polishing the tip on a zero grade polishing paper until the surface had a shiny appearance. The same surface of the CME could be used for 4–5 analyses (the surface being cleaned in between by repeated oxidative scans). Then, the surface had to be regenerated by pressing out about 1 mm of the paste. One gram of paste yielded about 50 cm of the paste, which means, at least 1000 analyses can be done using one gram of paste.

A platinum electrode served as auxiliary electrode and a saturated calomel electrode (SCE) as reference electrode.

Procedure. The response of CMEs prepared in the above manner was studied in aqueous and in 40% (v/v) ethanol-water mixture as follows:

Initially, cyclic voltammograms of Cu(II) solutions in different electrolytes were recorded with a plain carbon paste electrode at a scan rate of 100 mV/s from +0.5 to -0.5 V vs SCE. Then, cyclic voltammograms of Cu(II) solutions in aqueous and 40% ethanol-water media using 0.01 M HClO₄ and 0.05 M KCl as supporting electrolytes, respectively, were recorded with different CMEs under identical conditions. The B-15-C-5 CME was used to study the effect of scan rate on peak currents. The same CME was used for the quantification of copper by DPV and DPASV at a pulse amplitude of 100 mV and a scan rate of 10 mV/s. In DPASV the deposition was carried out at -0.3 V vs SCE with stirring. The artificial samples were prepared by mixing appropriate volumes of stock solutions and were analysed under identical conditions. The method of standard addition was used for quantification of copper in artificial and real alcoholic samples by DPASV (as above). Here, an appropriate quantity of solid KCl was directly added to the sample so as to make it 0.005 M with respect to KCl.

The real samples of rum were appropriately pre-concentrated and analysed by AAS at 324.7 nm for comparison of the results obtained by above method.

Results and discussion

A Voltammetry in aqueous medium

From the cyclic voltammograms obtained with the plain carbon paste electrode in 0.01 M HCl, 0.01 M HNO₃ and 0.01 M HClO₄ it was evident that the acid media used for cyclic voltammetry do not change the potential window for the redox process. Figures 1 and 2 show cyclic voltammograms for Cu(II) solutions obtained with unmodified and modified carbon paste electrodes in 0.01 M HClO₄ respectively. It is observed that the unmodified paste electrode shows a typical 'current cross over', which is a characteristic of an electrolytic deposition-stripping [11] mechanism; whereas no such behaviour was observed in case of the modified electrode, indicating the effect of complexation by crown ethers. The cyclic voltammograms show that both the cathodic as well as anodic peaks are enhanced as compared to the unmodified one. This happens due to increased uptake of copper ions

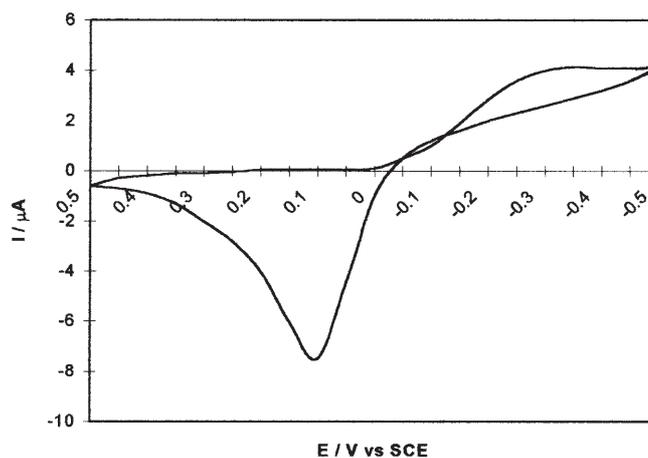


Fig. 1 Cyclic voltammogram obtained by unmodified carbon paste electrode for 5.77×10^{-4} M Cu(II) in 0.01 M HClO₄ at 100 mV/s in aqueous medium

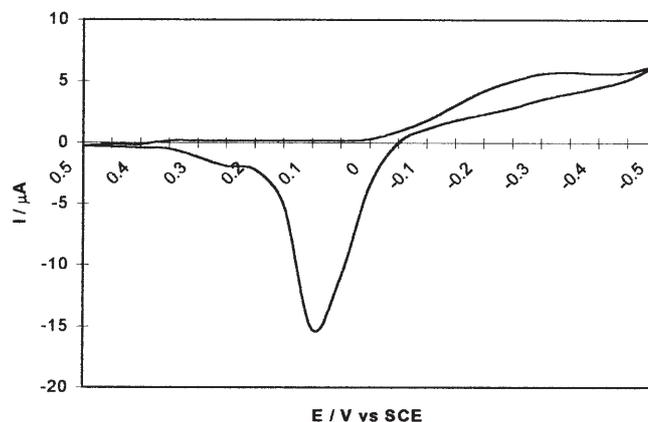


Fig. 2 Cyclic voltammogram obtained by benzo-15-crown-5 CME for 5.77×10^{-4} M Cu(II) in 0.01 M HClO₄ at 100 mV/s in aqueous medium

Table 1 Effect of modification on the cyclic voltammetric peak currents for 2.90×10^{-4} M CuSO_4 in 0.01 M HClO_4 at 100 mV/s

Electrodes	$I_{pc}/\mu\text{A}$	$I_{pa}/\mu\text{A}$
Unmodified	2.0	3.7
15-C-5	3.0	4.3
B-15-C-5	3.1	8.4
DB-18-C-6	2.2	3.8

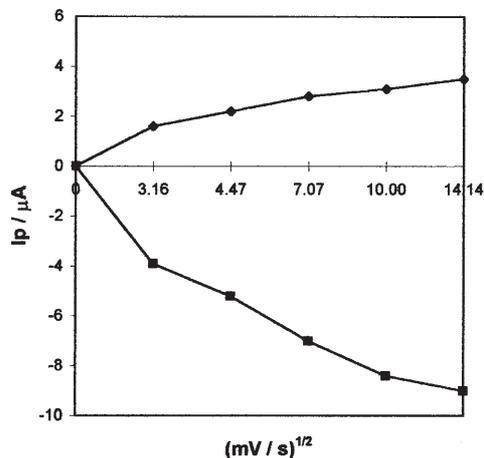


Fig. 3 Plot of I_{pc} and I_{pa} vs $v^{1/2}$ for 2.90×10^{-4} M Cu(II) at B-15-C-5 CME in 0.01 M HClO_4

by the CME through complexation. Table 1 shows the effect of modification on peak currents observed by cyclic voltammetry. The enhancement was maximum for the B-15-C-5 modified electrode and also the peaks are sharper. This could be expected, as the cavity size of B-15-C-5 is closer to the diameter of cupric ion (1.54 \AA) than that of the other crown ethers. As B-15-C-5 is insoluble in water it did not leach out. So, the B-15-C-5 modified electrode was used for further studies and perchloric acid was used as supporting electrolyte as it is the least complexing medium.

Voltammograms were recorded for Cu(II) solutions of two different concentrations at varying scan rates and peak currents. Figure 3 shows a representative plot of I_p vs $v^{1/2}$ which are not straight lines but curves at higher scan rates, indicating that the process is not totally diffusion controlled, but some kinetic parameter, i.e. complexation is effective. Also, a shift in peak potentials is observed with the value of $I_{pc}/v^{1/2}$ decreasing with increase in scan rates (Table 2). This implies that the chemical step precedes electron transfer.

The cathodic peak enhancement was used for the determination of copper in the range 0.1 to 1.0 ppm¹ by DPV. Well-defined peaks were obtained, within the potential range scanned (+0.3 V to -0.4 V vs SCE) with a current proportional to the concentration of copper ions

¹ The terms ppm and ppb which mean parts per million and parts per billion, respectively, have been used as they are more convenient and widely used in trace analysis, although not IUPAC convention. 1 ppm = 1 $\mu\text{g/mL}$ and 1 ppb = 1 ng/mL

Table 2 Effect of scan rate on the behaviour of B-15-C-5 CME for 2.90×10^{-4} M Cu(II) in 0.01 M HClO_4

Scan rate (mV/s)	$v^{1/2}$	E_{pc}/V	E_{pa}/V	$I_{pc}/\mu\text{A}$	$I_{pa}/\mu\text{A}$	$I_{pc}/v^{1/2}$
10	3.16	-0.2	0.03	1.6	3.9	0.51
20	4.47	-0.23	0.04	2.2	5.2	0.49
50	7.07	-0.26	0.05	2.7	7.0	0.38
100	10.00	-0.27	0.06	3.1	8.4	0.31
200	14.14	-0.28	0.07	3.7	9.0	0.26

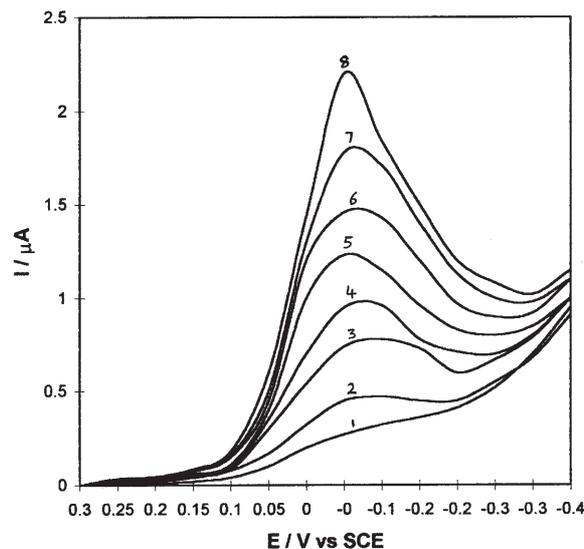


Fig. 4 Differential pulse voltammetric curves obtained by B-15-C-5 CME at a scan rate of 10 mV/s for 100 mV pulse amplitude in 0.005 M HClO_4 . Concentration of Cu(II) : 1: blank, 2: 0.148 ppm, 3: 0.296 ppm, 4: 0.443 ppm, 5: 0.590 ppm, 6: 0.737 ppm, 7: 0.884 ppm, 8: 1.030 ppm

(Fig. 4). A comparison of peak currents obtained under identical conditions with the plain carbon paste and the B-15-C-5 modified electrode by DPV showed that the sensitivity of the modified electrode is about 1.5–2 times higher than that of the unmodified one. A detection limit of 0.05 ppm (RSD = 2.32%, for $n = 7$) was obtained under these conditions.

Under these conditions, the effect of interference by Co(II) , Ni(II) , Mn(II) , Pb(II) and Fe(II) were studied. None of them were found to affect the Cu(II) peaks when present in 50 times excess concentration. A 60 fold excess of Ni(II) and Co(II) showed lowering of peak height (by about 5%), which may be due to blocking of the crown ether sites, whereas 70 times excess Pb(II) caused broadening of the peak, within the potential range studied. Mn(II) and Fe(II) did not seem to interfere even when present in 100 times excess concentration. Two artificial samples containing similar amounts (0.7 ppm each) of either Cu(II) , Mn(II) , Ni(II) and Pb(II) or Cu(II) , Mn(II) , Fe(II) and Co(II) were prepared and analysed. The peak currents obtained for the samples were the same as that obtained for pure Cu(II) solution which shows that these ions do not interfere even when present together in a sample.

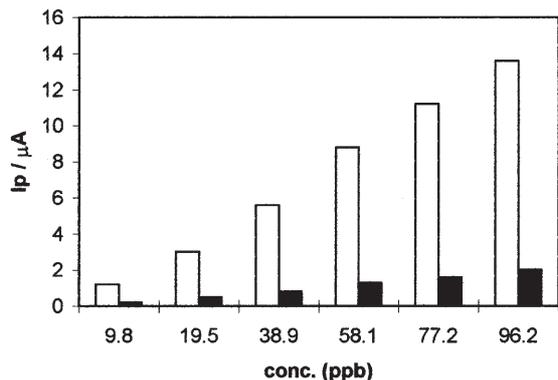


Fig. 5 Comparison of peak currents obtained by unmodified (■) and B-15-C-5 CME (□) for a deposition period of 1 minute at -0.3 V vs SCE in 0.001 M HClO_4 at a scan rate of 10 mV/s with 100 mV pulse amplitude

As the anodic peak was found to be much more enhanced, this observation was used to quantify copper at ppb levels by DPASV. After some trial experiments it was found that for 1 min deposition period, a linear calibration curve was obtained over the range 10 to 100 ppb. A linear curve was obtained over the range 1 to 10 ppb for a 2 min deposition period. The deposition potential used was -0.3 V vs. SCE, at which the other ions mentioned before do not get deposited and hence do not interfere. A detection limit of 0.1 ppb (RSD = 5.56%, for $n = 7$) was obtained for a deposition period of 5 min. Figure 5 shows the comparison of peak currents obtained by modified and unmodified electrodes under identical conditions of deposition period, pulse amplitude, concentration, etc. It is seen that an enhancement by about 6–7 times is obtained. It was also tried to accumulate copper at the working electrode at ‘open circuit’ as done for most of CMEs, but it was found that the quantity deposited was too low and was irreproducible. Also, it required longer accumulation periods due to weak complexation. The CME gave a similar performance when potassium chloride was used as the indifferent electrolyte.

Thus, the fact that B-15-C-5 does form a weak complex with Cu(II) can be advantageously used to enhance the voltammetric signals. Also, the interference from other transition metal ions is prevented by means of potential control. If a strong complexing agent is used then severe interference can be expected due to competition between the other transition metal ions and copper ions.

B Voltammetry in 40% (v/v) ethanol-water mixture

Figure 6 shows the cyclic voltammograms of copper perchlorate solution obtained with the plain carbon paste electrode and B-15-C-5 modified electrode, respectively, in ethanol-water mixture using 0.05 M KCl as supporting electrolyte. It was observed that with both electrodes (modified as well as unmodified) Cu(II) gives two cathodic and two anodic peaks indicating a two step redox

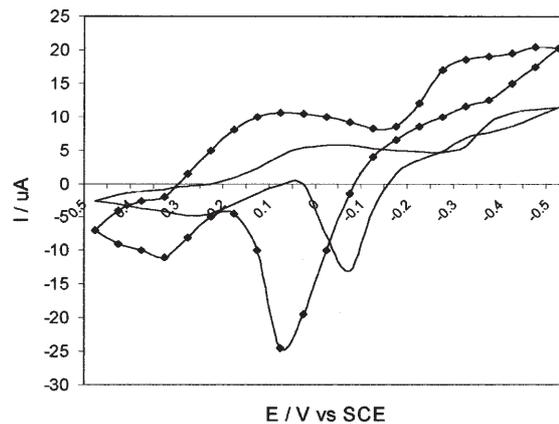


Fig. 6 Cyclic voltammograms obtained by unmodified (smooth curve) and B-15-C-5 CME (marked curve) for 2.346×10^{-3} M Cu(II) in 0.05 M KCl at 50 mV/s in 40% (v/v) ethanol – water medium

process. Here again, ‘current cross over’ was observed in case of the unmodified electrode, whereas the modified paste electrode showed increased peak currents without ‘current cross over’. The anodic peak at $+0.1$ V (vs SCE), being sharper and more enhanced, was used for quantitative analysis of copper by DPASV. In this medium, deposition times of 20 s and 50 s were sufficient to obtain well defined peaks and a linear calibration plot over the range 10 to 100 ppb and 1 to 10 ppb, respectively. This can be attributed to the fact that B-15-C-5 forms a more stable complex with Cu(II) in this medium. In case of artificial samples the percentage recovery was generally found to be $97.5 \pm 1.0\%$ and in particular for a 20 ppb sample the RSD was 4.4% ($n = 7$). Here again, no interference was observed from the ions mentioned above. This method was applied to the determination of copper in three commercial samples of rum and they were found to contain 28.7, 76.2 and 64.8 ppb of copper. The same samples were analysed by AAS and the results showed the presence of 24.2, 72.1 and 62.9 ppb of copper respectively, which are quite comparable.

Conclusion

The studies conducted in aqueous medium may be applied for trace analysis of copper in environmental samples like sea water, river water, etc. The studies conducted in ethanol-water mixture can be directly applied to check for contamination or leaching of copper into alcoholic beverages during processing.

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