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# DETERMINATION OF Ag(I) WITH CHEMICALLY MODIFIED CARBON PASTE ELECTRODE BASED ON 2,3-DICYANO 1,4-NAPHTHOQUINONE

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**Summary**—The utility of carbon paste modified with 2,3-dicyano 1,4-naphthoquinone (CYNQ) for the voltammetric determination of Ag(I) is demonstrated. The method is based on the formation of Ag(I) complex with CYNQ by accumulation from the aqueous solution to the electrode surface without an applied potential. Using the medium exchange technique, the electrode was transferred to another media followed by linear-scan voltammetric measurements. The reduction peak of the Ag(I)–CYNQ complex was observed at +0.22 V (*vs.* SCE). The silver response is studied with respect to paste composition, pH of the measurement solution, reproducibility, interference and other variables. A detection limit of $5 \times 10^{-8}M$ was obtained and the calibration curve was linear over the range $1 \times 10^{-6}$–$8 \times 10^{-5}M$.

The deliberate modification of electrodes has shown great promise for electroanalytical studies.[1] Generally the modification procedure consists of changing the chemical nature of the electrode surface by attaching chemical reagents to it, on the assumption that the surface would take on the properties of the attached reagent.[2] Modified carbon paste electrodes are commonly used in voltammetric analysis. The analyte is preconcentrated and accumulated into the electrode surface prior to the voltammetric measurements. The selectivity and sensitivity of such measurements can be improved substantially by preconcentration. The concept of MCPEs preconcentration is an important one in that it offers the potential for constructing and using electrodes specifically optimized for each analyte of interest.[3] Recently a variety of modifiers were incorporated into the carbon matrix to design electrodes with surfaces that have the ability to react with and bind the target solute via complexation,[4–8] ion exchange,[9,10] or covalent linkage.[11] Some organic compounds were determined using MCPEs depending on their hydrophobic character.[12–14]

The present study describes the construction of a new MCPE suitable for the selective preconcentration and quantitation of silver. Wang *et al.*[15] have determined Ag(I) using zeolite as a modifier and others determined metal ions by introducing a suitable complexing agent into carbon paste electrodes. Cheek and Nelson reported the determination of Ag(I) employing an MCPE containing amino salines.[4] Baldwin *et al.*[3] have described the use of carbon paste electrodes modified with dimethylglyoxime and 2,9-dimethyl 1,10-phenanthroline for the determination of nickel(II) and copper(II), respectively. Taga *et al.*[16] accumulated copper(II) into carbon paste electrode containing salicylideneamino-2-thiophenol as a complexing agent. Gao *et al.*[17] utilized carbon paste modified with 2,2′-bipyridyl and Nafion for the determination of iron(II). The method is based on formation of the 2,2′-bipyridyl complex of iron(II) and its accumulation by Nafion. The suggested ligand (CYNQ) forms a strong complex with $Ag^+$, as proved by other methods,[18] consequently it was used for the determination of silver(I). Kalcher[19] published a review of chemically modified carbon paste electrode and their use in voltammetric analysis. The review also discussed the various methods of modification as well as the types of interaction between substrate and modifier. The modified electrode in the present case was easily prepared by simple mixing of the required amount of the modifier with a carbon paste matrix.

## EXPERIMENTAL

A silver(I) ion stock solution ($10^{-3}M$) was prepared by dissolving the required amount of silver nitrate. Working solutions were prepared by diluting the stock solution with bidistilled water. Graphite powder (spectroscopic grade) was used in the study. Paraffin oil was used as a pasting medium. 2,3-Dicyano 1,4-naphthoquinone was prepared according to the method of Van Allen.[20] All other chemicals were of analytical grade and were used without further purification.

### *Apparatus*

A Sargent–Welch polarograph model 3001 was used to record the measurements. The reference electrode was a saturated calomel electrode (SCE) and a platinum wire was used as a counter electrode. The measurements were carried out at 25 ± 0.1°C. The pH of the solution was measured by an Orion ionanalyser digital 601A pH meter.

### *Electrodes and procedures*

Unmodified carbon paste electrode was made by mixing 1.0 g of graphite powder and 0.5 g of oil in a mortar. Modified electrodes were prepared in a similar fashion except that the graphite was first mixed with the desired weight of 2,3-dicyano 1,4-naphthoquinone. Both pastes were packed into the well of the Teflon body of homemade electrodes (2 mm deep × 3 mm in diameter). The electrode surface was smoothed against clean paper. Following this, the electrode was immersed in a stirred 25-ml silver test solution for a given period of time. The electrode was then removed from the preconcentration cell and was immersed for 15 sec in the washing cell and then transferred to the measurement cell. The initial potential (+0.45 V) was applied for 30 sec before recording the voltammogram over the +0.45 to −0.05 V range.

Silver was removed from the electrode surface by stirring the electrode in a solution containing 0.1*M* HCl, transferring to the measuring cell, after rinsing with water, and a voltammogram was recorded. After repeating this step several time, the electrode was rinsed with water and placed in the preconcentration cell for the next cycle.

## RESULTS AND DISCUSSION

The voltammograms obtained by the MCPEs with CYNQ in the absence and presence of silver(I) are shown in Fig. 1, no distinct redox peaks were observed in the potential range between +0.45 and −0.05 V when the accumulation process was carried out for 3 min without Ag(I) and the peak current was measured in a solution of 0.05 $NaNO_3$ at pH 9.8 using linear scan voltammetry. With $2.5 \times 10^{-5}$, $5 \times 10^{-5}$ and $1 \times 10^{-4}M$ Ag(I) solutions the reduction peak appeared at 0.22 V. The reduction peak was proportional to the concentration of Ag(I). It is thought that the reduction peak was due to the complexation between Ag(I) and CYNQ on MCPEs.[18] Accordingly it can be applied for the determination of Ag(I).

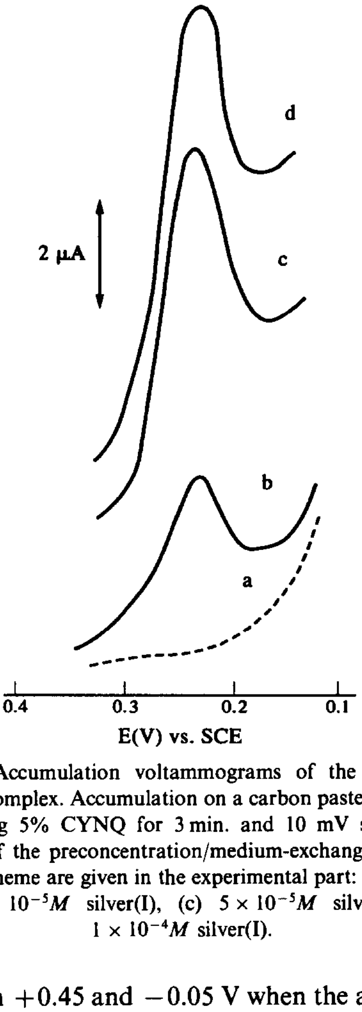

Fig. 1. Accumulation voltammograms of the silver(I)–CYNQ complex. Accumulation on a carbon paste electrode containing 5% CYNQ for 3 min. and 10 mV scan rate. Details of the preconcentration/medium-exchange voltammetric scheme are given in the experimental part: (a) blank, (b) $2.5 \times 10^{-5}M$ silver(I), (c) $5 \times 10^{-5}M$ silver(I), (d) $1 \times 10^{-4}M$ silver(I).

Silver ion is accumulated directly from its solution in which the modified carbon paste electrode was immersed in the test solution, depositing the target analyte (silver ion) via complex formation. Then the electrode (MCPE) was removed from the preconcentration solution, washed with distilled water thoroughly and transferred to the separate measuring cell. After this a voltammogram was recorded in a solution containing only 0.1*M* $NaNO_3$. It was found that the reduction peak of the complex appeared at +0.22 V. The electrode reaction of the analysis of Ag(I) with MCPE can be illustrated as:

$$\text{Ag(I)} + \text{CYNQ (on the MCPE)} \rightarrow$$
$$\text{Ag(I)(CYNQ) accumulation step}$$
$$\text{Ag(I)(CYNQ)} + e^- \rightarrow$$
$$\text{Ag(0)} + \text{CYNQ reduction step, } +0.22\text{ V}$$

The solution was employed in the determination step had a profound effect on the peak current enhancement. Several electrolytes were tested: potassium nitrate pH 9.8 proved to be better than the other solutions tested (0.1*M* sodium acetate, 0.1*M* sodium citrate, 0.1*M* disodium hydrogen phosphate, 0.1*M* sodium carbonate). The effect of pH on the peak current was studied in which a series of solutions of 0.1*M* potassium nitrate having different pH values were used. It was found that pH 9.8 produced the largest and sharpest peak. Using an acidic medium caused a decrease in the peak current. At the same time the use of a medium more alkaline than pH 10.5 decreased the peak response.

The effect of the amount of 2,3-dicyano 1,4-naphthoquinone in the accumulation of Ag(I) was investigated by changing the modifier ratio to the graphite powder in the mixture. The peak current increased with increasing amount of CYNQ up to 5% and above 10% it decreased. Since the signal-to-noise ratio increased with the modifier percentage, the ratio of CYNQ to graphite powder in the mixture was set at 5%.

The removal of an analyte from electrode surface (cleaning) and regeneration of an analyte-free surface is an important step for the successful analytical application of MCPE. In the present study, various cleaning methods were utilized for renewal of the modified electrode surface. It was found that renewal was easily attained by dipping the electrode in a solution containing 0.1*M* HCl and stirring for about 5 min. Then the electrode was transferred to the measuring cell after rinsing with water and a voltammogram was recorded. The renewal step must be repeated many times to obtain a good base line. The same electrode (the same paste) could be used for 4–8 hr performing nine to 15 preconcentration/determination/renewal cycles with no noticeable decrease of sensitivity or stability.

Figure 2 shows the dependence of the voltammetric peak current on accumulation time for different Ag(I) concentrations. The rate of Ag(I) uptake is dependent on concentration. The peak current increased linearly up to 5 min for the all concentrations. For 1 × $10^{-5}M$ Ag(I), the peak current increased up to 15 min, but become nonlinear over 5 min in 1 × $10^{-4}M$ Ag(I). This may be due to electrode surface saturation. From the graph it was found that more than 65% of the peak response generated with the first few minutes appeared to represent Ag(I) uptake kinetics.

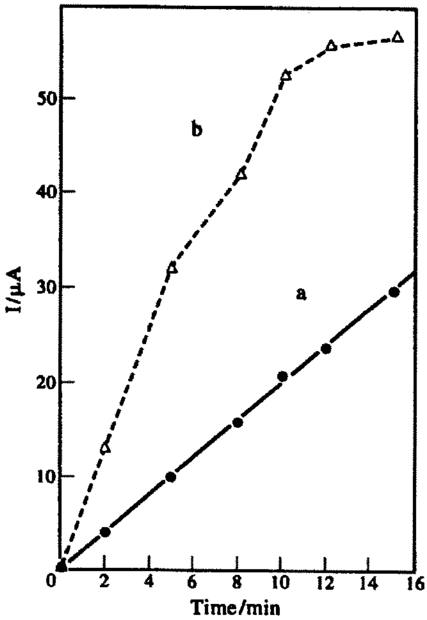

Fig. 2. Dependence of peak current on preconcentration time at different silver(I) concentrations: (a) 2 × $10^{-5}M$, (b) 1 × $10^{-4}M$. Other conditions as in Fig. 1.

The effect of co-existing metal ions (whether electroactive or not) was examined by introducing different concentrations of metal ions such as Co(II), Ni(II), Mn(II), U(IV), Bi(III), Fe(III), Hg(II) and Cu(II). Using a selective modifier avoids or at least decreases the effect of co-existing ions. Ions can interfere with the determination of Ag(I) if they compete for surface binding sites or yield an overlapping response. It was found that Co(II), Ni(II) and Mn(II) which can occupy the active sites in the electrode surface had no effect in the silver response. Metal ions which have reduction potential near to that of silver(I) [Bi(III), Hg(II), Cu(II) and U(IV)] also did not affect the peak current, but the presence of 5 × $10^{-4}M$ iron (III) yielded a depression of about 25% of the 5 × $10^{-5}M$ silver (I) response. The selective response in the presence of copper is significant because the presented method did not suffer from an overlapping copper response. The method also avoided the interferences of several metal ions (as indicated above) which cannot be avoided by other methods.[15]

Under the optimum experimental conditions, the linear-scan voltammetric peak current increased linearly with [Ag(I)] from $1 \times 10^{-6} M$ to $8 \times 10^{-5} M$ with a correlation coefficient of 0.994. The detection limit was found to be $5 \times 10^{-8} M$. For a series of six replicate determinations of $5 \times 10^{-5} M$ Ag(I) a relative standard deviation of 6.7% was obtained.

## CONCLUSIONS

The utility of carbon paste electrode modified with 2,3-dicyano 1,4-naphthoquinone for the determination of Ag(I) has been demonstrated. A highly selective analytical method for Ag(I) was developed by accumulation voltammetry. A linear range that extend from $1 \times 10^{-6 \text{ to } 8 \times 10^{-5} M}$ was obtained. The method avoids the overlapping of many metal ions response with the Ag(I) response.

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