

COBALT PHTHALOCYANINE MODIFIED CARBON PASTE ELECTRODE AS A POTENTIOMETRIC SENSOR FOR DETERMINATION OF ASCORBIC ACID

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Abstract

A carbon Paste electrode modified with cobalt (II) phthalocyanine (CoPC) was used as a sensitive potentiometric sensor for determination of ascorbic acid in aqueous solutions. The potential response of the electrode is a linear function of ascorbic acid concentration over the range 5×10^{-6} to 10^{-2} M ($\sim 1-1800 \mu\text{g ml}^{-1}$) with a Nernstian slope of 56 mV at pH 7. The limit of detection was $0.2 \mu\text{g ml}^{-1}$ ascorbic acid. The modified electrode was used to determine ascorbic acid in vitamin preparations. The recovery was 97-98% for the vitamin added to the preparations with a relative standard deviation of less than 5%.

Introduction

Ascorbic acid is a water soluble vitamin of great biochemical and medical importance. This compound has been the subject of many electrochemical investigations and on the basis of such studies, several methods have been developed for its determination [1-8].

It has been known for a number of years that some of the transition metal complexes, like biomimetic compounds can catalyze the oxidation of organic compounds [9]. Promising advances towards improved selectivity of carbon based electrochemical sensors have been achieved through judicious surface modification of the electrodes with these biocompatible complexes [10-12]. One of the important advantages of such modified electrodes can be seen in terms of faster electron transfer reactions. The design of chemically modified electrodes for electroanalysis has been the subject of much research

in recent years [12, 13]. One of the most attractive biocompatible electron mediators is cobalt (II) phthalocyanine (CoPC). This compound is known for its effective electrocatalytic action towards a wide range of redox systems. Electrodes modified with this compound have shown the most promise for the electrocatalytic determination of biochemically important compounds [14-19], mainly with regard to their catalytic oxygen reduction activity or the possibility of decreasing the effective oxidation or reduction potentials of various reactions.

Wring et al. [20] have investigated the electrochemical behaviour of CoPC modified carbon paste electrode for electrooxidation of reduced glutathione. They have observed an additional anodic wave for the oxidation of this compound, which they assumed to arise from the chemical reduction of Co (II) to Co (I) by reduced glutathione, followed by an electrochemical re-oxidation of Co (I) to Co (II). Previous studies have shown that the oxidation of ascorbic acid at carbon electrodes requires relatively high potentials [21-23]. However, chemical modification of such electrodes with suitable compounds results in low overpotentials and provides very sensitive

Keywords: Potentiometry; Carbon paste electrode; Modified electrode; Cobalt-phthalocyanine; Ascorbic acid

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and selective sensors for electrochemical studies. Carbon-based electrodes chemically modified with CoPC have been successfully applied for amperometric determination of ascorbic acid [24,25] and some other organic compounds [26,27]. Recently, Janda et al. [28] have reported on the use of a carbon fiber electrode coated with cobalt tetramethylpyridoporphyrine for potentiometric detection of ascorbic acid. To the best of our knowledge, this paper describes, for the first time, the application of a CoPC modified carbon paste electrode as a potentiometric sensor for determination of ascorbic acid. The electrode was used to determine ascorbic acid in vitamin preparations. Cyclic voltammetry was used to study the catalytic activity of the modified electrode.

Experimental Section

Materials

Cobalt phthalocyanine (β -form), ascorbic acid and spectroscopic grade mineral oil (Nujol) were obtained from Aldrich and used as received. Graphite powder, potassium hydrogen phosphate, potassium dihydrogen phosphate and potassium hydroxide (Merck) were used without further purification. All other chemicals were of analytical reagent grade. Doubly distilled water was used for preparing all of the solutions and throughout the experiments.

Phosphate buffers were prepared by mixing 0.1 M solutions of KH_2PO_4 and K_2HPO_4 . The resulting solutions were adjusted to the required pH by addition of dilute KOH and H_3PO_4 solutions using a pH meter. Solutions of ascorbic acid were freshly prepared as required in phosphate buffer at the desired pH and protected from light during the investigation.

Voltammetric experiments were carried out in 0.1 M phosphate buffers, deoxygenated by argon. Solutions for the potentiometric determination of ascorbic acid were equilibrated with oxygen at $25 \pm 1^\circ\text{C}$ by bubbling the solution with oxygen.

For determination of ascorbic acid in commercial vitamin preparations, each tablet was crushed with a mortar and pestle and 100 mg of the powder was dissolved in 100 ml distilled water. The resulting solutions were filtered as necessary and appropriately diluted with phosphate buffer (pH 7.0) to reach the linear range of the calibration graph. An aliquot of this solution (25 ml) was transferred to the measuring cell and potentials were recorded. Standard addition was subsequently performed by adding several separate 100 μl aliquots of a solution containing 0.1 M ascorbic acid and measuring the potential plateau in each case.

The recovery of the method was determined by adding ascorbic acid to 100 mg of the powdered vitamin preparations and then taking this mixtures through the

remainder of the procedure.

Apparatus

Voltammetric experiments were conducted with a Potentionstat/Galvanostat Analysis System Model BHP-2061-A (Behpajouh Eng. Co. Esfahan, Iran). A conventional three electrode system was employed incorporating either unmodified or modified carbon paste electrode, a saturated Ag/AgCl/KCl reference electrode and a Pt-wire counter electrode.

Potentiometric measurements were performed in a cell consisting of a CoPC modified carbon paste as the indicator electrode, a saturated Ag/AgCl/KCl reference electrode and a stirrer. The measuring cell was thermostated at $25 \pm 1^\circ\text{C}$ using a Haake Model FK2 circulation water bath. A digital pH/mV meter (Corning Model 125) was used for measuring pH and potentials. The meter was connected to a Philips Model PM-8277 X-Y recorder for plotting potential-time data.

Modified Electrode Preparation

The modified carbon paste electrode was prepared by mixing CoPC powder with graphite powder (5% w/w) and then adding mineral oil (Nujol). After thorough hand mixing with a mortar and pestle, a portion of the composite mixture was packed into the end of a glass tubing (ca. 3mm i.d.) and a copper wire was used to provide electrical contact. Unmodified electrodes were prepared in the same way without the addition of CoPC. The working surface of the electrodes was polished using a polishing cloth.

Results and Discussion

The catalytic function of CoPC modified electrode is demonstrated in Figure 1A by cyclic voltammogram of deoxygenated solution of 1.0×10^{-3} M ascorbic acid at pH 7.0, obtained at the surface of the chemically modified carbon paste electrode. Figure 1B shows the behavior of this electrode in the absence of ascorbic acid. Under the same experimental conditions, the direct oxidation of ascorbic acid at an unmodified carbon paste electrode shows an irreversible anodic wave with a peak potential, not well defined, around +600mV (vs. Ag/AgCl electrode), (Figure 1C). For both electrodes, the oxidation of ascorbic acid shows irreversible waves due to inactivity of dehydroascorbic acid. At the modified electrode, the oxidation of ascorbic acid gives rise to a typical electrocatalytic response with an anodic peak current that is greatly enhanced over that observed for the unmodified electrode. The maximum current for the oxidation of ascorbic acid with the modified electrode occurred at a potential some 150-200 mV more negative of that obtained in the presence of the unmodified electrode. This reduction of overvoltage for oxidation of ascorbic acid was also

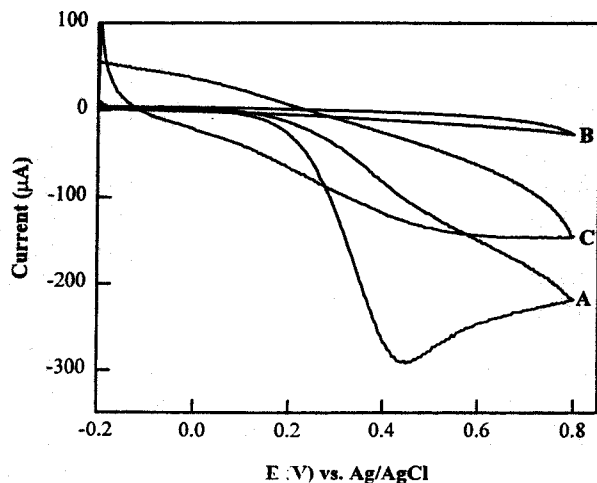


Figure 1. Typical cyclic voltammograms for oxidation of (A) 1×10^{-3} M ascorbic acid at the modified carbon paste electrode; (B) 1×10^{-3} M ascorbic acid at the unmodified carbon paste electrode; (C) plain supporting electrolyte at the modified electrode. In each case, the supporting electrolyte was 0.1 M phosphate buffer (pH 7). Scan rate, 100 mV s^{-1} .

observed for different concentrations and potential scan rates and clearly demonstrates that the CoPC mediator functions electrocatalytically. Similar observations have been previously reported for CoPC and cobalt tetramethylpyridodorphyrzine [21,28].

The effect of scan rate on the cyclic voltammograms for oxidation of 1.0×10^{-3} M ascorbic acid at the modified electrode is shown in Figure 2A. Plot of the experimental anodic peak currents, $(I_{p,a})$, vs. square root of the scan rate

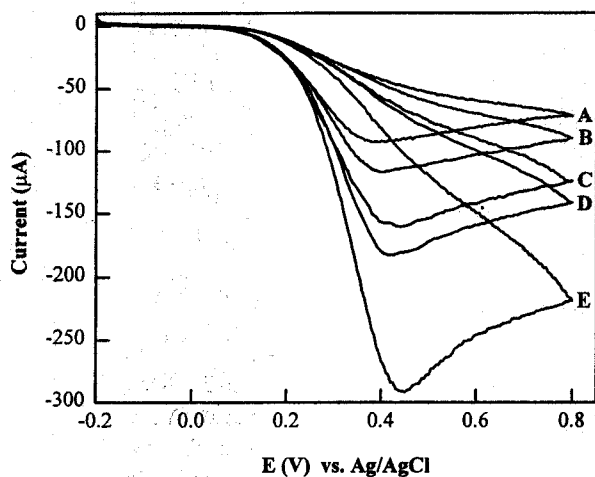


Figure 2. Cyclic voltammograms for oxidation of 1×10^{-3} M ascorbic acid at the modified electrode recorded at different scan rates; (A) 10, (B) 20, (C) 40, (D) 50 and (E) 100 mV s^{-1} at pH 7.

, $U^{1/2}$, shows a linear relationship, which suggests that the reaction is diffusion controlled.

In the light of our results and previous works [21,28], the catalytic effect of CoPC modified carbon paste electrode towards ascorbic acid can be explained by a CE (chemical reaction followed by an electron transfer process) mechanism; which consists of chemical reduction of Co(II)PC by ascorbic acid according to Equation(1),



and the subsequent electrochemical re-oxidation of Co(I)PC, Equation (2):



The direct oxidation of ascorbic acid by oxygen in acidic and neutral solutions in the absence of a catalyst is very slow [3]. Potentiometric methods using a redox mediator represent a convenient way to measure the equilibrium potential of such slow and irreversible reactions. The CoPC modified electrode can be used as a mediator for indirect oxidation of ascorbic acid by oxygen. The Co(II)PC is reduced by ascorbic acid forming Co(I)PC (equation 1), which can be re-oxidized back in the second step through a chemical reaction with oxygen according to Equation (3).



A similar mechanism has been recently proposed by Janda et al. [28] for a carbon fiber microelectrode. In fact, the CoPC mediator provides a reversible redox couple, Co(II)PC / Co(I)PC, for measuring the potential of the ascorbic acid-oxygen (as donor-acceptor couple) system. As can be seen from Equations (1) and (3), the potential of the electrode is determined by the Co(II)PC / Co(I)PC concentration ratio, which is determined not only by the ascorbic acid concentration, but also by pH and oxygen concentration in the solution. In the case that the concentration of oxygen and other parameters such as pH and temperature are kept constant, the potential of the electrode is determined by the concentration of ascorbic acid in the solution.

A typical potential vs. time curve for the response of the modified electrode to changes in ascorbic acid concentration is shown in Figure 3. This plot was obtained by the sequential addition of $100 \mu\text{l}$ of 0.100 M freshly prepared ascorbic acid to 25 ml of $1.0 \times 10^{-3} \text{ M}$ ascorbic acid solution buffered at pH 7.0 and saturated with oxygen at $25 \pm 1^\circ\text{C}$. The response time of the electrode is fast ($< 20\text{s}$), depending on the efficiency of stirring during injection of the sample.

The calibration plot of the potential of the modified electrode vs. logarithm of ascorbic acid concentration was linear over the concentration range 5×10^{-6} - 1×10^{-2} M, ~1-1800 $\mu\text{g ml}^{-1}$, (at pH 7.0, correlation coefficient=0.9989, n=8) (Figure 4A). The sensitivity expressed as the slope of the calibration graph was calculated to be 56 - 59 mV, depending on the pH of solution, which showed the Nernstian response of the electrode. The equilibrium potential of the electrode can be expressed by Equation (4):

$$E = Q + 59 \log C_{AA} \text{ mV (at } 25 \pm 1^\circ\text{C and pH 7.0)} \quad (4)$$

The effect of buffer concentration and pH on the electrode response to ascorbic acid additions was studied. The optimum buffer concentration was found to be 0.1 M. It was observed that pH affects both the potential shift of the electrode, Q in Equation (4), and slope of the calibration graph (Figure 4). Maximum sensitivity was observed at pH 7.0, with a Nernstian slope of 59 mV per decade of ascorbic acid concentration (Figure 4A). The calibration graph was linear in the pH range 5-7 with a slight decrease in sensitivity at pH values less than 7.0.

The theoretical limit of detection was 1×10^{-6} M (~0.2 $\mu\text{g ml}^{-1}$) ascorbic acid. The electrode retained its full

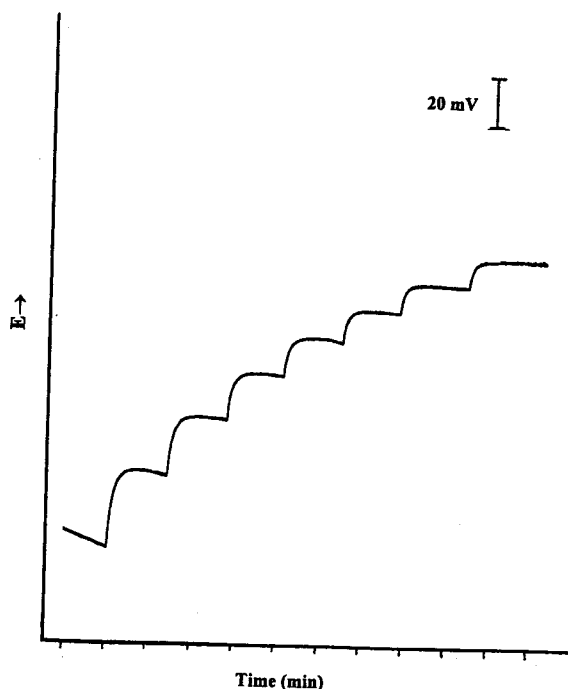


Figure 3. Potential-time curve for the response of the CoPC modified electrode to successive addition of ascorbic acid at pH 7.0 in solutions saturated with oxygen at 25°C.

Table 1. The results of analysis of vitamin preparations. The mean results are quoted $\pm 95\%$ confidence limit.

Vitamin Preparation	Quoted Content (mg)*	Weight of Sample (mg)	Ascorbic acid (mg)	Recovery %
A	78	100	75.8 \pm 3.0 (n=5)	-
B	-	-	149.4 \pm 5.4 (n=5)	98.1
C	25	100	22.1 \pm 1.4 (n=5)	-
D	-	-	46.4 \pm 2.6 (n=5)	97.2

- A: Vitamin tablets, Daro Pakhsh Co., Quoted content 250 mg per ~320 mg tablet.
- B: Sample A, 100 mg+75 mg ascorbic acid.
- C: Vitamin C effervescent tablets, Osvah Co., quoted content 1000 mg per 4 g tablet.
- D: Sample C, 100 mg+25 mg ascorbic acid.
- *: Quoted contents are mg ascorbic acid expected per 100 mg of the sample.

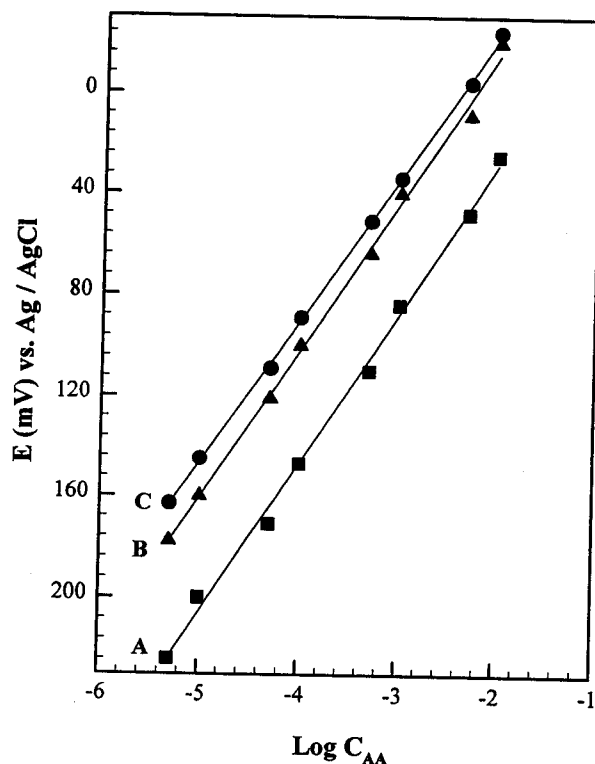


Figure 4. Calibration plot of potential of CoPC modified electrode vs. logarithm of ascorbic acid concentration; PH 7.0(■), pH 6.0 (▲), pH 5.0 (●), in solutions saturated with oxygen at 25°C.

activity during one month of operation. Since carbon paste is a reservoir of the modifier, the surface of the electrode can be easily renewed by slight polishing.

The modified electrode was applied to the determination of ascorbic acid in vitamin preparations using the standard addition method. Quantification was achieved by the linear regression of potentials vs. logarithm of ascorbic acid concentration and results are given in Table 1. The correlation coefficients of the calibration plots in the standard addition methods were between 0.9989 to 0.9998. The precision of the method was assessed by repeating the analyses of vitamin preparations. For vitamin C tablets, the RSD was 3.2% (n=5, mean=75.8 mg per 100 mg of the powdered sample) and 2.9% when spiked with ascorbic acid (n=5, mean=149.4 mg). The precision for the effervescent tablets was 5% (n=5, mean=22.1 mg) and 4.5% when spiked with ascorbic acid (n=5, mean=46.4 mg). The recovery of ascorbic acid added to 100 mg of vitamin preparations was 97-98% (Table 1).

In summary, the CoPC modified carbon paste electrode has been successfully applied as a sensitive potentiometric sensor for fast and accurate determination of ascorbic acid in commercial vitamin products. The electrocatalytic system for the determination of ascorbic acid shows relatively long-term operational stability (over a month). The proposed potentiometric method offers advantages of very simple instrumentation, a wide linear range of the calibration plot (about 4 decades of concentration), and the absence of deactivation processes often accompanying voltammetry at solid electrodes [29]. Voltammetric methods require a potentiostatic system and periodic regeneration of the working electrode to obtain reproducible responses [28] and generally offer lower linear range. The above advantages, together with the very easy preparation and easy regeneration of the electrode surface by simple polishing, makes the system useful in constructing simple devices for determination of ascorbic acid.

Acknowledgements

The authors gratefully acknowledge the support of this work by the Esfahan University Research Council.

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