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Detection of Ascorbic Acid in Biological Samples by a New Modified Glassy Carbon Electrode

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ABSTRACT

The present work describes the construction of a new modified electrode by casting the appropriate mixture of a metallocene, which has been introduced in the experimental part, as a mediator at the surface of glassy carbon (GC) electrode. The proposed modified GC electrode was used for the determination of ascorbic acid (AA) in phosphate buffer (PB) solution (pH = 4.0). When compared to bare GC electrode, the modified electrode not only shifted the oxidation potential of AA towards less positive potential but also enhanced its oxidation peak current. Further, the oxidation of AA was highly stable at modified electrode. The optimum analytical conditions were sought. The oxidation peak of AA increases linearly while increasing its concentration with a correlation coefficient of 0.9993 and a detection limit (3σ) was found to be quite desirable. The present modified electrode was also successfully used for the determination of AA in the presence of common interferences such as starch, glucose, citric acid Na^+, K^+, Mg^{2+} and Ca^{2+}. The proposed modified electrode was successfully demonstrated towards the determination of AA in pharmaceutical samples. It should be noted that procedure for preparation of this modified electrode is simple, inexpensive and rapid.

Keywords: Ascorbic acid, Sensor, Chloromercuriferrocene, Nafion, Electro catalytic, Glassy carbon electrode

INTRODUCTION

Ascorbic acid (AA) is an important molecule involved in many biological and biochemical processes. AA is found in numerous natural sources. It is of vital importance in the process of oxidation and reduction in human organism, participating of several metabolic reactions. AA has also been used for the prevention and treatment of the common cold, mental illness, infertility, cancer and AIDS [1]. However, excess of AA can cause gastric irritation and diarrhoea, giving as metabolic product oxalic acid, which can cause renal problems [2]. For this reason, it has gained important significance in areas of analytical chemistry such as pharmaceutical, food or clinical analysis [3].

Many methods have been developed for the determination of AA including titrimetry [4,5], spectrophotometry [6-15], spectrofluorimetry [16,17], calorimetry [18], potentiometry [19], enzymatic method [20], GC [21], HPLC [22,23], capillary electrophoresis [24] and voltammetric methods [25-34]. Among the different methods, electrochemical method of determination with modified electrode has several advantages over other methods such as less time consuming and more selectivity and sensitivity [25,26]. The direct electrochemical oxidation of AA is possible but requires high overpotentials. These high overpotentials result in electrode fouling, poor reproducibility, low selectivity and poor sensitivity and thus this technique is rarely employed analytically [27]. Chemically modified electrodes (CMEs) containing redox mediators provide a promising method to lower the overpotential have been used for the AA determination [25-34]. CMEs can be divided broadly into two main categories; namely, surface modified and bulk modified electrodes. Methods of surface modification include adsorption, covalent bonding, attachment of polymer films, *etc*. [35]. Polymer film modified electrodes can be differentiated from

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other modification methods such as adsorption and covalent bonding because they commonly involve multilayer adsorption, which can increase the concentration of the eletrocatalyst resulting in obvious analytical signals. Together with its ease of preparation, good stability and reproducibility, the polymer film modified electrode is particularly advantageous for electroanalytical research [36]. One of these polymers is Nafion (NF). NF, a perfluorinated sulfonate ionomer, has been widely employed to modify electrodes for a variety of sensor and fuel cell applications [37]. NF modified electrodes can be easily prepared by solvent casting the polymer directly on the electrode surface and provide several advantages over unmodified electrodes. NF acts as a protective coating for the electrode surface [38].

The present work describes the fabrication of a modified electrode using Chloromercuriferrocen (CMF) as a new mediator immobilized on the surface of glassy carbon electrode by NF as a covering agent. The electrochemistry behavior of GCE/NF/CMF and investigation of its electrocatalytic effect on AA determination was studied in details. It was found that the GCE/NF/CMF modified electrode showed an electrocatalytic activity towards the oxidation of AA at pH = 4.0 by enhancing its oxidation current with 120 mV less positive potential shift when compared to bare GC electrode. The practical application of the present modified electrode was demonstrated by measuring the concentration of AA in real samples.

EXPERIMENTAL

Reagents and Materials

Nafion (5 wt% solution) and AA were purchased from Fluka-Sigma and were used as received. Chloro-mercuriferrocene and other chemical compounds such as H_3PO_4, NaH_2PO_4 and NaOH were purchased from Merck. Phosphate buffer solutions (PBS) were prepared from H_3PO_4 and NaH_2PO_4 (0.1 M) and adjusted the pH range 2-8 with 0.1 M H_3PO_4 and NaOH solutions and used as supporting electrolyte. All solutions were prepared using doubly distilled water. The electrolyte solutions were deoxygenated with nitrogen bubbling before each voltammetric experiment. All experiments were performed under nitrogen atmosphere at room temperature.

Instrumentation

Electrochemical measurements were carried out with a SAMA500 Electroanalyser (SAMA Research Center, Iran) controlled by a personal computer. All electrochemical experiments were carried out in a conventional three-electrode cell at room temperature. A platinum electrode and a saturated calomel electrode (SCE) were used as the counter and reference electrodes, respectively. All potentials were reported with respect to this reference electrode.

Preparation of Working Electrodes

All glassware was thoroughly cleaned with freshly prepared aqua regain (3:1; HCl/HNO_3) and rinsed comprehensively with double distilled water prior to use. Glassy carbon electrodes (GCEs) were polished with 0.05 μm alumina slurry, followed by rinsing thoroughly with doubly distilled water. Then, the electrodes were successively sonicated in H_2SO_4 1 M. 0.1 ml NF 5 wt% was diluted by 0.9 ml methanol to obtain the NF 0.5 wt % solution. 0.01 g CMF was dissolved in 2 ml dimethyl-formamide (DMF). These two solutions were mixed and a result mixture was stirred for 20 min. Each time, 4 μl from the resulted solution was coated on the surface of the GCE and allowed to dry at room temperature for 2 h and was used as working electrode.

RESULTS AND DISCUSSION

The Electrochemical Study of GCE/NF/CMF

Figure 1 shows three cyclic voltammograms that are related to GCE, GCE/NF and GCE/NF/CMF. The third cyclic voltammogram can be referred to the presence of CMF at the electrode surface. The electrochemical properties of GCE/NF/CMF were studied by cyclic voltammetry in pure buffered aqueous solution at various scan rates. Figure 2a shows the cyclic voltammograms of GCE/NF/CMF at various scan rates. The corresponding reactions of these voltammograms are as following:

$$\text{Chloromercuriferrocene} \longrightarrow \text{Chloromercuriferrocenium}^{+} + e^{-} \quad (1)$$

$$\text{Chloromercuriferrocenium}^{+} + e^{-} \longrightarrow \text{Chloromercuriferrocene} \quad (2)$$

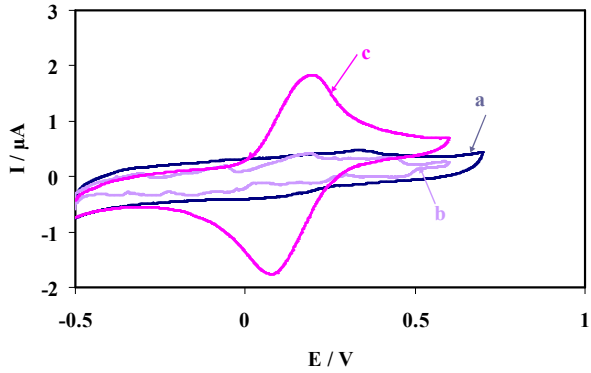

Fig. 1. Cyclic voltammograms of (a) bare GCE, (b) GCE/NF and (c) GCE/NF/CMF in PBS (pH = 4.0) at the scan rate 50 mV s^{-1}.

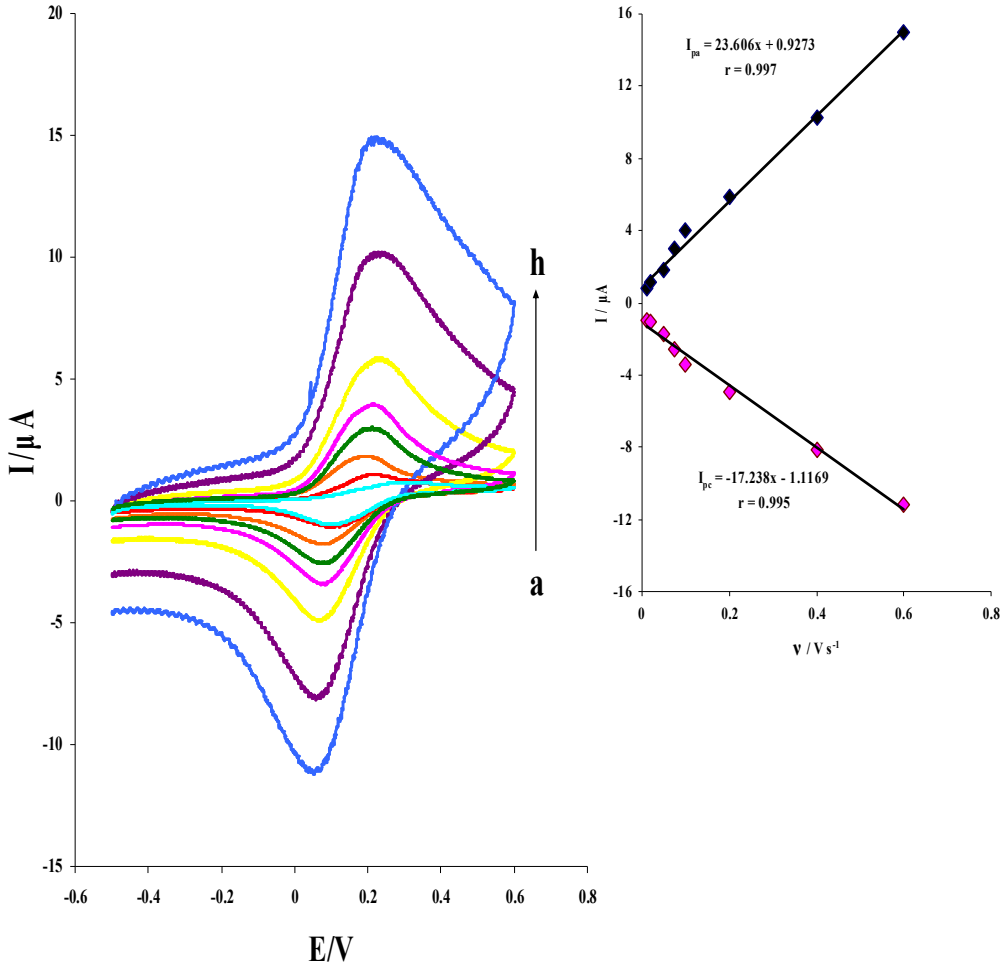

Fig. 2. (A) Cyclic voltammograms of GCE/NF/CMF in 0.1 M phosphate buffer pH 5, at various scan rates: (a) 10; (b) 50; (c) 100; (d) 200; (e) 400; (f) 600 mV s^{-1}. (B) Plots of anodic and cathodic peak currents of GCE/NF/CMF *vs.* $\upsilon^{1/2}$ from cyclic voltammograms of (A).

The Eqs. ((1) and (2)) include the oxidation and reduction of CMF and production of chloromercuriferrocenium ion (CMF^+) with loss of one electron in anodic sweep. A summary of electrochemical data for the mediator obtained at the CNTPE/CMF is shown in Table 1. As can be seen, the peak separation potential, ΔEp (ΔEp = E_{pa} - E_{pc}), is greater than the 59/n mV expected for a reversible system; this result suggests that CMF does not act as a reversible system in the GCE/NF/CMF matrix. These cyclic voltammograms were used to examine the variation of peak current versus sweep rate. Figure 2a shows that the modified electrode had a chemically quasi-reversible redox couple in PBS (pH = 4.0) solution and the peak currents were increased due to the cyclic voltammetric scan rate. As shown in Fig. 2b, I_{pa} and I_{pc} were linearly dependent on scan rate, as expected for surface confined redox process. And the ratio of the anodic peak current to the cathodic peak current Ipc:Ipa, is almost close to unity. These behaviors are consistent with a diffusionless system, reversible electron transfer process at low scan rates [39].

Based on the electrochemical studies of some ferrocenium compounds modified electrodes involving in a one electron transfer process [40,41] we suggested that the modified electrode reaction could be a one electron transfer process (n = 1).

An approximate amount of the electroactive species can be estimated by the method suggested by Sharp *et al.* [42] According to this method, the peak current is related to the surface concentration of electroactive species, Γ, by Eq. (3):

$$I_p = \frac{n^2 F^2 A \Gamma v}{4RT} \quad (3)$$

Where n represents the number of electrons involved in the reaction, A is the geometric surface area (0.0314 cm^2) of the electrode, Γ (mol cm^{-2}) is the surface coverage, v is the scan rate, R (8.314 J mol^{-1} K^{-1}), F (96485 C mol^{-1}) and T (298 K) denote as usual for the gas constant, the temperature, and the Faraday constant, respectively. From the slope (from Fig. 1b) of anodic peak currents *versus* scan rate, the surface concentration of CMF was calculated to be 8.0 × 10^{-10} mol cm^{-2} for n = 1.

The stability of modified electrode was studied by noting the decrease in anodic charge, q_a, in repetitive potential scan cycles. The rate of loss of electrochemical activity for the modified electrode was investigated prior to use. Cyclic voltammograms of GCE/NF/CMF in consecutive 10 potential scan cycles in PBS at scan rate 50 mV s^{-1} were shown in Fig. 3. As shown in Fig. 3, a little change of the anodic and cathodic peak currents has been observed and these results could prove the stability of the modified electrode.

Electrocatalytic Oxidation of AA at the Surface of GCE/NF/CMF

The prime objective of the present work is to determine the concentration of AA using GCE/NF/CMF modified electrode. Figure 4 shows the CVs obtained for bare GCE and GCE/NF/CMF modified electrodes in 0.1 M PB solution (pH = 4.0) containing 0.31_mM AA. The bare GC electrode showed an oxidation wave for AA at 390 mV (curve b), whereas no oxidation wave was observed at GCE/NF modified electrode (not shown) due to the formation of compact NF film on GC electrode. On the other hand, GCE/NF/CMF modified electrode showed the oxidation peak for AA at 270 mV (curve d). When compared to bare GC electrode (curve b), the oxidation peak potential of AA was shifted to 120 mV less positive potential. Also, the oxidation current was greatly increased over that ordinarily observed just for the incorporated chloromercuriferrocene/chloromercuriferrocenium couple while the corresponding cathodic wave was depressed on the reverse cyclic voltammetry scan. The mechanism of this phenomenon can be written as follows:

$$\text{Chloromercuriferrocene} \longrightarrow \text{Chloromercuriferrocenium}^+ + e^- \quad (4)$$

$$2\text{Chloromercuriferrocenium}^+ + \text{AA} \longrightarrow 2\text{Chloromercuriferrocene} + \text{DHAA} + 2H^+ \quad (5)$$

These results showed that the electrooxidation of AA to dehydroascorbic acid (DHAA) can be catalyzed by chloromercuriferrocene/chloromercuriferrocenium couple as a mediator at the surface of GCE/NF/CMF.

It has been already shown that the oxidation of AA is very sensitive to pH of the solution. Hence, a series PBS with different pH values were prepared and tested as

Table 1. Electrochemical Data for GCE/NF/CMF

E_{pa} (mV)	E_{pc} (mV)	$E_{1/2}$ (mV)	ΔE_p (mV) [a]
203.0 (0.34)[b]	67.0 (0.69)	135.0 (0.44)	136.0

[a]Peak separation potential scan rate, υ = 50 mV s^{-1}. [b]The values in parentheses indicate the calculated R.S.D. (%).

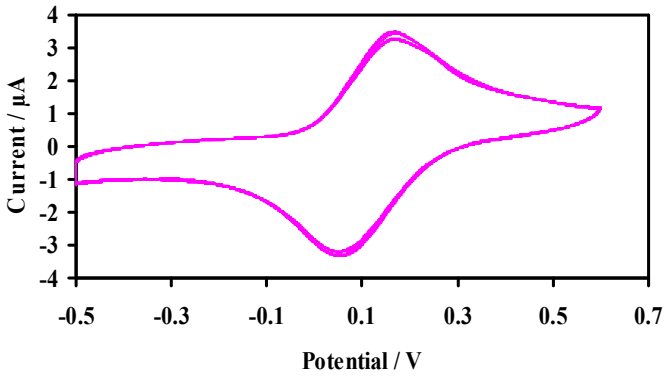

Fig. 3. Cyclic voltammograms of GCE/NF/CMF in consecutive 6 potential scan cycles in PBS (pH 5) at scan rate 50 mV s^{-1}.

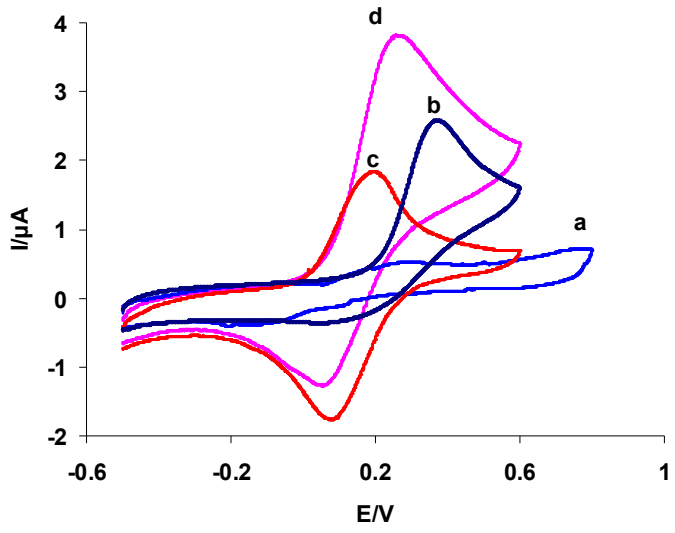

Fig. 4. Cyclic voltammograms of (a) unmodified and (c) GCE/NF/CMF in absence of AA and (b) unmodified and (d) GCE/NF/CMF in present of AA in PBS (pH 4) at scan rate 50 mV s^{-1}.

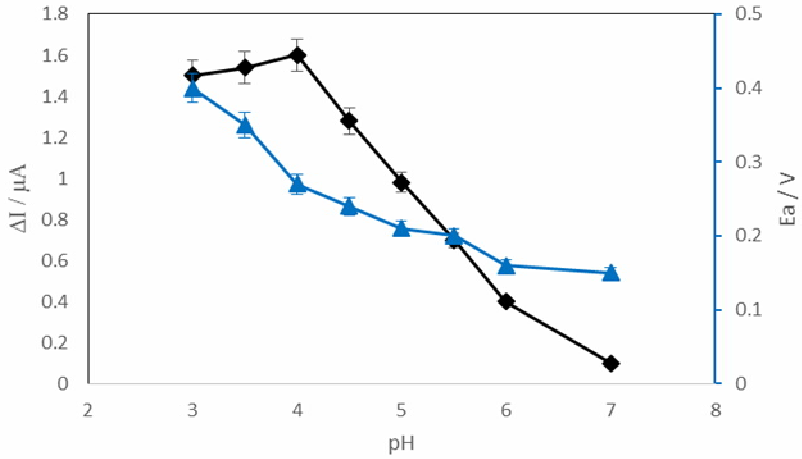

Fig. 5. The effect of pH of the anodic peak current and electrooxidation potentional of 0.31 mM of AA, in PBS (pH 4) at scan rate 50 mV s^{-1}.

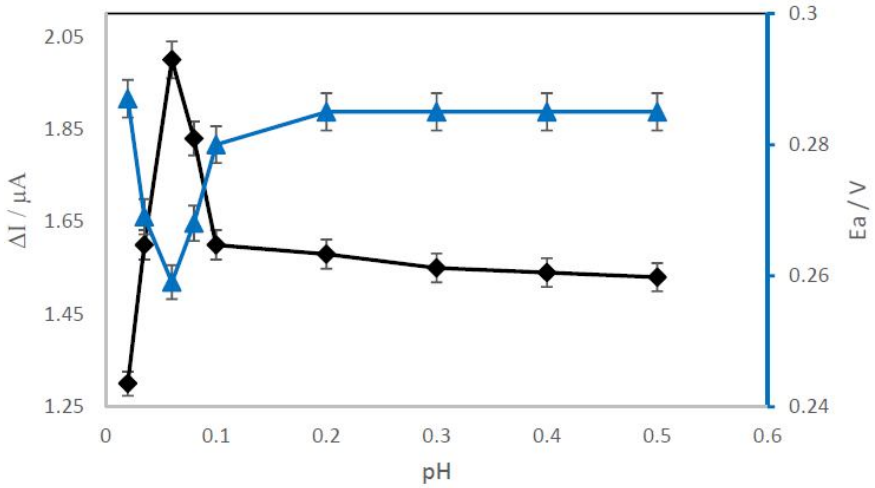

Fig. 6. The effect of NF (%) of the anodic peak current and electrooxidation potentional of 0.31 mM of AA, in PBS (pH 4) at scan rate 50 mV s^{-1}.

supporting electrolyte for electrocatalytic determination of AA at the surface of GCE/NF/CMF by cyclic voltammetry. The variations of anodic peak potential and anodic peak current with respect to the change in the pH of the electrolyte in the pH range from 3.0-7.0 were shown in Fig. 5. Variation in the electrolyte pH will result in variation in the formal potential of the AA, the value of potential shift and the height of peak corresponding to the oxidation of AA. For the electrocatalytic oxidation of AA using GCE/NF/CMF, with increasing the pH of the buffer solution from 3.0 to 4.0, the anodic peak currents were increased and then decreasing with increasing pH from 4.0 to7.0. Also, the anodic peak potentials were decreased with increasing pH from 3 to 7. So, pH 4 was chosen as optimum.

In order to obtain the best composition of this modified electrode, we used the different quantities of NF to preparation of modified electrodes. For this work, four electrodes with different percent of NF were prepared and

studied in the presence of the 0.31mM AA using cyclic voltammetry. Figure 6 shows the result. According to this figure, we selected the NF 0.05% in all experimental works.

To understand the fast electron transfer reaction of AA at GCE/NF/CMF modified electrode quantitatively, we have calculated the standard heterogeneous rate constant (k_s) for AA at GCE/NF/CMF and bare GC electrodes using Velasco equation [43] as given below:

$$k_s = 1.11\, D_o^{1/2} (E_p - E_{p1/2})^{-1/2} v^{1/2} \quad (6)$$

Where, k_s is standard heterogeneous rate constant; D_o is the apparent diffusion coefficient; E_p is oxidation peak potential; $E_{p1/2}$ is half-wave oxidation peak potential and v is the scan rate. In order to determine the k_s, it is necessary to find the diffusion coefficient for AA. The apparent diffusion coefficient (D_o) value was determined by a single potential chronoamperometry technique based on the Cottrell slope obtained by plotting *vs.* $1/\sqrt{time}$. Chronoamperometry measurements were carried out for AA both at bare GC and GCE/NF/CMF electrodes. Based on Cottrell equation, the diffusion coefficient of AA was found to be 6.47×10^{-5} cm^2 s^{-1} for GCE/NF/CMF electrode [44]. The estimated standard heterogeneous rate constant (k_s) values for totally irreversible oxidation of AA both at bare GC and GCE/NF/CMF electrodes were found to be 6.470×10^{-3} cm s^{-1} and 3.361×10^{-3} cm s^{-1} respectively. The obtained higher k_s value for AA at GCE/NF/CMF modified electrod indicated that the oxidation of AA was faster at the GCE/NF/CMF electrode than at bare GC electrode.

Evaluation of the Proposed Modified Electrode

Under optimum conditions, determination of AA was carried out at the potential range of -500-600 mV using cyclic voltammetry mode. The AA electro-oxidation peak was observed at the potential of about 270 mV *vs*. SCE. The electrocatalytic peak current of AA at the surface of GCE/NF/CMF was linearly dependent on the AA concentration. These peak currents were linear up to 3.6 mM and was described by the equation $\Delta I_{(\mu A)} = 5.903[AA]_{(mM)} + 0.1451$, r = 0.9993, n = 12, where $\Delta I_{(\mu A)}$ is the difference of the oxidation peak currents CMF before and after addition of AA, [AA] is the AA concentration, r is the correlation coefficient and n represents the number of determinations (Fig. 7). The detection limit (3σ) was 2.8×10^{-5} M Relative standard deviation (%RSD) for 5 determinations of AA (0.31 mM) using CV were 1.71 %.

Interference Study

For investigating the interference, several compounds were selected. If the tolerance limit was taken as the maximum concentration of the foreign substances, which caused an approximately 5% relative error, for 1.2×10^{-4} M AA, no interference was observed for the following compounds: starch, citric acid and glucose, K^+, Na^+, Mg^{2+}, Ca^{2+},. The results are listed in Table 2.

Application in Real Samples

In order to prove the capability of this modified electrode for catalytic oxidation of AA in the real samples, we examined this ability in the voltammetric determination of AA in some pharmaceutical preparations, such as effervescent, chewable tablets and vials available in local pharmacies. Therefore, pharmaceutical tablet solutions were prepared by accurately weighing, grinding of tablets and then filtering of dissolved obtained powder in the working buffer solution. The determination of AA in pharmaceutical preparations was carried by the standard addition method in order to prevent on any matrix effect. The results were compared with those obtained using the official iodometric titration method [45]. The paired t-test equation, applied in statistics is;

$$t = \left| \frac{\bar{d}\sqrt{n}}{s_d} \right| \quad (7)$$

Where $\bar{d}$ and s_d are the mean and standard deviation respectively of $\bar{d}$ (the difference between paired values). For the pairs of values in Table 3, the mean difference, $\bar{d}$, is -8.37 and the standard deviation of the differences, s_d, is 8.19. The calculated t was found to be 2.04. The critical value of t (tabulated t) for n-1 degrees of freedom (in this work 3) is 3.18 (P = 0.05). Since the calculated value of t is less than this the null hypothesis is not rejected: the methods do not give significantly different results for AA concentration.

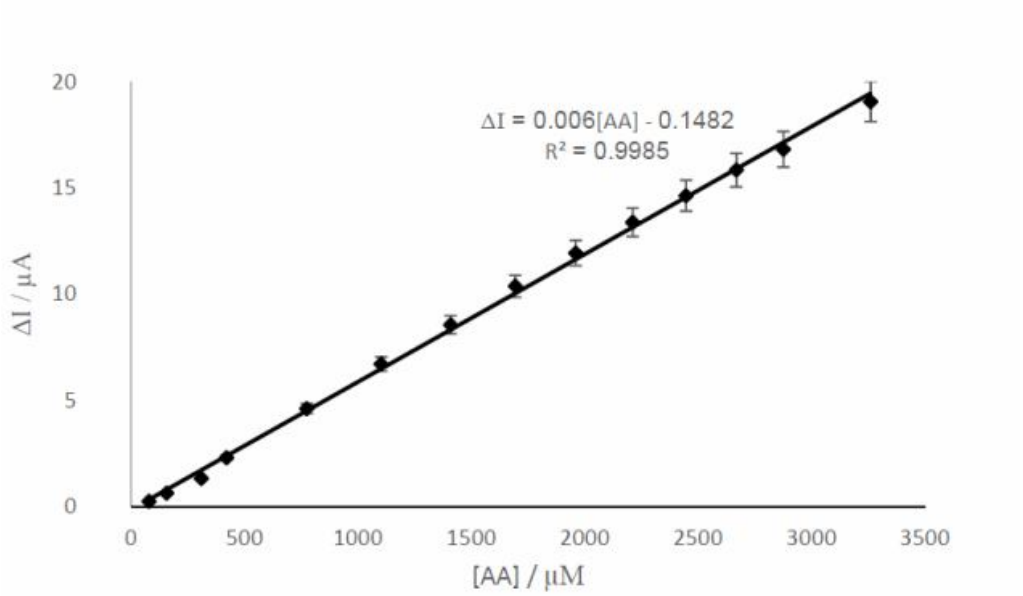

Fig. 7. Calibration curve; Plot of peak currents of AA at various concentrations: (1) 0.00; (2) 0.42; (3) 0.78; (4) 1.1; (5) 1.4; (6) 1.7; (7) 2.0; (8) 2.2; (9) 2.4; (10) 2.7; (11) 2.9; (12) 3.3; (13) 3.6; (14) 3.8; (15) 3.9 mM at the surface of GCE/Nf/CMF from CV vs. the AA concentrations, respectively. Solutions were PBS (pH 5). Scan rate was 50 mV s^{-1}.

Table 2. Influence of Foreign Compounds. AA Concentration 0.12 mM

Interferent	Tolerance limit (Inter/AA^-)[a]
Starch	520
Na^+, K^+	340
Ca^{2+}, Mg^{2+}	220
Citric acid	115
Glucose	95

CONCLUSIONS

The construction of GCE/NF/CMF and its use for electrocatalytic oxidation and determination of different concentrations of AA was described. NF had good properties as a covering agent and CMF showed the electrocatalytic activity for AA oxidation. The overpotential was reduced with the value of 120 mV for the oxidation of AA. Experimental conditions such as pH 4 of supporting electrolyte, scan rate 50 mV s^{-1} and %0.05 NF have been used for the determination of AA. For study the capability of this modified electrode in the real samples, some pharmaceutical preparations were used and the compared with standard titrimetric method. There was no significant

Table 3. Determination of AA in Pharmaceutical Real Samples

Sample	Proposed method (mg)	Iodometric standard method (mg)
Vitamin C tablet (250 mg)[a]	247.27	246.67
Vitamin C tablet (250 mg)[b]	242.00	249.32
Vitamin C injection (500 mg)[a]	478.46	494.21
Vitamin C tablet (1000 mg)[a]	980.80	995.10

[a]Osveh Co. [b]Darou Pakhsh Co.

Table 4. Comparsion the Proposed Modified Electrode GCE/NF/CMF with others Electroanalytical Methods for Determination of AA

Electroanalytical method	Modifier	Sample	pH	Linear range (μM)	Detection limit (μM)	Ref.
DPV	Chitosan-Graphene	-	7	50-1200	50	[46]
CV	ZnO/RM	Pharmaceutical	1.5	15-240	1.4	[47]
CV, DPV	Pt-Au hybrid	Pharmaceutical	4	103-165	103	[48]
CV	p-ATD	Biological	5	30-300	2.01	[49]
CV	CMF	Pharmaceutical	5	79-3300	28	This work

difference between the two methods. Simple fabrication procedure, wide linear range, high stability and good reproducibility for repeated determination, suggest this electrode as a good and attractive candidate for practical applications. In comparison with other electroanalytical methods that reported for the determination of ascorbic acid, this method has satisfy figures of merit (Table 4).

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