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Simultaneous Voltammetric Determination of Norepinephrine and Acetaminophen at the Surface of a Modified Carbon Nanotube Paste Electrode

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A modified carbon nanotube paste electrode was used for the sensitive and selective voltammetric determination of norepinephrine (NE). The mediated oxidation of NE at the modified electrode was investigated by cyclic voltammetry (CV). Under the optimum conditions, the calibration curve for NE was obtained in the range of 0.03-500.0 μM with a detection limit (3σ) of 22.0 nM using differential pulse voltammetry (DPV). DPV was used for simultaneous determination of NE and acetaminophen (AC) at the modified electrode, and quantitation of NE and AC in some real samples by the standard addition method.

Keywords: Noreponephrine, Acetaminophen; Carbon Nanotubes; Modified Carbon paste Electrode; Voltammetry

1. INTRODUCTION

Application of chemically modified electrodes (CMEs) in the electrochemical determinations has been widely considered as a sensitive and selective analytical method for the detection of trace amounts of biologically important compounds [1–3]. One of the most important properties of CMEs, in comparison to unmodified electrodes, has been their ability to catalyze the electrode process by significant decrease in the needed overpotential. With respect to relatively selective interaction of the electron mediator with the target analyte in a coordination fashion, these electrodes are capable to considerably enhance the selectivity in the electroanalytical methods [4-6].

Carbon nanotubes have attracted much attention during the past decade [7] due to their unique mechanical, chemical and electrical properties [8]. Carbon nanotubes (CNT) with diameters in the range of 5–40 nm and up to several microns in length can now be produced in macro quantities [9]. According to their atomic structure, carbon nanotubes behave electrically as a metal or as a semiconductor [10-15].

They have many significant properties and can be used as attractive novel materials in electrochemical fields [16-22]. The subtle electronic properties suggest that carbon nanotubes should have the ability to mediate electron transfer reactions with an electroactive species in solution when used as an electrode. The reactivities of CNT in solution have been demonstrated, resulting in specific reactive (oxidative) sites on the CNT surfaces. Thus, an important application of CNT is that they can be used as the electrode material in CNT paste electrodes or CNT modified glassy carbon electrodes [23-27] to investigate the electrochemical properties of biomolecules.

Norepinephrine (NE) is a very important catecholamine neurotransmitter in the mammalian central nervous system [28]. Along with epinephrine, NE also underlies the fight-or-flight response, directly increasing heart rate, triggering the release of glucose from energy stores and increasing blood flow to skeletal muscle [29].

However, extreme abnormalities of NE concentration levels lead to several diseases such as nueroblastoma, ganglioneuroblastoma, ganglioneuroma, paraganglioma, diabetes mellitus ketoacidosis and Parkinson's diseases [30]. The selective detection of NE from its major interferents AC, is a problem of critical importance not only in the fields of biomedical chemistry and neurochemistry but also in diagnostic and pathological researches.

Therefore, it is very important to develop sensitive, selective and reliable methods for the direct determination of trace NE. Various methods have been employed for the determination of NE including high performance liquid chromatography [31], electrochemical [32], gas chromatography [33], ion chromatography [34] and spectrophotometry [35]. Among the different methods, the determination of NE by electrochemical method has several advantages such as high sensitivity, selectivity, easy and less time consumption.

At unmodified electrodes, selective determination of NE in the presence of AC is not possible because the oxidation potentials of AC is very close to the oxidation potential of NE. To overcome these problems, various chemically modified electrodes have been used for the determination of NE [36-40].

AC is a widely used anti-pyretic and analgesic drug with actions similar to aspirin. It is an effective and safe agent for the relief of mild to moderate pain associated with headache, arthritis and postoperative pain. Its ready access has resulted in its increased use in attempted suicide [41].

Hence, it is very important to establish a rapid, sensitive and reliable method for the determination of AC. Current methods for the analysis of AC include spectrophotometric [42], chromatographic [43], mass spectrometry [44] and electrochemical approaches [45–49].

AC administration is known to increase brain serotonin (5-HT) levels as a result of liver tryptophan-2,3-dioxygenase (TDO) inhibition [50] and 5-HT is known to play a role in NE release in the brain [51,52]. Therefore, simultaneous determination of NE and AC is very important. Thus, in the present work, we describe the preparation of a new electrode composed of CNPE modified with

ferrocene dicarboxylic acid (FCDCNPE) and investigate its performance for the electrocatalytic determination of NE in aqueous solutions. We also evaluate the analytical performance of the modified electrode for quantification of NE in the presence of AC.

2. EXPERIMENTAL

2.1. Apparatus and chemicals

The electrochemical measurements were performed with an Autolab potentiostat/galvanostat (PGSTAT-302 N, Eco Chemie, The Netherlands), and Metrohm 797 VA Computrace Model. A conventional three electrode cell was used at 25 ± 1 °C. An Ag/AgCl/KCl (3.0 M) electrode, a platinum wire, and the FCDCNPE were used as the reference, auxiliary and working electrodes, respectively. A Metrohm 691 pH/Ion Meter was used for pH measurements.

All solutions were freshly prepared with double distilled water. NE, AC, FCD and all other reagents were of analytical grade from Merck (Darmstadt, Germany). Graphite powder and paraffin oil (DC 350, density = 0.88 g cm^{-3}) as the binding agent (both from Merck) were used for preparing the pastes. Multiwalled carbon nanotubes (purity more than 95%) with o.d. between 10 and 20 nm, i.d. between 5 and 10 nm, and tube length from 10 to 30 μm were prepared from Nanostructured & Amorphous Materials, Inc. The buffer solutions were prepared from orthophosphoric acid and its salts in the pH range of 2.0-11.0.

2.2. Preparation of the electrode

The FCDCNPEs were prepared by hand mixing 0.01 g of FCD with 0.89 g graphite powder and 0.1 g CNTs with a mortar and pestle. Then, ~ 0.7 mL of paraffin was added to the above mixture and mixed for 20 min until a uniformly-wetted paste was obtained. The paste was then packed into the end of a glass tube (ca. 3.4 mm i.d. and 10 cm long). A copper wire inserted into the carbon paste provided the electrical contact. When necessary, a new surface was obtained by pushing an excess of the paste out of the tube and polishing with a weighing paper.

2.3. Procedure of real Samples Preparation

The NE injection and AC oral solutions were diluted 1000 times with water; then, different volume of the diluted solution was transferred into a 10 mL volumetric flask and diluted to the mark with phosphate buffer (pH 5.0).

3. RESULTS AND DISCUSSION

3.1. Electrochemical Behavior of FCDCNPE

We have previously shown that a carbon paste electrode spiked with FCD can be constructed by the incorporation of FCDCNPE in a graphite powder-paraffin oil matrix [4]. The experimental

results show well-defined and reproducible anodic and cathodic peaks related to ferrocene dicarboxylic acid / ferricenium dicarboxylic acid (Fc/Fc^+) redox system, which show a quasireversible behavior in an aqueous medium [4]. The electrode capability for the generation of a reproducible surface was examined by cyclic voltammetric data obtained in optimum solution pH 7.0 from five separately prepared FCDCNPE. The calculated RSD for various parameters accepted as the criteria for a satisfactory surface reproducibility (about 1 – 4%), which is virtually the same as that expected for the renewal or ordinary carbon paste surface [4]. However we regenerated the surface of FCDCNPE before each experiment according to our previous results [4].

3.2. Electrocatalytic oxidation of NE at a FCDCNPE

The utility of the modified electrode for oxidation of NE was evaluated by cyclic voltammetry. The cyclic voltammetric responses of a bare carbon-paste electrode in 0.1M phosphate buffer (pH 5.0), without and with NE, are shown in Fig. 1 (curves c and d, respectively).

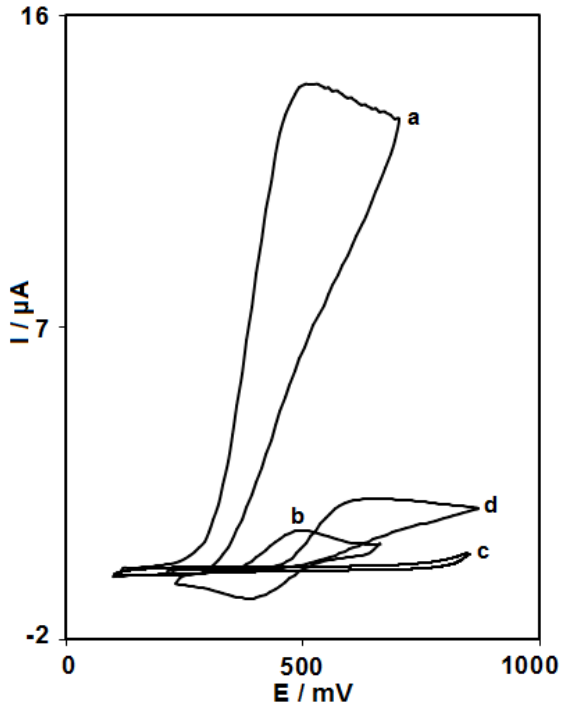

Figure 1. Cyclic voltammograms of FCDCNPE at 10 mV s^{-1} in 0.1M phosphate buffer (pH 5.0): (a) In the presence and (b) in the absence of 200.0 µM NE; (c) and (d) for an unmodified carbonpaste electrode in the absence and presence of 200.0 µM NE, respectively.

Figures 1a and b show cyclic voltammograms of modified electrode in the buffer solution with 200.0 µM of NE and without NE, respectively. The results show that the sensor produces a large anodic peak current in the presence of NE without a cathodic counterpart (Fig. 1, curve a). That the current observed is associated with NE oxidation and not the oxidation of modifier is demonstrated by

comparing the current in Fig. 1 (curve b, without NE) with the one in the presence of NE in Fig. 1 (curve a).

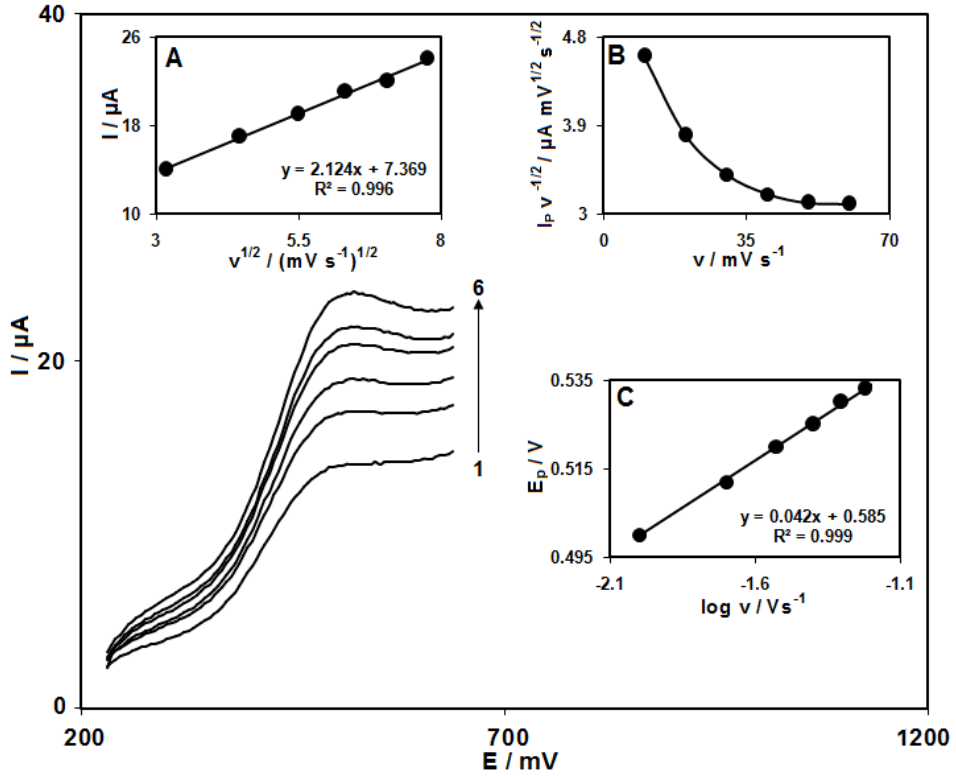

Figure 2. Linear sweep voltammograms of FCDCNPE in 0.1 M phosphate buffer solution (pH 5.0) containing 200.0 µM NE at various scan rates; From inner to outer scan rates of 10, 20, 30, 40, 50 and 60 mV s^{-1}, respectively. Insets: Variation of (A) anodic peak current vs. $\nu^{1/2}$; (B) normalized current ($I_p/\nu^{1/2}$) vs. ν; (C) anodic peak potential vs. log ν.

It is apparent that the anodic current associated with the surface-attached materials is significantly less than that obtained in the solution containing NE. At the surface of a bare electrode, NE was oxidized around 600 mV. As can be seen, the electroactivity of NE on the modified electrode was significant (Figs. 1 curve a), with strongly defined peak potential, around 500 mV *vs.* Ag/AgCl/KCl (3.0 M) electrode. Thus, a decrease in overpotential and enhancement of peak current for NE oxidation are achieved with the modified electrode. Such a behavior is indicative of an EC´ mechanism [53].

The effect of scan rate on the electrocatalytic oxidation of NE at the FCDCNPE was investigated by linear sweep voltammetry (Fig. 2). As can be observed in Fig. 2, the oxidation peak potential shifted to more positive potentials with increasing scan rate, confirming the kinetic limitation in the electrochemical reaction. Also, a plot of peak height (I_p) vs. the square root of scan rate ($\nu^{1/2}$) was found to be linear in the range of 10–60 mV s^{-1}, suggesting that, at sufficient overpotential, the process is diffusion rather than surface controlled. A plot of the scan rate-normalized current ($I_p/\nu^{1/2}$) vs. scan rate (Fig. 2B) exhibits the characteristic shape typical of an EC´process [53].

The Tafel slope (b) can be obtained from the slope of E_p *vs.* log v using Eq. (1) [54]:

$$Ep = b/2 \log v + constant \qquad (1)$$

The Tafel slope was found to be 85.6 mV (Fig. 2, inset C), which indicates that a one-electron transfer process is the rate limiting step assuming a transfer coefficient (α) is about 0.31.

3.3. Chronoamperometric measurements

Chronoamperometric measurements of NE at FCDCNPE were carried out by setting the working electrode potential at 0.6 V *vs.* Ag/AgCl/KCl (3.0 M) for the various concentration of NE in buffered aqueous solutions (pH 5.0) (Fig.3).

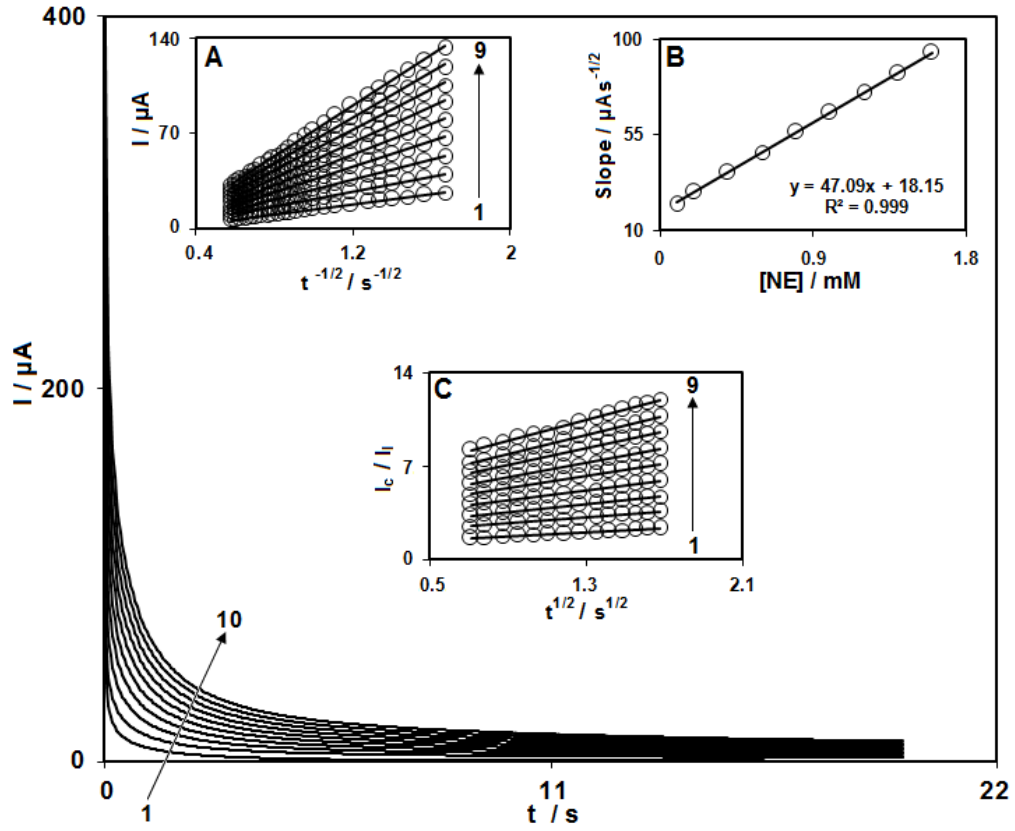

Figure 3. (A) Chronoamperograms obtained at FCDCNPE in 0.1 M phosphate buffer solution (pH 5.0) for different concentration of NE. The numbers 1–10 correspond to 0.0, 0.1, 0.2, 0.4, 0.6, 0.8, 1.0, 1.2, 1.4 and 1.6 mM of NE. Insets: (A) Plots of I vs. $t^{-1/2}$ obtained from chronoamperograms 2–10. (B) Plot of the slope of the straight lines against NE concentration; (C) dependence of I_{cat}/I_l on $t^{1/2}$ derived from the data of chronoamperograms 1-10.

For an electroactive material (NE in this case) with a diffusion coefficient of D, the current observed for the electrochemical reaction at the mass transport limited condition is described by the

Cottrell equation [54]. Experimental plots of I vs. $t^{-1/2}$ were employed, with the best fits for different concentrations of NE (Fig. 3A). The slopes of the resulting straight lines were then plotted vs. NE concentration (Fig. 4B). From the resulting slope and Cottrell equation the mean value of the D was found to be 2.3×10^{-5} cm^2/s.

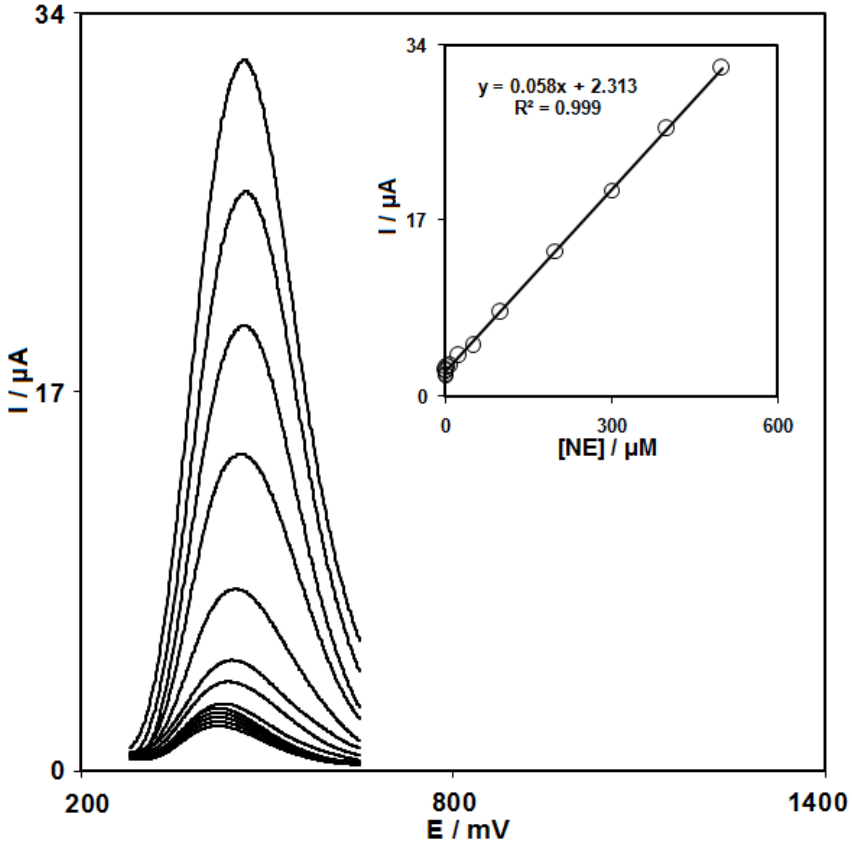

Figure 4. Differential pulse voltammograms of FCDCNPE in 0.1 M phosphate buffer solution (pH 5.0) containing different concentrations of NE. From inner to outer correspond to 0.03, 0.1, 0.5, 1.0, 5.0, 10.0, 25.0, 50.0, 100.0, 200.0, 300.0, 400.0 and 500.0 µM of NE. Inset show the plots of the electrocatalytic peak current as a function of NE concentration in the range of 0.03 to 500.0 µM.

Chronoamperometry can also be employed to evaluate the catalytic rate constant, k, for the reaction between NE and the FCDCNPE according to the method of Galus [55]:

$$I_C / I_L = \gamma^{1/2}[\pi^{1/2} \text{erf}(\gamma^{1/2}) + \exp(-\gamma) / \gamma^{1/2}] \qquad (2)$$

where I_C is the catalytic current of NE at the FCDCNPE, I_L is the limited current in the absence of NE and $\gamma = kC_bt$ is the argument of the error function (C_b is the bulk concentration of NE). In cases where γ exceeds the value of 2, the error function is almost equal to 1 and therefore, the above equation can be reduced to:

$$I_C / I_L = \pi^{1/2} \gamma^{1/2} = \pi^{1/2} (kC_b t)^{1/2} \quad (3)$$

where t is the time elapsed. The above equation can be used to calculate the rate constant, k, of the catalytic process from the slope of I_C/I_L vs. $t^{1/2}$ at a given NE concentration. From the values of the slopes, the average value of k was found to be 2.99×10^{3} M^{-1} s^{-1}.

3.4. Calibration plot and limit of detection

The electrocatalytic peak current of NE oxidation at the surface of the modified electrode can be used for determination of NE in solution. Therefore, DPV experiments were performed using modified electrode in phosphate buffer solution containing various concentration of NE. The results show the electrocatalytic peak current of NE oxidation at the surface of modified electrode was linearly dependent on the NE concentrations. The mediated oxidation peak currents of NE at the surface of a modified electrode were proportional to the concentration of the NE within the ranges 0.03-500.0 μM in the DPV. The detection limits (3σ) was 22.0 nM.

3.5. Simultaneous determination of NE and AC

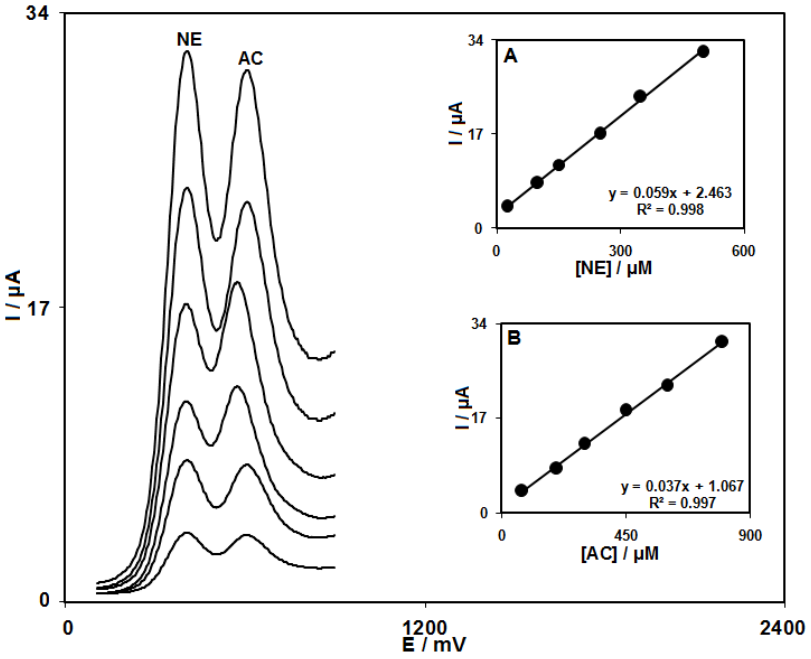

Figure 5. DPVs of FCDCNPEin 0.1 M phosphate buffer solution (pH 5.0) containing different concentrations of NE+AC in μM, from inner to outer: 25.0+75.0, 100.0+200.0, 150.0+300.0, 250.0+450.0, 350.0+600.0 and 500.0+800.0 respectively. Insets (A) and (B) are plots of I_p vs. NE and AC concentrations, respectively.

One of the main objects of this study was to detect NE and AC simultaneously using FCDCNPE. This was performed by simultaneously changing the concentrations of NE and AC, and

recording the DPVs. The voltammetric results showed well-defined anodic peaks at potentials of 415 and 625 mV, corresponding to the oxidation of NE and AC, respectively, indicating that simultaneous determination of these compounds is feasible at the FCDCNPE as shown in Fig. 5.

The sensitivity of the modified electrode towards the oxidation of NE was found to be 0.059 µA/ µM. This is very close to the value obtained in the absence of AC (0.058 µA/ µM, see Section 3.4), indicating that the oxidation processes of these compounds at the FCDCNPE are independent and therefore, simultaneous determination of their mixtures is possible without significant interferences.

3.6. Real sample analysis

3.6.1 Determination of NE and AC in pharmaceutical preparations

In order to evaluate the analytical applicability of the proposed method, also it was applied to the determination of NE and AC in NE ampoule and AC oral solution respectively. Based on the repeated differential pulse voltammetric responses (n=5) of the diluted analytes and the samples that were spiked with specified concentration of NE and AC, measurements were made for determination of NE and AC concentrations in the pharmaceutical preparations. The results are listed in table1.

Table 1. The application of FCDCNPE for simultaneous determination of NE and AC. All concentrations are in µM (n=5).

Sample	Original content		Added		Found		Recovery (%)		RSD (%)	
	NE	AC	NE	AC	NE	AC	NE	AC	NE	AC
NE ampoule										
	5.0	-	-	25.0	4.9	25.4	98.0	101.6	3.1	1.7
	5.0	-	5.0	30.0	10.1	29.3	101.0	97.7	2.4	2.7
	5.0	-	10.0	35.0	15.5	34.8	103.3	99.4	1.9	3.4
Oral solution of AC										
	-	30.0	10.0	-	9.8	31.1	98.0	103.7	1.4	2.3
	-	30.0	20.0	10.0	20.2	39.1	101.0	97.7	2.6	3.2
	-	30.0	30.0	20.0	29.1	50.3	97.0	100.6	3.3	1.5

Table 2. Comparison of the total values of NE and AC of some pharmaceutical preparations obtained using FCDCNPE with declared values in the lable of the samples (n=5).

Samples	Declared value	Found value	RSD%
NE ampoule (mg mL^{-1})	1.0	1.1	2.5
Oral solution of AC (mg mL^{-1})	24.0	26.16	2.3

The reliability of the proposed modified electrode was also evaluated by comparing the obtained results with those declared in the label of the pharmaceutical preparations (Table 2). The results in table 1 show the relative standard derivations (RSD%) and the recovery rates of the spiked samples are acceptable. Also, the data in table 2 indicate that the results obtained by utilizing FCDCNPE are in good agreement with those declared in the label of the preparations. Thus, the modified electrode can be efficiently used for individual or simultaneous determination of NE and AC in pharmaceutical preparations.

4. CONCLUSIONS

In the present study, a ferrocene dicarboxylic acid modified carbon nanotube paste electrode was used for the determination of NE in the presence of AC. The CV and DPV investigations showed effective electrocatalytic activity of the modified electrode in lowering the anodic over potential for the oxidation of NE and complete resolution of its anodic wave from AC. The detected potential differences of 210 mV between NE–AC, is large enough to allow simultaneous determination of NE and AC in mixtures without significant interferences.

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