

## Simultaneous Voltammetric Determination of Norepinephrine, Uric Acid and Folic Acid at the Surface of Modified Chloranil Carbon Nanotube Paste Electrode

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The electrochemical behavior of norepinephrine (NE) is investigated on the surface of a carbon-paste electrode modified with chloranile (CA) and carbon nanotubes. The prepared modified electrode showed an efficient catalytic role in the electrochemical oxidation of NE, leading to remarkable decrease in oxidation overpotential and enhancement of the kinetics of the electrode reaction. Differential pulse voltammetric peak currents of NE increased linearly with its concentrations at the range of 0.03  $\mu\text{M}$  to 500  $\mu\text{M}$  and the detection limit ( $3\sigma$ ) was determined to be 11.2 nM. This modified electrode exhibits well-separated oxidation peaks for NE, uric acid (UA) and folic acid (FA). The modified electrode is successfully applied for the accurate determination of NE, UA and FA in some real samples.

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**Keywords:** Norepinephrine, Uric acid, Folic acid, Carbon nanotube; Carbon paste electrode

### 1. INTRODUCTION

NE is one of the derivatives of catecholamines secreted in the adrenal medulla and plays important physiological roles in the central nervous system. It affects muscle and tissue control, stimulates arteriole contraction, decreases peripheral circulation and activates lipolysis in adipose tissue [1]. It is also critical in mental disease, heart failure, DNA breaks in cardiac myoblast cells, and diabetes. Recent reports have indicated that NE enhances adhesion of human immunodeficiency virus-1 (HIV-1)-infected leukocytes to cardiac microvascular endothelial cells and also accelerates HIV replication via proteinkinase [2]. Hence, it is very necessary to develop sensitive, selective and reliable methods for the direct determination of trace NE due to its physiological function and the diagnosis of

some diseases in clinical medicine. Various methods including spectrophotometry, capillary electrophoresis and high-performance liquid chromatography (HPLC) have been employed to the determination of NE. Because NE is an electroactive compound, its electrochemical detection has been the focus of research for electroanalytical researchers and neurochemists and some modified electrodes have been used to determine NE [3,4].

Uric acid (UA), the end metabolic product of purine through the liver, is present in blood and urine. Monitoring UA in the blood or urine is important because it can be used as a powerful indicator for an early warning sign of kidney diseases. Abnormal UA level in a human body could be caused by several diseases such as gout, hyperuricemia, Lesch-Nyan syndrome, cardiovascular and chronic renal disease [5]. Furthermore, other diseases such as leukemia and pneumonia are also related with the urate levels. Various electrochemical methods have been employed to monitor the level of UA [6-8]. The advantages of electrochemical technique for determining UA is its high sensitivity, low cost and less time consumption.

Similarly, folic acid (FA) is an important component of the haematopoietic system and is the coenzyme that controls the generation of ferrohaeme. Lack of FA gives rise to the gigantocytic anemia, associated with leucopenia, devolution of mentality and psychosis etc. Numerous methods for the measurement of FA are available, including enzyme-linked immunosorbent assays (ELISAs), liquid chromatography/tandem mass spectrometry (LC/MS/MS), capillary electrophoresis (CE), microemulsion electrokinetic chromatography (MEEKC) and high-performance liquid chromatography (HPLC). As FA is an electroactive component, some electrochemical methods have been reported for its determination [9, 10]. Comparing with other technologies, electrochemical method is more desirable because of its convenience and low cost.

So, the determination of NE, UA and FA is an important topic in clinic medicine. NE is an electroactive compound and its electrochemical behavior has been studied extensively. Unfortunately, its oxidation potential overlaps with that of UA and FA which coexists with NE in biological fluids. This led to the difficulty in the direct electrochemical determination of NE. Moreover, the oxidation potentials of UA and FA also are usually too close to be separated at the bare electrode. Therefore, some chemically modified electrodes have been developed to eliminate the interference of UA or FA to NE determination or separate the electrochemical response of NE-UA or NE-FA [11,12]. But to the best of our knowledge, no study has hithered been reported for the simultaneous determination of NE, UA and FA using modified carbon nanotube paste electrodes.

Electrochemical sensors based on carbon nanotubes (CNTs) represent a new and interesting alternative for quantification of different analytes. CNTs have attracted enormous interest because of their unique structural, mechanical and electronic properties. Some of these properties include high chemical and thermal stability, high elasticity, high tensile strength, and in some instances, metallic conductivity. Many studies have demonstrated that the list of unique features of carbon nanotubes could be extended to include the electrocatalytic properties of carbon nanotube modified electrodes [13-23].

The chemical modification of electrodes using electron transfer mediators is an interesting field in analytical chemistry. One of the most important effects of any mediator is a reduction of the overpotential required for electrochemical reaction, which enhances the sensitivity (current) and

selectivity of the method. Electrochemical detection using mercury-based electrodes, for example, has been used for the determination of thiols and disulfides in complex matrices, including biological fluids [24]. Carbon-based electrodes are among the most commonly used electrodes in voltammetric techniques because of their low cost, wide potential windows, low electrical resistances and versatility of chemical modification.

Many types of carbon-based electrodes, such as glassy carbon [25-27], carbon composites [28] and carbon pastes [29-40], are used as modified electrodes. In the present work, we described initially the preparation and suitability of a chloranil modified carbon nanotube paste electrode (CAMCNPE) as a new electrode in the electrocatalysis and determination of NE in an aqueous buffer solution, then we evaluated the analytical performance of the modified electrode in quantification of NE in the presence of UA and FA.

Finally, in order to demonstrate the catalytic ability of the modified electrode in the electrooxidation of NE, UA and FA in real samples, we examined this method for the voltammetric determination of NE, UA and FA in NE ampoule and urine samples.

## 2. EXPERIMENTAL

### 2.1. Apparatus and chemicals

All the cyclic voltammetric measurements were performed using a BHP 2063<sup>+</sup> Electrochemical Analysis System, Behpajoo, Iran potentiostat/galvanostat coupled with a Pentium IV personal computer connected to a HP laser jet 6L printer. An Ag / AgCl / KCl 3 M, a platinum wire, and a CAMCNPE were used as reference, auxiliary and working electrodes, respectively.

A digital pH/mV meter (Metrohm model 710) was applied for pH measurements. Graphite powder, paraffin oil and reagents were analytical grade from Merck. NE, UA, FA and carbon nanotubes were purchased from Merck. The buffer solutions were prepared from ortho phosphoric acid and its salts in the pH range 2.0-12.0.

### 2.2. Preparation of the electrode

Modified carbon nanotube paste electrodes were prepared by dissolve 0.01 g of CA in diethyl ether and hand mixing with 89-times its weight of graphite powder and 10-times its weight of carbon nanotube with a mortar and pestle. The solvent was evaporated by stirring.

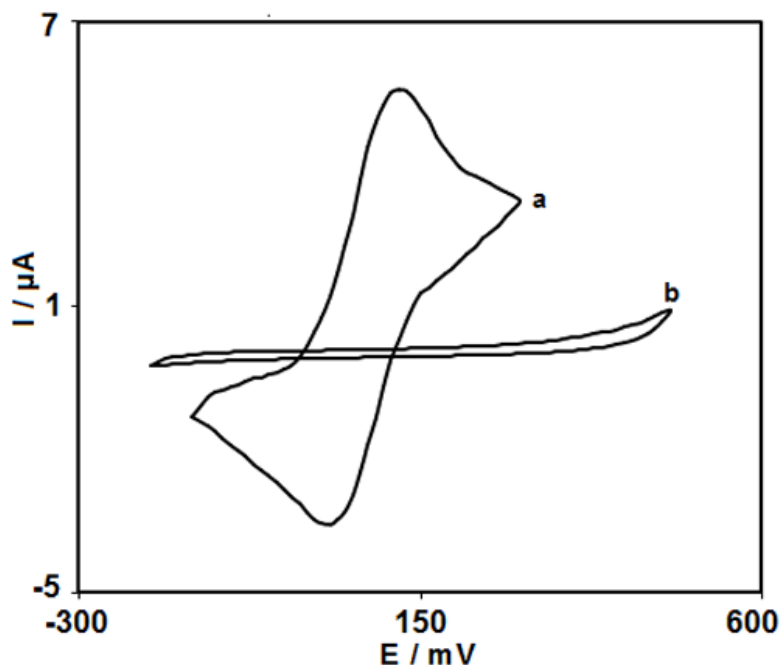
A 70:30 (w/w) mixture of CA spiked carbon nanotube powder and paraffin oil was blended by hand mixing for 20 min until a uniformly-wetted paste was obtained.

The paste was then packed into the end of a glass tube (*ca.* 3.4 mm *i.d.* and 10 cm long). Electrical contact was made by inserting a copper wire into the glass tube at the back of the mixture. Unmodified carbon paste, prepared in the same way without adding CA and carbon nanotube to the mixture and was used for comparison purposes.

### 3. RESULTS AND DISCUSSION

#### 3.1. Cyclic voltammetric investigations

Cyclic voltammetry was employed for investigation the electrochemical properties of CAMCNPE in a pure buffered aqueous solution (pH 7.0). The cyclic voltammogram exhibits an anodic and corresponding cathodic peaks with  $E_{pa}=120$  mV and  $E_{pc}=20$  mV vs. Ag / AgCl / KCl 3 M (Fig. 1).



**Figure 1.** The cyclic voltammograms of a) CAMCNPE and b) bare CPE in 0.1 M phosphate buffer solution (pH 7.0) at a scan rate  $100 \text{ mV s}^{-1}$ .

The electrode capability for the generation of a reproducible surface was examined by cyclic voltammetric data obtained in optimum solution pH from five separately prepared CAMCNPEs. The calculated RSDs for various parameters such as  $E_{pa}$ ,  $E_{pc}$ ,  $I_{pa}$  and  $I_{pc}$  accepted as the criteria for a satisfactory surface reproducibility (1 – 4%). This degree of reproducibility is virtually the same as that expected for the renewal or ordinary carbon paste surface.

#### 3.2. Electrocatalytic oxidation of NE at the surface of CAMCNPE

Fig. 2 depicts the cyclic voltammetric responses from the electrochemical oxidation of  $150 \mu\text{M}$  NE at CAMCNPE (curve f), CA modified CPE (CAMCPE) (curve e), CNPE (curve d) and bare CPE (curve a). As can be seen, the anodic peak potentials for the oxidation of NE at CAMCNPE (curve f) and CAMCPE (curve e) are about 120 mV, while at the CNPE (curve d) peak potential is about 370 mV, and at the bare CPE (curve b) peak potential is about 460 mV for NE. From these results it is

concluded that the best electrocatalytic effect for NE oxidation is observed at CAMCNPE (curve f). For example, the results are shown that the peak potential of NE oxidation at CAMCNPE (curve f) shifted by about 250 and 340 mV toward the negative values compared with that at a CNPE (curve d) and bare CPE (curve b), respectively. Similarly, when we compared the oxidation of NE at the CAMCPE (curve e) and CAMCNPE (curve f); there is a dramatic enhancement of the anodic peak current at CAMCNPE relative to the value obtained at the CAMCNPE. In the other words, the data obtained clearly show that the combination of carbon nanotube and mediator (CA) definitely improve the characteristics of NE oxidation. The CAMCNPE in 0.1M phosphate buffer (pH 7.0), without NE in solution, exhibits a well-behaved redox reaction (curve c) upon the addition of 150  $\mu\text{M}$  NE, the anodic peak current of mediator was greatly increased, while the corresponding cathodic peak was disappear on the reverse scan of the potential (curve f). This behavior is typical of that expected for electrocatalysis at chemically modified electrodes [41].

The effect of scan rate on the electrocatalytic oxidation of 150  $\mu\text{M}$  NE at the CAMCNPE was investigated by cyclic voltammetry (Not shown). The oxidation peak potential shifts with increasing scan rates towards a more positive potential, confirming the kinetic limitation of the electrochemical reaction. Also, a plot of peak height ( $I_p$ ) against square root of scan rate ( $v^{1/2}$ ), in range of 10-80  $\text{mVs}^{-1}$ , was constructed, which was found to be linear, suggesting that at sufficient overpotential the process is diffusion rather than surface controlled.

From the slope of  $E_p$  vs.  $\log v$ , the Tafel slope can also be obtained from the following equation [41]:

$$E_p = (b/2) \log v + \text{constant} \quad (1)$$

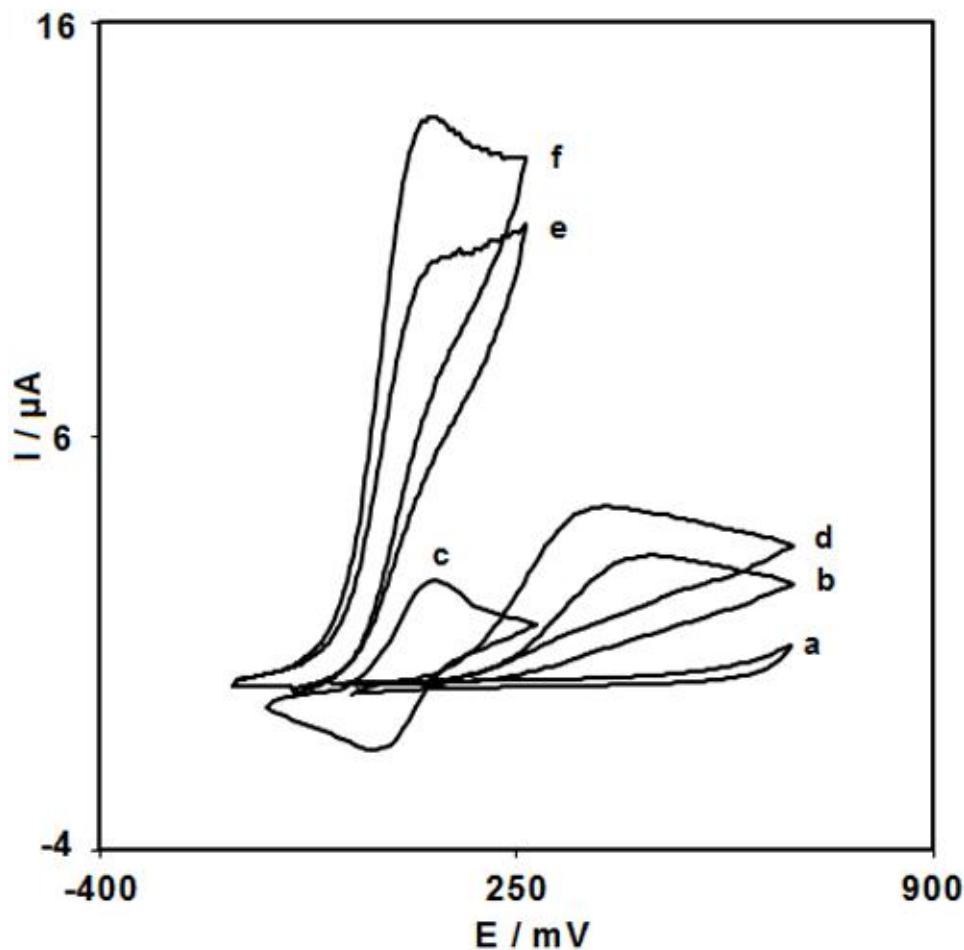
The slope of  $E_p$  vs.  $\log v$  plot is  $b/2$ , where  $b$  indicates the Tafel slope. The slope of  $E_p$  vs.  $\log v$  plot is  $\partial E_p / \partial (\log v)$  and was found to be 0.051 V in this work, so,  $b = 2 \times 0.051 = 0.102$  V. The value of Tafel slope indicates that a one-electron transfer process is the rate limiting step assuming a transfer coefficient of  $\alpha$  about 0.42.

### 3.3. Chronoamperometric studies

The catalytic oxidation of NE by a CAMCNPE was also studied by chronoamperometry. Chronoamperometric measurements of different concentrations of NE at CAMCNPE were done by setting the working electrode potential at 150 mV. In chronoamperometric studies, we have determined the diffusion coefficient,  $D$ , of NE. The experimental plots of  $I$  versus  $t^{-1/2}$  with the best fits for different concentrations of NE were employed (Fig. 3.A). The slopes of the resulting straight lines were then plotted versus the NE- concentrations (Fig. 3.B), from whose slope and using the Cottrell equation [41]:

$$I = nFAD^{1/2}C_b\pi^{-1/2}t^{-1/2} \quad (2)$$

we calculated a diffusion coefficient of  $2.82 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$  for NE .

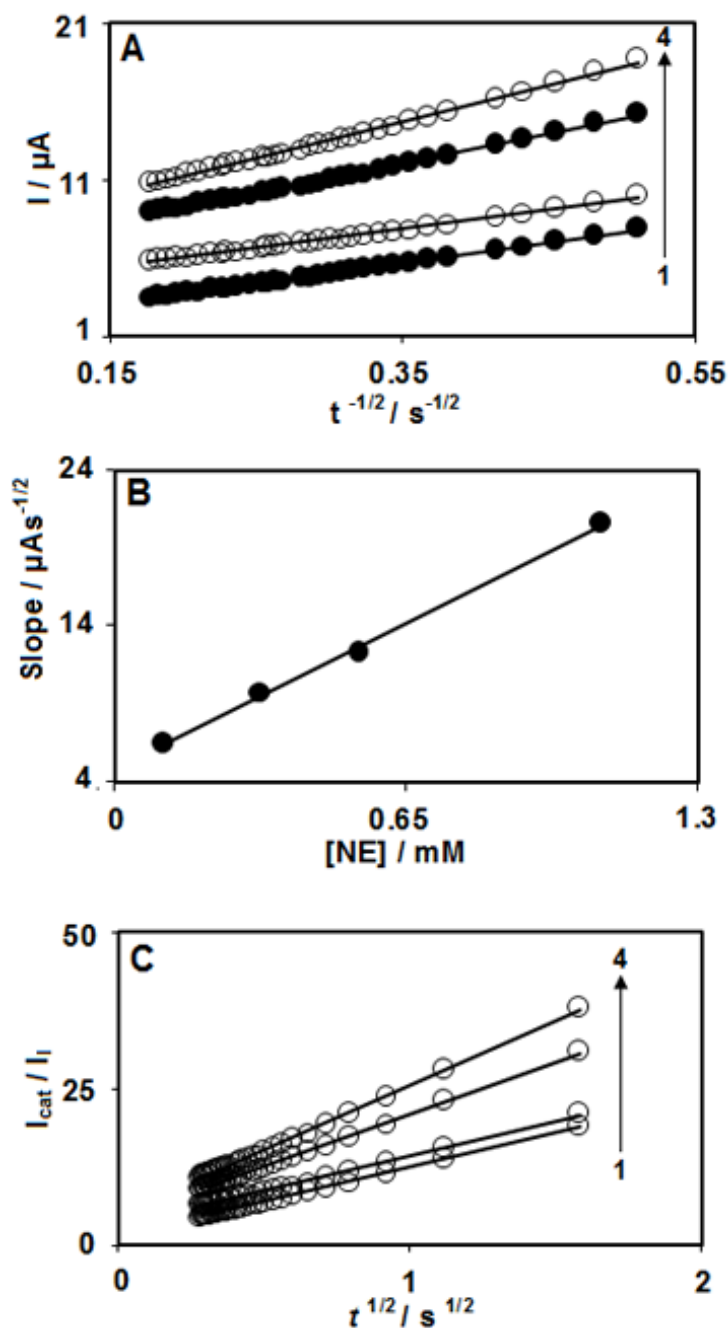


**Figure 2.** Cyclic voltammograms of (a) CPE in 0.1M PBS (pH 7.0) at scan rate  $20 \text{ mV s}^{-1}$  and (b) as (a) +  $150 \text{ μM}$  NE; (c) as (a) and (d) as (b) at the surface of CAMCNPE and CNPE respectively. Also, (e) and (f) as (b) at the surface of CAMCPE and CAMCNPE respectively.

The rate constant for the chemical reaction between NE and redox sites in CAMCNPE,  $k_h$ , can be evaluated by chronoamperometry according to the method of Galus [42]:

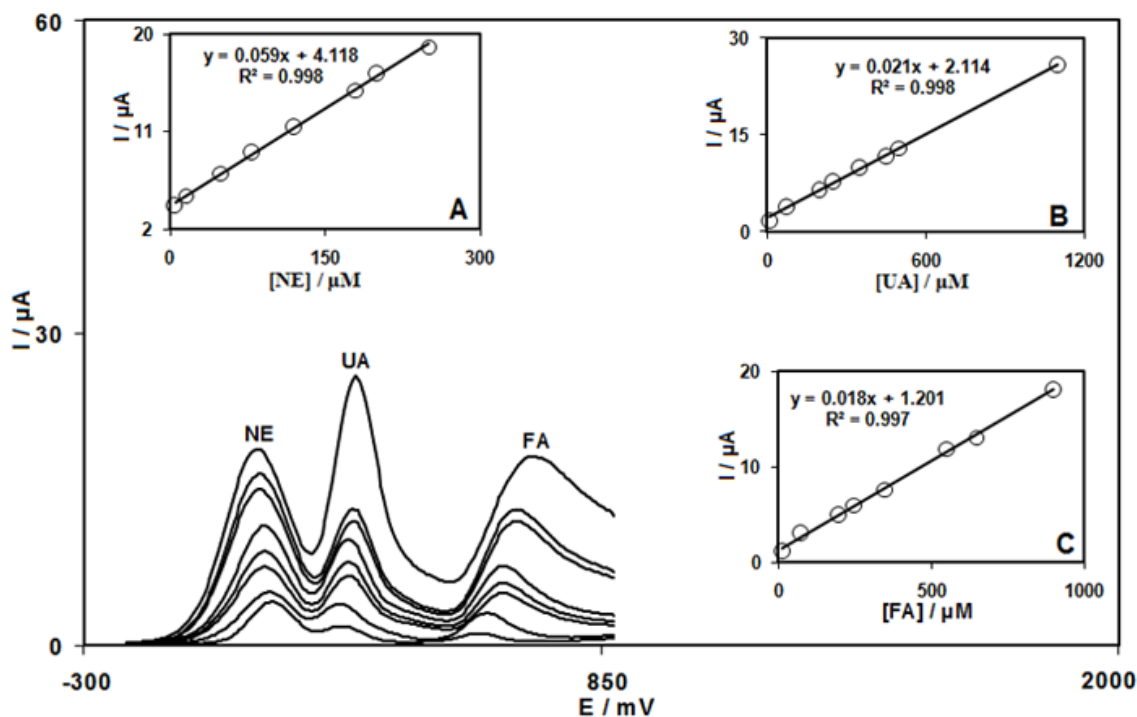
$$I_C / I_L = \pi^{1/2} \gamma^{1/2} = \pi^{1/2} (kC_b t)^{1/2} \quad (3)$$

where  $I_C$  is the catalytic current of NE at the CAMCNPE,  $I_L$  the limited current in the absence of NE and  $t$  is the time elapsed (s). The above equation can be used to calculate the rate constant of the



**Figure 3.** A. Plots of  $I$  vs.  $t^{-1/2}$  obtained at CAMCNPE in 0.1 M phosphate buffer solution (pH 7.0) for different concentration of NE by setting potential step at 150 mV. B. Plot of the slope of the straight lines against the NE concentration. (C) Dependence of  $I_{cat}/I_L$  on  $t^{1/2}$ .

process  $k_h$ . Based on the slope of the  $I_C / I_L$  versus  $t^{1/2}$  plots (Fig. 3.C),  $k_h$  can be obtained for a given NE concentration. From the values of the slopes an average value of  $k_h$  was found to be  $k_h = 4.96 \times 10^3 M^{-1} s^{-1}$ .



**Figure 4.** Differential pulse voltammograms of CAMCNPE in 0.1M PBS (pH 7.0) containing different concentrations of NE, UA and FA (from inner to outer) mixed solutions of 5+10+15, 15+75+75, 50+200+200, 80+250+250, 120+350+350, 180+450+550, 200+500+650 and 250+1100+900 respectively, in which the first value is concentration of NE in  $\mu\text{M}$  and the second value is concentration of UA in  $\mu\text{M}$  and the third value is FA in  $\mu\text{M}$ . Insets: (A) Plots of the peak currents as a function of NE (B) UA and (C) FA concentrations respectively.

### 3.4. Calibration plot and limit of detection

The electrocatalytic peak current of NE oxidation at the surface of CAMCNPE can be used for determination of NE in solution. Therefore, differential pulse voltammetry experiments were performed using CAMCNPE in a phosphate buffer solution containing various concentration of NE. The results show that the electrocatalytic peak current of NE oxidation at the surface of CAMCNPE was linearly dependent on NE concentration. The mediated oxidation peak currents of NE at the surface of a 1% CAMCNPE were proportional to the concentration of NE within the ranges of 0.03  $\mu\text{M}$  to 500  $\mu\text{M}$  (with the correlation coefficients of 0.998). The detection limits ( $3\sigma$ ) was 11.2 nM.

### 3.5. Simultaneous determination of NE, UA and FA at CAMCNPE

One of the main objectives of the present study was the development of a modified electrode capable of the electro-catalytic oxidation of NE and separation of the electrochemical responses of NE, UA and FA.



The utilization of the CAMCNPE for the simultaneous determination of NE, UA and FA was demonstrated by simultaneously changing the concentrations of NE, UA and FA. The DP voltammetric results show three-well-defined anodic peaks (Fig. 4). The sensitivity towards NE found to be  $0.074 \mu\text{A} \cdot \mu\text{M}^{-1}$  (absence of UA and FA) and  $0.075 \mu\text{A} \cdot \mu\text{M}^{-1}$  (presence of UA and FA). It is very interesting to note that the sensitivities of the modified electrode towards NE in the absence and presence of UA and FA, are virtually the same, which indicate the fact that the oxidation processes of NE, UA and FA, at the CAMCNPE are independent and therefore simultaneous or independent measurements of the three analytes are possible without any interference. If the NE signal was affected by the UA and FA, the above-mentioned slopes would be different.

### 3.6. Determination of NE, UA and FA in real samples

In order to assess the applicability of the proposed electrode, an attempt was made to determine NE in NE injection using the standard addition method. The average determination results of NE in the injection were  $0.94 \text{ mg mL}^{-1}$ , which were quite corresponding to the value that was given by injection specification ( $1.0 \text{ mg mL}^{-1}$ ). Also, to a series of 10 mL measuring flasks, different capacity diluted NE injection solution, standard UA and FA solutions were added and diluted to the mark with phosphate buffer. The DPVs were recorded and the anodic peak currents were measured at their own oxidation potentials for NE, UA and FA. Also, the recovery results are shown in Table 1. Simultaneous determination of drugs in the urine sample was also performed. Therefore different amounts of NE, UA and FA were spiked to the sample and analyzed by the proposed method (Table 2).

**Table 1.** The application of CAMCNPE for simultaneous determination of NE, UA and FA in NE ampoule.

No	NE	UA	FA	NE			UA			FA		
	injection <sup>a</sup> ( $\mu\text{M}$ )	Added ( $\mu\text{M}$ )	Added ( $\mu\text{M}$ )	Found ( $\mu\text{M}$ )	Recovery (%)	RSD (%)	Found ( $\mu\text{M}$ )	Recovery (%)	RSD (%)	Found ( $\mu\text{M}$ )	Recovery (%)	RSD (%)
1	2.5	0	0	2.53	101.2	1.8	----	----	----	----	----	----
2	5	10	20	4.91	98.2	2.8	10.24	102.4	3.1	20.56	102.8	1.4
3	7.5	20	30	7.31	97.5	2.3	20.22	101.1	1.3	29.2	97.3	4.1
4	10	30	40	10.31	103.1	3.4	29.66	98.87	2.4	39.23	98.1	2.5

**Table 2.** The application of CAMCNPE for simultaneous determination of NE, UA and FA in urine samples.

Sample	Spiked ( $\mu\text{M}$ )			Found ( $\mu\text{M}$ )			Recovery (%)			R.S.D. (%)		
	NE	UA	FA	NE	UA	FA	NE	UA	FA	NE	UA	FA
Urine	0	0	0	-	-	-	-	-	-	-	-	-
	5	15	25	5.12	14.89	25.93	102.4	99.26	103.72	3.4	2.1	1.6
	10	25	35	9.72	25.38	34.12	97.2	101.52	97.48	1.3	1.4	2.3
	15	35	45	15.16	36.12	44.41	101.1	103.2	98.69	2.8	2.5	3.7

#### 4. CONCLUSION

This work demonstrates the construction of a carbon nanotube paste electrode chemically modified by incorporation of CA. The carbon nanotube paste electrode modified with CA was quite stable. This electrode is simple to prepare, and surface renewal is easy. The electrochemical behavior of CA has been studied by cyclic voltammetry and chronoamperometry in both the absence and presence of NE. The results show that the oxidation of NE is catalyzed at pH 7.0, where the peak potential of NE is shifted by  $-340$  mV at the surface of the CAMCNPE. The CAMCNPE exhibits highly electrocatalytic activity for oxidation of NE, UA and FA. The modified electrode displays improved selectivity for voltammetric measurement of NE, UA and FA in solutions containing three analytes.

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