

Full Paper

Simultaneous Determination of Ascorbic Acid, Paracetamol and Phenylephrine: Carbon Nanotubes Ceramic Electrode as a Renewable Electrode

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Abstract- In this paper, we fabricated a renewable and mechanical rigid electrode that we named it carbon nanotubes ceramic electrode (CNTsCE). The physicochemical properties of the obtained electrode were characterized by scanning electron microscopy and electrochemical methods. Comparing with carbon powder ceramic electrode (CPCE), the CNTsCE exhibited excellent electrochemical catalytic activities for the oxidation of ascorbic acid (AA), paracetamol (PA) and phenylephrine (PP) and three well shaped and separated anodic peaks were observed. Differential pulse voltammetry (DPV) technique was employed for the simultaneous determination of AA, PA and PP and the obtained results confirmed that the oxidation peak currents increased linearly with AA, PA and PP concentrations in the ranges of 5.0-350.0, 0.1-3.5 and 1.0-70.0 μM with detection limit of 2.0, 0.04 and 0.3 μM for AA, PA and PP, respectively. Finally, the CNTsCE was successfully used for the determination of AA, PA and PP in biological and pharmaceutical samples.

Keywords- Carbon nanotubes ceramic electrode, Simultaneous determination, Electrooxidation, Ascorbic acid, Paracetamol, Phenylephrine

1. INTRODUCTION

Ascorbic acid (AA) or vitamin C is a very important factor in human diet. The role of AA is very important in some of the significant biological reactions such as improving immunity,

free radical scavenging and cancer preventing. Paracetamol (PA) or acetaminophen is categorized as a mild analgesic and antipyretic drug. It is usually used for the sedation of headaches and other slight pains and it is a major element in various cold and flu therapies. Phenylephrine (PP) is an α -1-adrenergic receptor agonist utilized chiefly as a decongestant and as an agent to expand the pupil and to increase blood pressure. It exists in the formulations of some vasopressor medicines, in nasal decongestants, in eye-washes, and in syrups.

AA, PA and PP are frequently used as the components of antirheumatic, anti-inflammatory and antipyretic drugs with different brands such as Beechams Cold and Flu. These medicines help relieve symptoms such as aches and pains, headache, fever, sore throat, nasal catarrh, blocked nose and sinuses associated with the common cold and flu. On the other hand, the preparations containing these components offer the advantage of parallel activity of all three components and are in great demand. However, because of similar physical and chemical properties of these three components, determination of their exact content is difficult. Several methods such as high-performance liquid chromatography [1-3], liquid chromatography-tandem mass spectrometry [4], capillary electrophoreses [5], spectroscopy [6-8] and enzymatic [9] methods have been developed for quantifying some of these compounds alone or in different combinations. However, very few literature reports are available for the simultaneous determination of AA, PA and PP. De Fabrizio [10] reported the simultaneous determination of AA, PA and PP in a capsule preparation via a column chromatographic procedure. El-Shanawany et al. [11] studied the use of LC method for quantitative determination of AA, PA, PP and caffeine mixture. Muszalska et al. [12] reported the HPLC technique for simultaneous determination of PA, caffeine, AA and PP in pharmaceutical formulations; and recently Koblová et al. [13] have developed a rapid HPLC method for the determination of AA, PA, PP and caffeine using a monolithic column.

Because of their simplicity and selectivity, electrochemical procedures, particularly voltammetric techniques, have been extensively applied for individual determination [14-21] of AA, PA and PP due to their electrochemical activity. However, one of the major problems in the voltammetric simultaneous determination of AA, PA and PP is high signal overlapping between their voltammograms. Hence, it is important to develop a simple and reliable electroanalytical method for simultaneous determination of these compounds via modified electrodes with good electron transfers for electrocatalysis and separation of electrochemical signals of these compounds. To the best of our knowledge, there is not any report about the simultaneous electrochemical determination of AA, PA and PP in the literature.

In the last two decades, carbon nanotubes (CNTs) have received much attention because of their unique structure and properties. They have extraordinary properties such as large specific surface areas, distinctive ability to promote electron transfer, high stability and strong adsorption properties [22], so they have driven an unusual research effort in electrochemical

sensors and biosensors. Various approaches have been reported for the fabrication of CNTs modified electrodes. Surface modification of bare electrodes with CNTs via coating approach is the most frequently used methods [23-28]. The carbon nanotubes (CNTs) modified electrodes were prepared by surface coating always suffer from: Mechanical instability or electrode fouling during in electrocatalytic applications, especially in complex matrix analysis, limitations including non-reproducible results, time consuming and high costs, and not renewability of electrode surfaces. To overcome the above problems and to broaden the application of the CNTs-based modified electrodes as the electrochemical sensors, the CNTs modified electrodes were prepared by an alternative promising approach and through mechanical mixing CNTs with some binding substances. Sol-gel technology is very flexible in adapting matrices to electrochemical procedure [29-30]. Lev et al. [31] established the sol-gel derived carbon powder ceramic electrodes (CPCEs) which involved dispersion of carbon powder into the sol-gel solution and this electrode has been largely used in the electrochemical devices. Other than carbon powder, CNTs can also be doped into sol-gel matrix during the hydrolysis of alkoxysilane and gelation process as a binding substance to construct a stable and surface renewable CNTs modified electrode. By this way, the advantages of the sol-gel technique integrate with the favorable electrochemical characteristics of CNTs and consequently excellent properties such as surface renewability, the electrode surface could be renewed by a simple mechanical polishing step in the case of contamination or fouling and even after each use, mechanical rigidity, high stability, and ease of fabrication are obtained.

In this paper, we apply the multi walled carbon nanotubes (MWCNTs) instead of carbon powder in the sol-gel method and fabricate a renewable electrode that we named carbon nanotubes ceramic electrode (CNTsCE). The obtained electrode was characterized by scanning electron microscopy (SEM) and cyclic voltammetry (CV) methods. The CNTsCE was then described for the simultaneous determination of AA, PA and PP. Interestingly, the electrooxidation of these three species on the obtained electrode in the mixture solution appeared as three well-defined voltammetric peaks. It was shown that the current peak for the oxidation of AA, PA and PP in their ternary mixture could be very well resolved by differential pulse voltammetry (DPV), and, accordingly, a sensitive and selective electrochemical sensor for the simultaneous determination of these three compounds was established for the first time. Finally, the analytical performance of this sensor for simultaneous determinations of AA, PA and PP in pharmaceutical and biological samples was evaluated by DPV method.

2. EXPERIMENTAL

2.1. Chemicals

Methyl trimethoxy silane (MTMOS), ascorbic acid, paracetamol, phenylephrine and other chemicals were purchased from Merck or Fluka and used without any additional purification. MWCNTs (95% purity, 10-20 nm diameter and 1 μm length) were obtained from Nanolab (Brighton, MA). Beechams Cold and Flu Sachets were obtained from GlaxoSmithKline Consumer Healthcare Company. Stock solutions of 0.1 M H_3PO_4 , NaH_2PO_4 , Na_2HPO_4 and NaOH were applied to prepare phosphate buffer solutions (PBS) with 0.1 M at different pH values. Doubly distilled water was used throughout the experiments.

2.2. Apparatus

An Autolab100 (Potentiostat/Galvanostat) was used through the electrochemical process. It was interfaced with an individual computer and controlled by GPES 4.7 software. A customary three-electrode cell was used in the electrochemical investigations. The CNTsCE or CPCE, saturated calomel electrode (SCE) and a platinum wire were used as the working electrode, reference electrode and counter electrode, respectively. Scanning electron microscopy (SEM) (LEO 440i Oxford) was applied to characterize the surface morphology of the CNTsCE.

2.3. Preparation of the CNTsCE

The CNTsCE was prepared according to the following procedure. A portion of 0.15 mL MTMOS was mixed with 0.3 mL methanol and 10 μL hydrochloric acid (11 M) as the catalyst. The mixture was stirred on the conventional stirrer for 5 minutes, after which 0.2 g MWCNTs was added to it and the subsequent mixture was shaken for 5 min. A Teflon tube with 5 mm length and 3-4 mm inner diameter was used as the template and was filled with the sol-gel MWCNTs mixture and was dried in the room temperature. The electrode surface was polished with 2000 emery paper and rinsed thoroughly with distilled water and sonicated water for 2 minute. Electrical contact was made with copper wire through the other side of the electrode. The CPCE was also prepared in the same way as above, except that the carbon powder was used instead of carbon nanotubes in the final step.

3. RESULTS AND DISCUSSION

3.1. Surface characterization of the CNTsCE

SEM was applied to investigate the surface of the CNTsCE. The corresponding results are shown in Figure 1. Figure 1A shows the surface of the CNTsCE immediately after being polished with 2000 emery paper. As it can be seen in this image, the surface of the CNTsCE consists of a clump of ceramic material rocks containing MWCNTs and the homogeneous MWCNTs can be observed at the surface of each ceramic bullet. On the other hand, it can be clearly seen that bundles of MWCNTs were surrounded with the silica gel and the obtained

composite displays porous assembly. Figure 1B shows one of the ceramic bullets with high magnification.

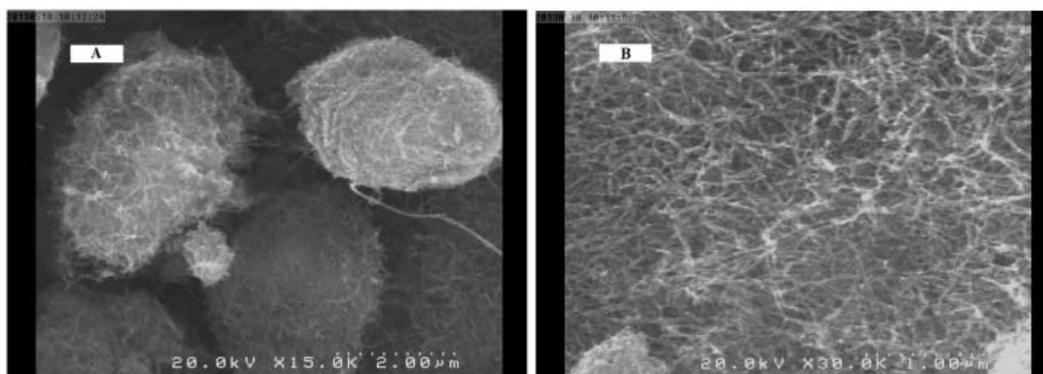


Fig. 1. SEM image of the CNTsCE (A), with high magnification (B)

3.2. Electrochemical characterization of the CNTsCE

Cyclic voltammetry in 1.0 mM $\text{Fe}(\text{CN})_6^{3-/4-}$ was employed to evaluate the electrochemical performance of CNTsCE and also to compare its electrochemical performance with that of CPCE; both of the electrodes were fabricated in the similar conditions. The peak-peak separation (ΔE_p) of anodic and cathodic peak potentials (E_{pa} and E_{pc}) of 91 mV at CPCE was observed corresponding to a quasi-reversible electron transfer process (Figure 2, curve a). After that the CPCE was modified by replacing the carbon powder with MWCNTs, the peak current greatly increased together with the obvious decrease of ΔE_p (78 mV; Figure 2, curve b) which results from the formation of high conductivity and enlarged surface area of electrode. On the other hand, as it can be seen in Figure 2, the smaller peak separation and higher peak current were obtained when we used CNTsCE as the working electrode. These results show that MWCNTs improved electron kinetics.

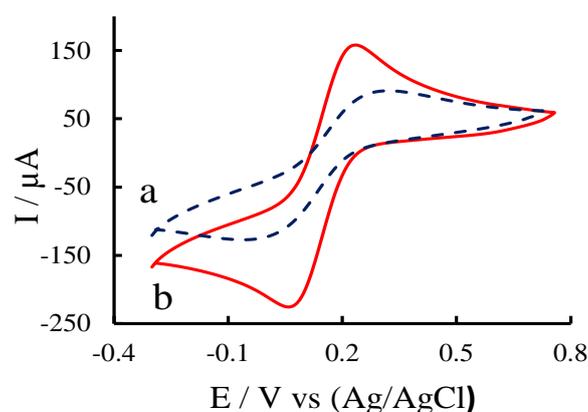


Fig. 2. Cyclic voltammograms of 1.0 mM ferricyanide at the CPCE (dashed line) and CNTsCE (solid line). Scan rate 50 mV s⁻¹

Also the electroactive surface area of the CNTsCE was estimated by cyclic voltammetry in $\text{Fe}(\text{CN})_6^{3-/4-}$ probe solution according to the Randles-Sevcik equation [32]. The calculated electroactive surface area for the CNTsCE is 0.325 cm^2 which was higher than that of CPCE (the real surface area for bare CPCE was already obtained: 0.162 cm^2) [26]. The higher electroactive surface area for CNTsCE suggests that the CNTsCE is promising for electrochemical reactions and measurements. On the other hand, cyclic voltammetry in $\text{Fe}(\text{CN})_6^{3-/4-}$ solution was applied to survey the stability of the CNTsCE and the reproducibility of the electrochemical procedure. After 100 cycles, the peak current of $1.0 \text{ mM Fe}(\text{CN})_6^{3-/4-}$ at the CNTsCE was about 99% of its initial value (Figure 3A) and no decrease was observed by replacing the electrolyte used for 200 repetitive cycles with fresh solution.

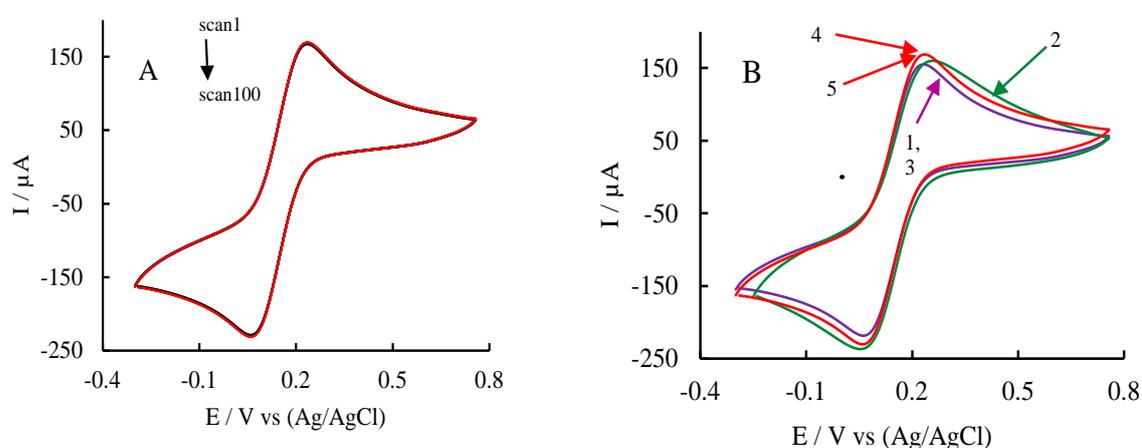


Fig. 3. Cyclic voltammograms of 1.0 mM ferricyanide at the CNTsCE of 1, 20, 50 and 100 th cycles (A), and Cyclic voltammograms of the same solution at the CNTsCE after 1, 2, 3, 4, 5th polish (B). Scan rate 50 mV s^{-1}

Moreover, the activity of the electrode remained at 98% of its initial activity for more than 30 days when it was kept in the laboratory at room temperature, and only a 3% drop was found when the CNTsCE was immersed in 0.1 M sulfuric acid buffer solution ($\text{pH } 1.0$) for 50 h. In order to investigate the reproducibility of the electrode preparation process, the CVs of four independent CNTsCE in $1.0 \text{ mM Fe}(\text{CN})_6^{3-/4-}$ solution were recorded. The relative standard deviation (R.S.D.) value of the measured anodic peak currents was 3.3%. In order to study the reproducibility and renewability of the individual CNTsCE, the CV of CNTsCE in $1.0 \text{ mM Fe}(\text{CN})_6^{3-/4-}$ was recorded after each polish (Figure 3B). The R.S.D. value of the measured anodic peak currents for five times polish and use was about 3.2%, which reveals very good reproducibility of the electrode preparation and polishing procedure. As it can be seen, the sol-gel derived CNTsCE was stable in the air just as the stability of the conventional graphite or glassy carbon electrodes, but its surface could be refreshed by polishing. It can

also be continuously immersed in water solution for a very long time (at least 10 days) without splitting or dissolution because of the hydrophobicity of electrode surface which was endowed by the organic sol precursor. These results show that the CNTsCE as a renewable and mechanical rigid electrode can be used in the electrochemical investigation and determination.

3.3. Electrooxidation of the AA, PA and PP

The electrochemical behaviors of AA, PA and PP in the mixture solution of these three drugs were investigated at the CNTsCE by means of cyclic voltammetry. The CVs of AA, PA and PP at the CNTsCE (curve a) and also CPCE (curve b) are shown in Figure 4. The oxidation of AA on the CNTsCE occurs at 142 mV, which is around 50 mV more negative than that of the CPCE. Also, the oxidation peak potential of PA occurs at 424 mV, which is about 121 mV more negative than that of CPCE and the peak potential due to the oxidation of PP happens at 736 mV, which is almost 161 mV more negative than that of CPCE. Then negative shifts of potential with much increased peak current confirm an enhanced electron transfer rate for AA, PA and PP oxidation at the CNTsCE. All these facts demonstrate that CNTsCE have more favorable electron transfer kinetics than CPCE. Table 1 shows the associated voltammetric records for AA, PA and PP using CNTsCE and CPCE as working electrodes.

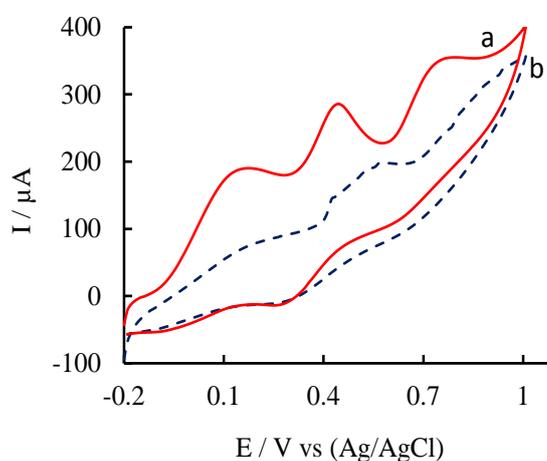


Fig. 4. Cyclic voltammograms of 10.0 mM AA, 0.5 mM PA and 1.0 mM PP at the CPCE (dashed line) and CNTsCE (solid line) in 0.1 M PBS (pH 7.0). Scan rate 100 mVs⁻¹

The dependence of the peak potentials of the AA, PA and PP oxidation on the pH was studied and the obtained results show that by increasing the pH of the measurement solution, the peak potentials of the AA, PA and PP shift to more negative values. This is the consequence of a deprotonation step involved in all oxidation processes that is facilitated at

higher pH values. Also, the effect of pH on the separation of peak potentials was studied and the maximum separation of peak potentials for AA-PA and PA-PP was observed at pH 6-8. In order to obtain high sensitivity and selectivity, pH 7.0 (pH of biological medium) was selected as an optimum pH value for the determination of AA, PA and PP in their mixture.

Table 1. Cyclic voltammetric analysis of AA, PA and PP at the surface of CPCE and CNTsCE

Parameter	CPCE			CNTsCE		
	AA	PA	PP	AA	PA	PP
E_p (mV)	192	545	897	142	424	736
I_p (μ A)	67	190	315	187	279	346

3.4. Simultaneous determination of AA, PA and PP

One of the main purposes of this work was to develop a modified electrode with the ability of separating the electrochemical responses of AA, PA and PP. Therefore, DPV was used for the simultaneous determination of these compounds because this method had low charging contribution to the background current and high current sensitivity. By means of CNTsCE as the working electrode, the analytical experiments were carried out by varying the concentration of one compound in the presence of constant concentrations of two other compounds in 0.1 M PBS (pH 7.0). Therefore, we carefully investigated the oxidation current of AA in the presence of constant concentration of PA and PP at the CNTsCE. No significant change in the PA and PP oxidation currents was perceived by altering the concentration of AA. However, when the concentration of AA increased, its peak current increased linearly too (Figure 5A). The linear range for detection of AA in the presence of constant concentration of PA and PP was at range of 5.0-350 μ M. The linear regression equation is written as $I_{pa} (\mu A) = 0.0937C_{AA} (\mu M) + 0.89199$, $R^2 = 0.9994$ (inset of Figure 5A). Various concentrations of PA in the presence of constant concentration of AA and PP show excellent differential pulse voltammetric responses with the almost constant responses to AA and PP (Figure 5B).

The PA peak current increased linearly with PA concentration increasing from 0.1 to 3.5 μ M. The linear regression equation is expressed as $I_{pa} (\mu A) = 10.051 C_{PA} (\mu M) + 2.2098$ ($R^2 = 0.9952$) (inset of Figure 5B). We also carefully examined the oxidation currents of AA and PA at the CNTsCE in the presence of increasing concentration of PP (Figure 5C). No noticeable change in the AA and AP oxidation currents was perceived whenever varying the concentration of PP, and the peak current of PP increased linearly with increasing PP concentration from 1 to 70 μ M. The linear regression equation is obtained as $I_{pp} (\mu A) = 0.2885 C_{PP} (\mu M) + 2.5039$ ($R^2 = 0.9929$) (inset of Figure 5C).

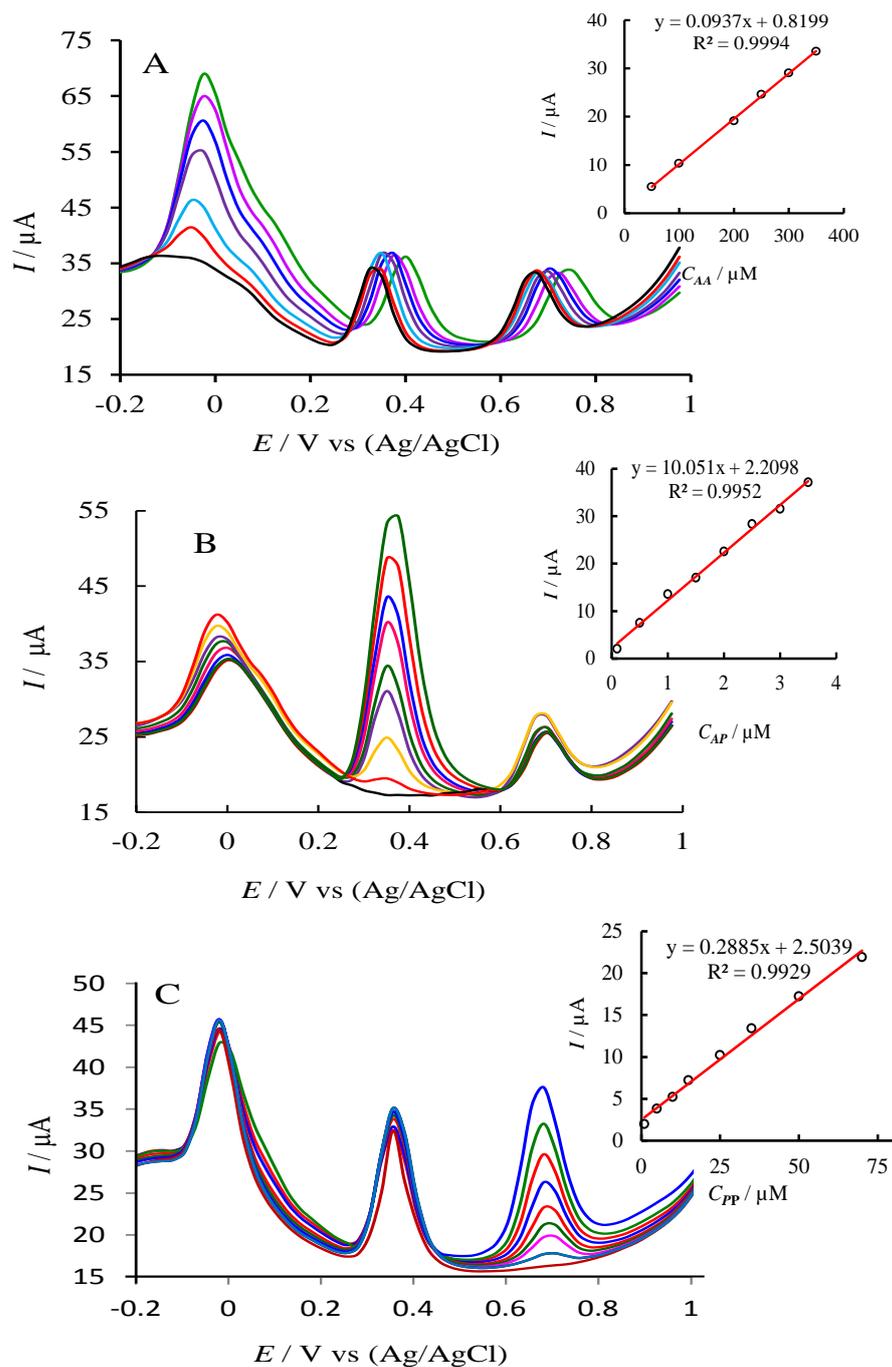


Fig. 5. DPVs of (A) AA at CNTsCE in the presence of 2 μM PA and 30 μM PP in 0.1 M PBS (pH 7), AA concentrations (from 50 to 350 μM): 50, 100, 200, 250, 300 and 350, (B) DPVs of PA in the presence of 50 μM AA and 30 μM PP, PA concentrations (from 0.1 to 3.5 μM): 0.1, 0.5, 1, 1.5, 2, 2.5, 3, and 3.5 and (C) DPVs of PP in the presence of 100 μM AA and 1 μM PA, PP concentrations (from 1 to 70 μM): 1, 5, 10, 15, 25, 35, 50 and 70. DPV conditions: scan rate, 20 mVs^{-1} ; pulse amplitude, 50 mV; pulse width, 50 ms; pulse period, 200 ms

The limit of detection for AA, AP and PP was founded 2.0, 0.04, and 0.3 μM , respectively. Thus, simultaneous determination of the three analytes is conceivable.

Additionally, to estimate the reproducibility of CNTsCE toward AA, PA and PP oxidation, the peak currents of 10 successive measurements by DPV in ternary mixture solution of 50 μM AA, 0.5 μM PA and 30 μM PP was determined (Figure 6). The RSD of 3.1%, 2.7% and 2.9% was obtained for AA, PA and PP, respectively, demonstrating that the CNTsCE is not subject to surface fouling by the oxidation products.

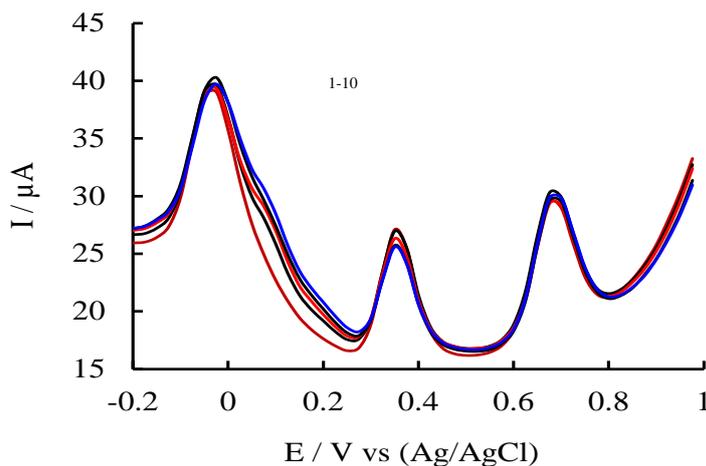


Fig. 6. DPVs of 10 successive measurements in ternary mixture solution of 50 μM AA, 0.5 μM PA and 30 μM PP in 0.1 M PBS (pH 7.0). DPV conditions are the same as in Figure 5

3.5. Interference study in the electrochemical determination of AA, PA and PP

Possible interference in the detection of AA, PA and PP at CNTsCE was investigated by adding of various ions to 0.1 M phosphate buffer solution in the presence of 100 μM AA, 2 μM PA and 20 μM PP. The common ions such as Na^+ , K^+ , Cl^- , NO_3^- , CO_3^{2-} , and SO_4^{2-} did not show interference with AA, PA and PP detection. As for the common interference in biological and pharmaceutical samples for the simultaneous determination of AA, PA and PP 500-fold concentration of glucose, caffeine, vitamin B₆, tyrosine, and cysteine had no effective interference with the current response of AA, PA and PP (signal change below 5%). This suggests that the proposed method has good selectivity toward simultaneous determination of AA, PA and PP in pharmaceutical and biological samples.

3.6. Determination of AA, PA and PP in human serum sample

The considered method was validated for the determination of AA, PA and PP in human serum samples. Serum samples were prepared as follows: 5% (v/v) of methanol was added and carefully mixed and the obtained samples were diluted 10 times with PBS (pH 7.0).

The diluted serum samples were spiked with standard solutions of AA, PA and PP respectively.

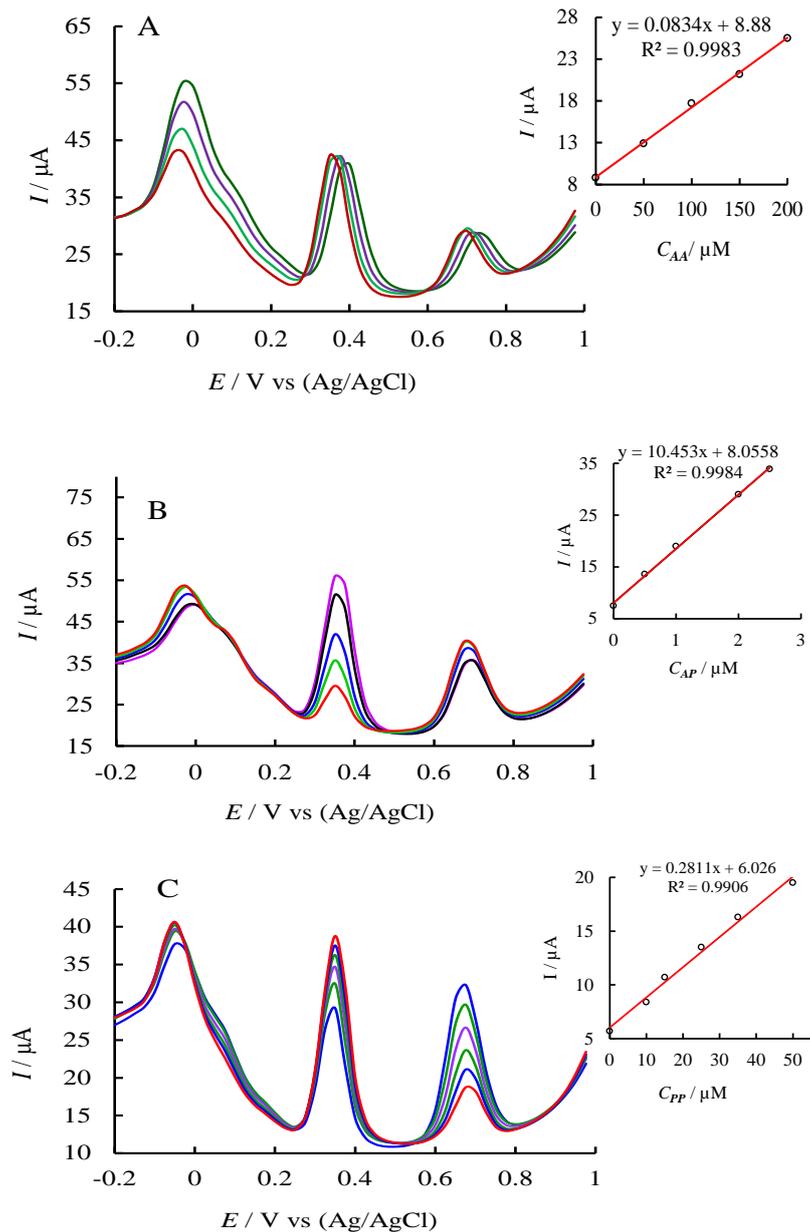


Fig. 7. DPVs for the (A) addition of the different amounts of AA (50, 100, 150, and 200 μM) in the presence of 2 μM PA and 30 μM PP, (B) addition of the different amounts of PA (0.5, 1, 2, and 2.5 μM) in the presence of 100 μM AA and 50 μM PP, and (C) addition of the different amounts of PP (1, 10, 15, 25, 35 and 50 μM) in the presence of 50 μM AA and 1 μM PA in the human serum samples diluted with 0.1 M PB solution (pH 7). DPV conditions are the same as in Figure 5

After the preparation of the sample and the appropriate dilution stages which were depicted above, the DPV technique was applied to the determination of AA, PA and PP in human serum samples (Figure 7). The summarized results of the analysis are given in Table 2. To check the accuracy of the investigated process, the recovery studies were performed.

The obtained recovery results in Table 2 indicate that CNTsCE can be successfully used for the determination of AA, PA and PP in a real sample such as human serum.

Table 2. Results of the recovery analysis of AA, PA and PP in human serum samples

	No.	Added (μM)	found (μM)	Recovery (%)	Average recovery (%)
AA	1 ^a	50.00	52.00	104.0	
	2	100.00	101.00	101.0	102.3
	3	150.00	153.00	102.0	
PA	1	1.00	1.02	102.0	
	2	2.00	1.94	97.0	99.3
	3	3.00	2.97	99.0	
PP	1	5.00	5.07	101.5	
	2	10.00	10.30	103.0	101.5
	3	15.00	15.00	100.0	

a: Number of sample assayed=5

Table 3. Measurement results for AA, PA and PP in pharmaceutical samples

Sample	No.	Analyte	Content (μM)	Added (μM)	Found(μM)	Recovery (%)	R.S.D (%)
Beechams	1	AA	100.00	---	101.40 ^a	101.40	3.20
Cold & Flu		PA	2.00	---	2.04	102.20	3.12
Sachet		PP	40.00	---	39.52	98.80	3.11
	2	AA	100.00	10.00	111.23	101.11	3.15
		PA	2.00	0.50	2.49	99.60	3.20
		PP	40.00	5.00	44.91	99.80	3.10
	3	AA	100.00	20.00	120.72	100.60	3.20
		PA	2.00	1.00	3.04	101.30	3.16
		PP	40.00	10.00	50.71	101.42	3.24

a: Number of sample assayed=5

3.7. Determination of AA, PA and PP in the pharmaceutical sample

The obtained electrode was used for the determination of AA, PA and PP in the pharmaceutical sample (Beechams Cold and Flu were obtained from GlaxoSmithKline Consumer Healthcare Company). The DPV method was used for the determination of AA,

PA and PP using a standard additional method in order to minimize possible matrix effects. 2 Sachets of Beechams Cold and Flu containing AA (40 mg), PA (600 mg) and PP (10 mg) were precisely weighted and transmuted to a fine powder. Then certain amount of obtained powder was dissolved in 100 mL distilled water. A portion of the resultant solution was diluted with PBS (pH 7.0) and then was taken out and subjected as the sample for the detection of AA, PA and PP concentrations. The obtained results are shown in Table 3. As it can be seen in Table 3, the added and measured concentrations were generally in good agreement.

4. CONCLUSION

A renewable electrode was fabricated through sol-gel method by replacing the carbon powder with CNTs. The physicochemical properties of the obtained electrode were characterized by SEM and electrochemical methods. The CNTsCE showed higher electroactivity than the CPCE in $\text{Fe}(\text{CN})_6^{3-/4-}$ solution due to high conductivity and high real surface area. The CNTsCE showed very good electrocatalytic effect in the electrooxidation of AA, PA and PP. In DPV method, the AA, PA and PP had different oxidation peak potentials and as a result, separated oxidation peaks at the CNTsCE due to distinctive properties of the MWCNTs. This sensor showed high sensitivity with low detection limits for AA, PA and PP. The CNTsCE was successfully applied to determine the AA, PA and PP in human blood serum and pharmaceutical samples.

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