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A Gold Nanoparticle-Modified Carbon Paste Electrode as a Sensor for Simultaneous Determination of Acetaminophen and Atenolol

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A simple, rapid and sensitive electrochemical method for simultaneous determination of acetaminophen and atenolol was developed in Britton-Robinson buffer solution on a gold nanoparticles carbon paste electrode (GN-CPE). Differential pulse voltammetry (DPV) was used for determination of both drugs. The modified electrode exhibited electrocatalytic properties toward acetaminophen and atenolol oxidation with a peak potential of 20.0 and 50.0 mV lower than that at the bare carbon paste electrode, respectively. Also the enhanced peak current response is a clear evidence of the catalytic of the gold nanoparticles modified carbon paste electrode towards oxidation of acetaminophen and atenolol. Linear calibration curves were obtained in the range of 0.770 μM – 0.375 mM and 0.990 μM – 0.167 mM with detection limits of 0.058 μM and 0.073 μM for acetaminophen and atenolol, respectively. The proposed method was successfully applied in the simultaneous determination of acetaminophen and atenolol in several pharmaceutical formulations and human plasma.

Keywords: Gold nanoparticles, acetaminophen, atenolol, simultaneous determination, differential pulse voltammetry, drug formulation

1. INTRODUCTION

Acetaminophen (Paracetamol, N-acetyl-p-aminophenol, ACEP) is a long-established substance, being one of the most extensively employed drugs in the world. It is noncarcinogenic and an effective substitute for aspirin for patients with sensitivity to it [1-4]. Because acetaminophen (ACEP) is being increasingly used for therapeutic purposes, its determination and quality control are of

vital importance [5]. Numerous methods have been reported for the determination of ACEP including chromatography [6-12], chemiluminescence [13,14], spectrophotometry [15], spectrofluorimetry [16-19], Flow-injection [20], near infrared [21] and electrochemical techniques [22-32]. Shang Guan et al. [33] studied the electrochemical determination of ACEP using differential pulse voltammetry (DPV) at a carbon ionic liquid electrode. The peak oxidation current at this electrode was linear with the ACEP concentration in the range of 1.0 μM - 2.0 mM (r = 0.9992), with a detection limit of 0.3 μM. Fatibello-Filho et al. [34] studied the simultaneous voltammetric determination of ACEP and caffeine at a cathodically pretreated boron-doped diamond (BDD) electrode using square wave voltammetry (SWV) and DPV. The diamond electrode provided a linear dynamic range from 0.500 μM to 0.083 mM and a detection limit of 0.490 μM for acetaminophen. The mechanism of ACEP electrooxidation involves two electrons and two protons to generate N-acetyl-p-quinoneimine [35,36].

Atenolol (ATN) is a cardioselective β1-adrenergic receptor-blocking agent. ATN is used therapeutically in the treatment of angina pectoris, hypertension and migraine. β-blockers are exceptionally toxic and most have a narrow therapeutic range; i.e., the differences between the lowest therapeutic and the highest tolerable doses are small [37-39]. Hence, accurate methods for the measurement of ATN are of great importance in pharmaceutical research. Several methods have been reported for the single or simultaneous determination of ATN including spectrofluorimetry [40], capillary zone electrophoresis [41], chromatography [42-47] and electrochemistry [48-53]. However, chromatographic methods (for single or simultaneous determination) require expensive instrumentation, time-consuming, sample extraction and high running costs [54,55].

In this paper, we prepare a simple, sensitive and selective gold nanoparticles modified carbon paste electrode (GN-CPE) for simultaneous determination of ACEP and ATN in a variety of samples with differential pulse voltammetry in Britton-Robinson (BR) buffer solution. The advantages of carbon paste electrodes include the diverse range of paste modifications available and the convenience in handling.

2. EXPERIMENTAL

2.1. Reagents and chemicals

All chemicals used were of analytical or pharmaceutical grade and solutions were prepared in deionized water. Carbon graphite powder, paraffin oil, $HAuCl_4$ and sodium citrate were supplied by Merck. The pure forms of ACEP and ATN were supplied by local pharmaceutical company (Iran) and stock solutions of 0.01 M of ACEP and also 0.01 M of ATN were prepared in BR buffer solution, pH 9.

2.2. Preparation of gold nanoparticles

Colloidal gold nanoparticles were prepared by adding 0.5 ml of 1% sodium citrate solution to 50 ml of a boiling solution of 0.01% $HAuCl_4$. The mixture was maintained at boiling point for 15

minutes, and then stirred for another 15 minutes after removing the heating source. The method produced 24 nm-diameter colloidal gold nanoparticles [56]. The maximum UV-Vis absorption of the colloidal gold was 520 nm. The solution was stored in a refrigerator in a dark-colored glass bottle.

2.3. Preparation of carbon paste electrodes

The bare carbon paste electrode (CPE) was prepared by thoroughly hand-mixing 0.50 g graphite powder with approximately 0.2 ml of paraffin oil. The colloidal gold nanoparticles modified carbon paste electrode (GN-CPE) was prepared by thoroughly mixing 0.50 g graphite powder and 1.5 ml of colloidal gold nanoparticles solution prior to adding paraffin oil. A portion of the paste was put into plastic syringe tubes with the inner diameter of 2.0 mm to form the GN-CPE. Electrical contact to the paste was established by inserting a copper wire into the plastic syringe tube.

2.4. Electrochemical measurements

Voltammetric measurements were carried out with a potentiostat/galvanostat EG&G (model 273A) and a conventional three-electrode system was adopted. The working electrode was the above described CPEs and the auxiliary and reference electrodes were platinum wire and Ag/AgCl electrode, respectively. The electrochemical measurement was conducted in BR buffer solution. DPV analysis was used for determination of ACEP and ATN in samples. All electrochemical measurements were done in an unstirred electrochemical cell at 25 ± 0.5 ºC.

3. RESULTS AND DISCUSION

3.1. DPV study of acetaminophen and atenolol with CPE

Initial studies of the voltammetric behavior of the drugs were performed using differential pulse voltammetry. DPV was used in the voltammetric measurement owing to its good sensitivity and resolving power. It is well known that DPV is suitable for the analysis of the drug mixtures of electrochemically active substances because a relatively small difference in peak potentials of the analytes is needed for their simultaneous determination. Fig. 1 compares typical differential pulse voltammograms of 38.5 μM ACEP and 38.5 μM ATN in BR buffer solution (pH 9) recorded at two different working electrodes (i.e. bare CPE and GN-CPE). At the GN-CPE, compared to the bare CPE, the oxidation peak of ACEP shifted negatively to 20.0 mV and also the peak current increased (Fig. 1A). On the other hand the oxidation peak of ATN shifted negatively to 50.0 mV and also the peak current increased (Fig. 1B).

The enhanced peak current response is a clear evidence of the catalytic effect of the GN-CPE towards oxidation of ACEP and ATN. A shift in the oxidation potential by about 20.0 mV and 50.0 mV was observed at the modified electrode for ACEP and ATN, respectively, which further supports the catalytic effect of GN-CPE. Fig. 2 presents the DPV of the mixture of ACEP and ATN at bare CPE

and GN-CPE. It is noticed that the peak potential of both ACEP and ATN shifted to less positive potentials at GN-CPE and also the peak currents of both drugs increased. It has been reported that gold nanoparticles exhibit catalytic activity and lower oxidation potential [57].

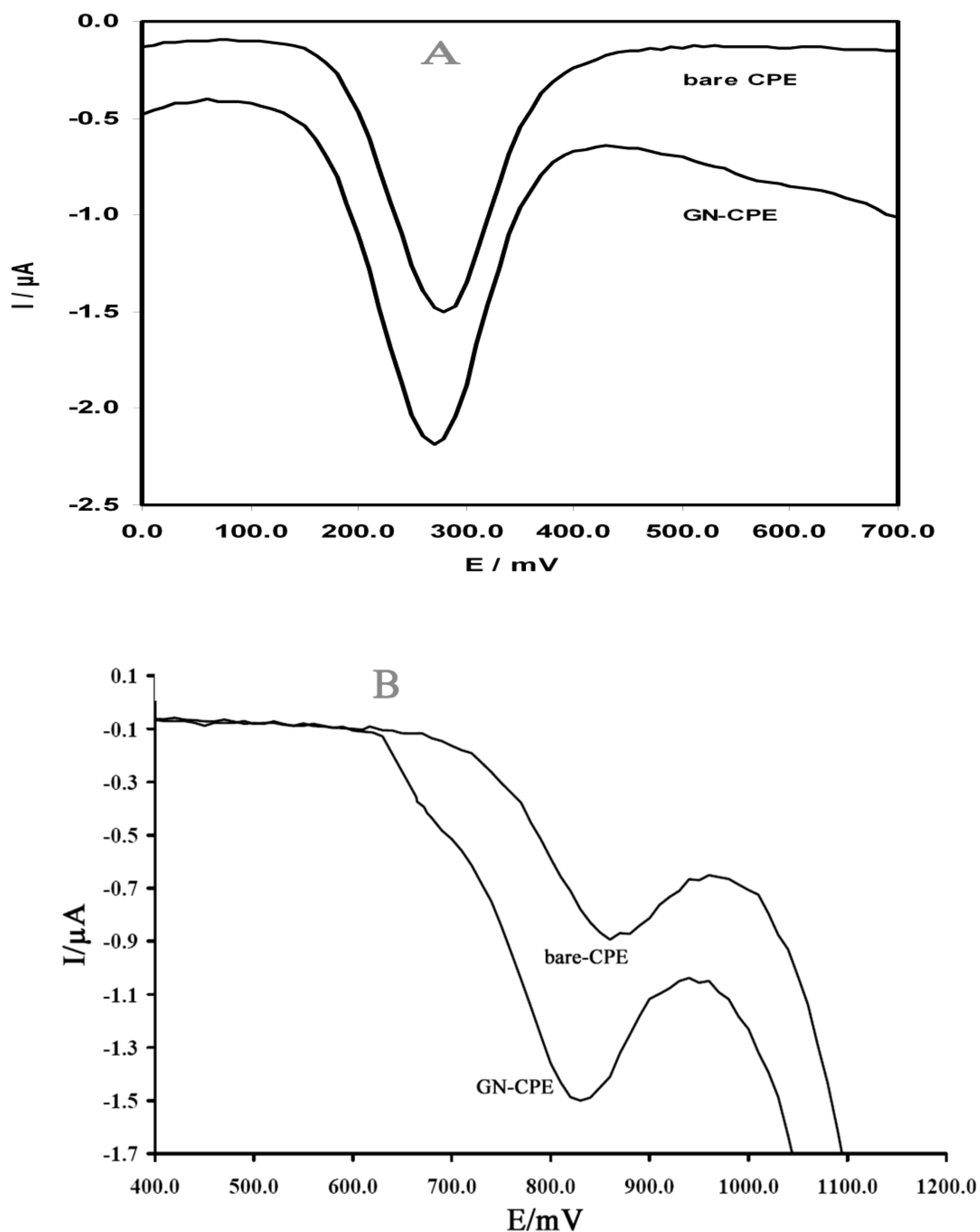

Figure 1. DPV of (A) 38.5 µM ACEP and (B) 38.5 µM ATN at bare CPE and GN-CPE in BR buffer solution (pH 9). Pulse height: 100 mV; pulse width: 50 ms; scan increment: 10 mV; scan rate: 15mV s^{-1}.

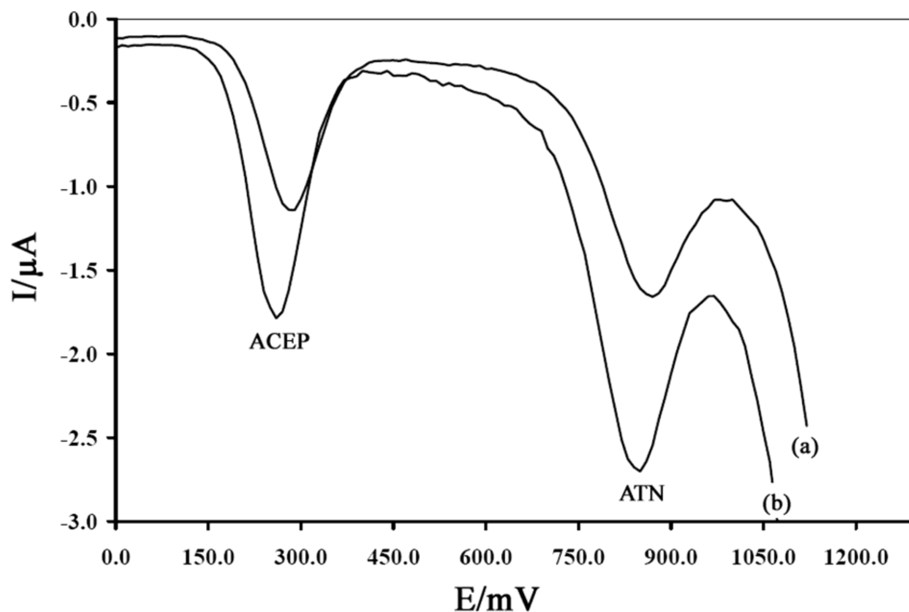

Figure 2. DPV of mixture of ACEP (38.5 μM) and ATN (3.85 μM) at pH 9 at (a) bare CPE and (b) GN-CPE.

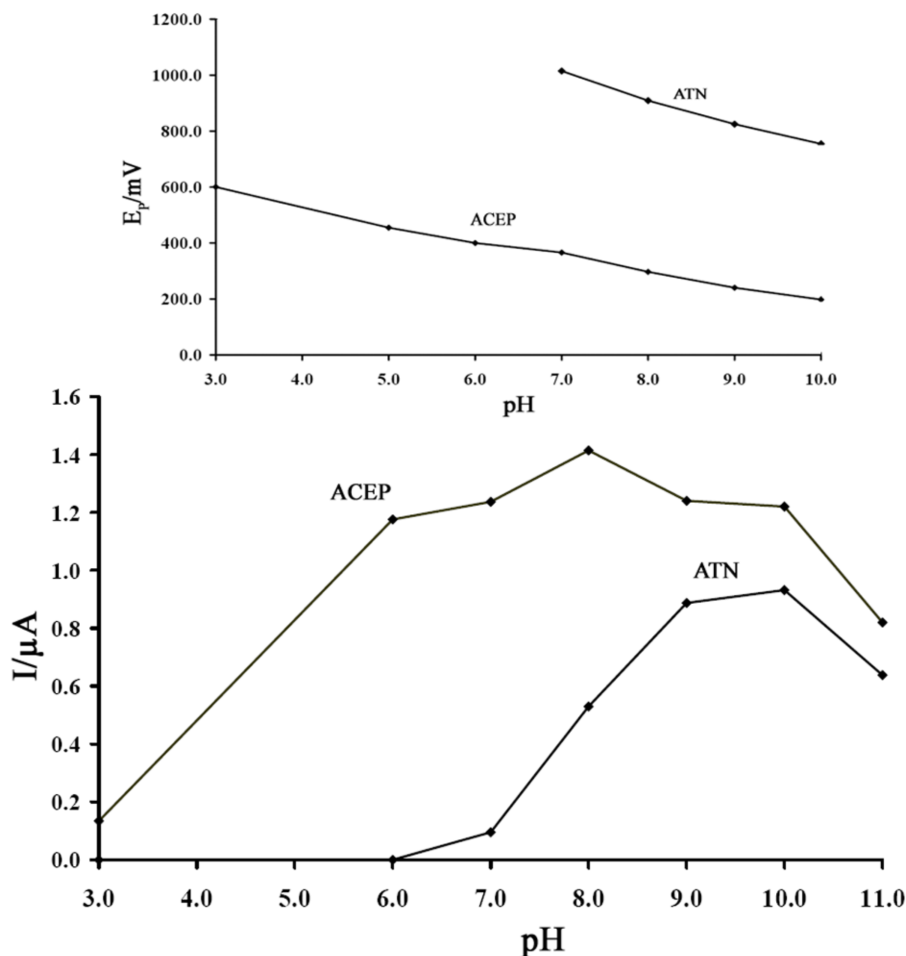

Figure 3. Peak currents vs. pH in the range of 3.0 to 11.0 for 40 μM ACEP and 50 μM ATN in BR buffer solution. The insert shows the linear dependence of Peak potentials vs. pH in the range of 3.0 to 10.0 for ACEP and 7.0 to 10.0 for ATN.

3.2. Effect of pH

Effect of pH was studied on the current responses and Peak potentials of oxidation peaks of ACEP and ATN in the range of 3.0 - 11.0 in BR buffer solutions (Fig. 3).

The optimum pH value was found to be 9. The peak potentials of oxidation peaks of both the drugs were found to be dependent on pH and shifted to less positive potentials with increasing pH. There is a linear relationship between the peak potentials (E_p) and pH in the range of 3.0 - 10.0 for ACEP and 7.0 - 10.0 for ATN, can be expressed as E_p (3.0 - 10.0) = [-53.5 pH + 739] mV versus Ag/AgCl and E_p (7.0 - 10.0) = [-68.7 pH + 1443.2] mV versus Ag/AgCl, having correlation coefficients of 0.99 and 0.9973, for ACEP and ATN, respectively.

3.3. Individual determination of ACEP and ATN

The oxidation peak currents of ACEP and ATN were measured in 0.2 M BR buffer solutions pH 9, and plotted against the bulk concentration of ACEP and ATN (Fig. 4).

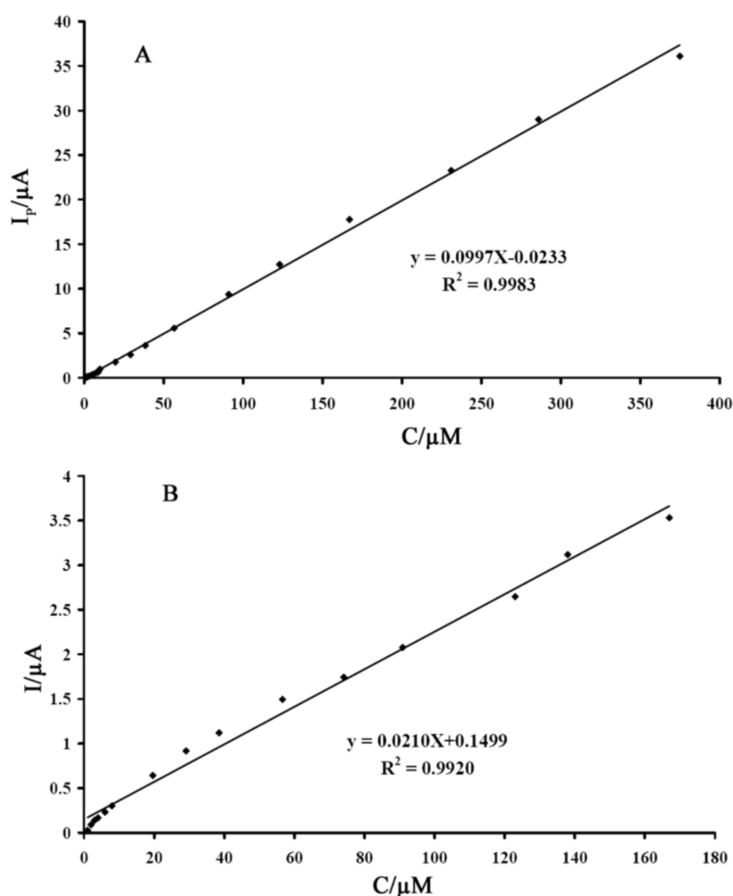

Figure 4. Dependence of the observed peak current against concentration of (A) ACEP and (B) ATN at the GN-CPE in 0.2 M BR buffer solution (pH 9).

The dependence of peak currents on the concentration of ACEP and ATN is a linear relationship in the range of 0.770 μM – 0.375 mM and 0.990 μM – 0.167 mM, respectively. The linear regression equations of ACEP and ATN can be expressed as I_p (μA) = 0.0997 C (μM) - 0.0233 (r = 0.9983) and I_p (μA) = 0.0210 C (μM) + 0.1499 (r = 0.9920), respectively. The detection limits are 0.058 μM and 0.073 μM for ACEP and ATN, respectively. The relative standard deviations of 8 successive scans are 1.4% and 1.6% for 40 μM ACEP and 60 μM ATN, respectively.

3.4. Simultaneous determination of ACEP and ATN

The main aim of our present study is to simultaneously determine the concentration of ACEP and ATN using GN-CPE in the BR buffer solution (pH 9). The DPV curves presented peak oxidation potentials at 0.265 V for ACEP and 0.85 V for ATN: this good peak potential separation of about 0.6 V clearly allows the simultaneous determination of the drugs.

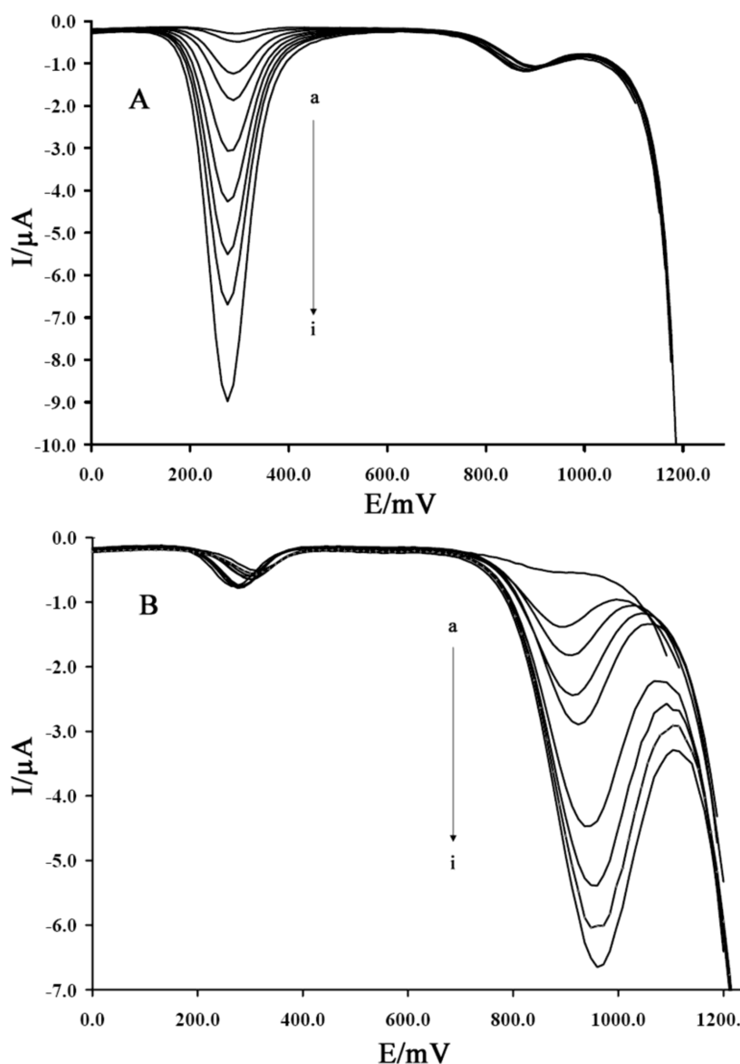

Figure 5. Observed DP voltammograms of a mixture of ACEP and ATN at GN-CPE at pH 9: (A) Concentration of ATN 40.0 μM and ACEP: (a) 2.0 , (b) 4.0 , (c) 12.0 , (d) 19.6, (e) 38.5, (f) 56.6, (g) 74.1, (h) 91.0 and (i) 123.0 μM. (B) Concentration of ACEP 10.0 μM and ATN: (a) 6.0, (b) 56.6, (c) 91.0, (d) 138.0, (e) 194.0, (f) 286.0, (g) 375.0, (h) 444.0 and (i) 500.0 μM.

To further investigate the electrochemical response when both substances are present in solution, DPV curves were obtained in the presence of a large excess of ACEP (or ATN) in the BR buffer solution (pH 9). Fig. 5A shows the DP voltammograms for different concentrations of ACEP and keeping the concentration of ATN constant (40 μM) and Vice Versa (Fig. 5B). An examination of Fig. 5A allows concluding that the peak oxidation current for ACEP increases regularly as its concentration is increased at a fixed concentration of ATN (its peak oxidation current remains fairly constant).

Similarly the Fig. 5B clearly depicts that ATN signal increases with increase in its concentration without affecting the ACEP signal. After this previous study, ACEP and ATN were determined by simultaneously changing their concentrations.

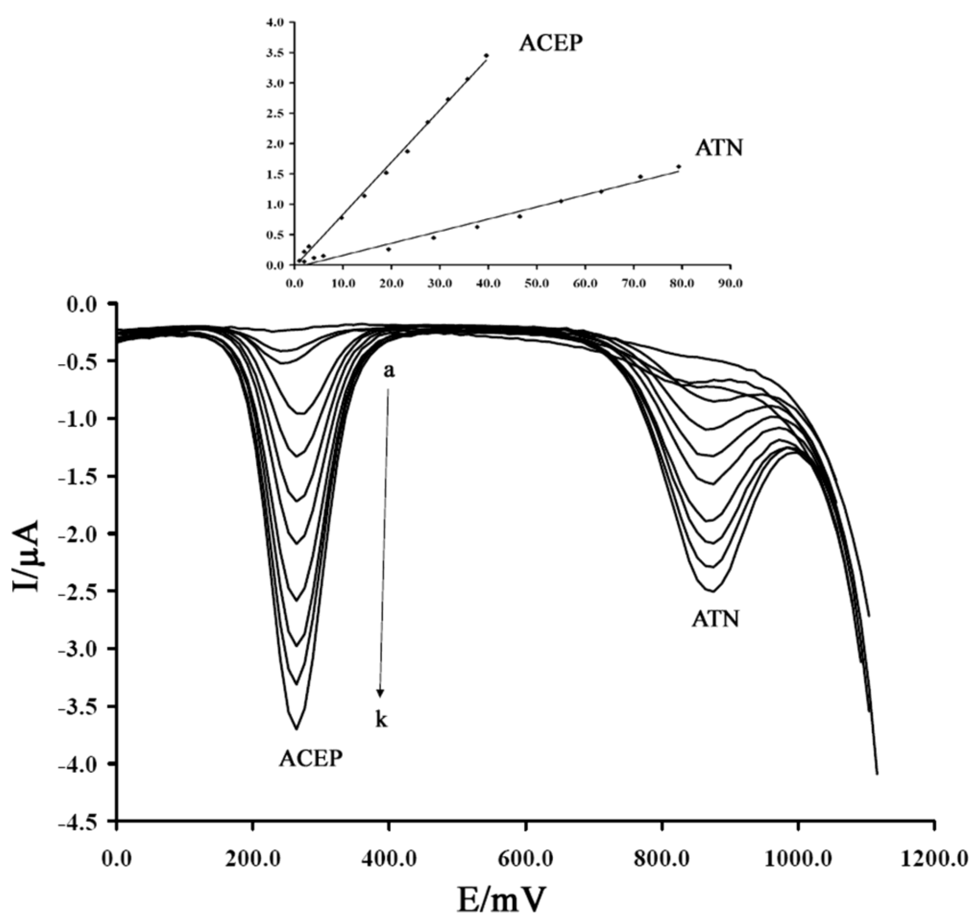

Figure 6. Differential pulse voltammograms recorded at different concentration of ACEP: (a-k: 0.99, 1.99, 2.97, 9.71, 14.40, 18.90, 23.30, 27.50, 31.70, 35.70, 39.6 μM) and ATN (a-k: 1.99, 3.98, 5.95, 19.40, 28.70, 37.70, 46.50, 55.00, 63.30, 71.40, 79.30 μM). The insert shows the calibration curves for ACEP and ATN. Pulse height: 100 mV; pulse width: 25 ms; scan increment: 12 mV; scan rate: 15 mV s^{-1}.

The electrooxidation processes of ACEP and ATN in the mixture have been investigated when the concentrations of ACEP and ATN were changed and the DPV of both species were recorded at the GN-CPE. Fig. 6 is DPV recording of different concentrations of ACEP and ATN at the GN-CPE. As shown in Fig. 6, the oxidation peak currents of ACEP and ATN increased linearly with the concentration of their own in the range of 0.99 to 39.60 µM [I_p (µA) = 0.0859 C (µM) - 0.0270, r = 0.9971] for ACEP and 1.99 to 79.30 µM [I_p (µA) = 0.0199 C (µM) - 0.0435, r = 0.9822] for ATN. The oxidation peaks of ACEP and ATN were well separated even in higher concentrations. The precision (n=11) assessed at relative standard deviation (R.S.D) were 2.5% for 20 µM ACEP and 1.5% for 40 µM ATN.

3.5. Interferences

The influence of common interfering species was investigated in the presence of 20 µM ACEP and 20 µM ATN. The results showed that the concentrations of Na^+, K^+, Ca^{2+}, Mg^{2+} and Cl^- have not significantly influence the height of the peak currents. The tolerance concentration level is 100 µM for dopamine, 40 µM for ascorbic acid and 20 µM for propranolol and uric acid. The results are listed in Table 1. The tolerance limit was defined as the concentrations which give an error of < 5.0% in the determination of ACEP and ATN compounds.

Table 1. Influence of some foreign substances for 20 µM ACEP and 20 µM ATN

Foreign substances	Tolerance level (µM)
Na^+, K^+, Ca^{2+}, Mg^{2+}, Cl^-	10000
Dopamine	100
Ascorbic acid	40
Propranolol, Uric acid	20

Table 2. Recovery results for ACEP and ATN in human serum samples at the GN-CPE.

Serum no.	Added (µM)		Found (µM)		Recoveries (%)	
	ACEP	ATN	ACEP	ATN	ACEP	ATN
1	4.0	16.0	4.2	17.0	105.0	106.2
2	10.0	40.0	9.3	37.8	93.0	94.5
3	38.5	152.0	41.0	160.0	106.4	105.0

4. ANALYTICAL APPLICATIONS

4.1. Simultaneous determination of ACEP and ATN in human blood plasma

In order to verify the reliability of the method for simultaneous determination of the considered compounds in clinical samples, the prepared modified electrode was also applied for the analysis in

human blood serum samples. The serum sample was centrifuged and then after filtering, diluted with BR buffer solution of pH 9 without any further treatment. The diluted serum sample was spiked with different amounts of ACEP and ATN. In these measurements, the concentration of one species changed in the presence of a constant concentration of another compound. Using the DPV method, the oxidation peak currents were linearly proportional to ACEP and ATN concentration with good correlation coefficients. The results indicated good recoveries (Table 2) for the determinations of these species in clinical samples, in the range of 93.0% to 106.0%. Therefore, it is possible to simultaneously determine ACEP and ATN by using the GN-CPE modified electrode in complex matrix samples.

4.2. Pharmaceutical product

The utility of GN-CPE for determination of ACEP and ATN in pharmaceutical formulations was tested by measuring the ACEP concentration in an oral solution and tablets and also the ATN concentration in tablets .The ACEP oral solution was diluted and the tablets of each compound were grounded to powder, dissolved in water, filtered with sinter glass and diluted so that the concentrations of ACEP and ATN were in the working range. A standard addition method was applied to measure accuracy. The values of experimentally determined ACEP and ATN were compared to the reported their amounts in various tablets and oral solution and the results are summarized in Table 3.

Table 3. Determination results of ACEP in tablets and oral solution, ATN in tablet.

Sample		Content (μM)	Found (μM)	RSD (%)	Recovery (%)
ACEP	Tablet without codeine	20.0	21.0	1.00	105.0
	Tablet containing codeine	19.8	20.0	1.75	101.0
	Oral solution	16.0	15.8	2.20	98.8
ATN	Tablet	37.5	35.7	1.20	95.2

5. CONCLUSION

The results obtained in this work demonstrated the potentiality of the GN-CPE modified electrode for simultaneous determination of ACEP and ATN. The modified electrode exhibits electrocatalytic activity for the oxidation of ACEP and ATN associated with negative shifts in anodic peak potentials. Thus, large peak separations obtained with this electrode allow it to simultaneously detect these drugs. Moreover, high selectivity, good sensitivity, low detection limits with the low cost of the sensor, makes this method suitable for accurate determinations in pharmaceutical and clinical preparations. The proposed method could be applied to the determination of ACEP and ATN in real samples (commercial drugs and biological fluids; plasma) with satisfactory results.

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