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On the Electrochemical Oxidation of Dopamine, Ascorbic Acid and Uric Acid onto a Bare Carbon Paste Electrode from a 0.1 M NaCl Aqueous Solution at pH 7

E. Colín-Orozco[1], *S. Corona-Avendaño*[1,*] *M. T. Ramírez-Silva*[2,*], *M. Romero-Romo*[1],
M. Palomar-Pardavé[1]

[1] Universidad Autónoma Metropolitana Azcapotzalco, Departamento de Materiales, Av. San Pablo #180, Col. Reynosa-Tamaulipas, C.P. 02200, D.F., México.
[2] Universidad Autónoma Metropolitana Iztapalapa, Departamento de Química, Av. San Rafael Atlixco #186, Col. Vicentina, C.P. 09340, D.F., México.
[*]E-mail: scav@correo.azc.uam.mx; mtrs218@xanum.uam.mx

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From cyclic voltammetry, CV, and differential pulse voltammetry, DPV, the dopamine, DA, ascorbic acid, AA, and uric acid, UA, electrochemical behavior were studied using a bare carbon paste electrode, CPE, immersed in a 0.1 M NaCl aqueous solution (pH 7). The results proved that DA, AA and UA oxidation were all diffusion-controlled processes. For DA, from CV experiments, the heterogeneous standard rate constant, k^0, and energy transfer coefficient, α, were evaluated as 0.008 cm^2s^{-1} and 0.45 respectively however, for AA and UA these parameters could not be measured because in both cases, during the cathodic potential scan no significant currents were detected, thus both oxidation processes are irreversible. From the DPV recorded in the system CPE / 0.1 M NaCl at pH 7 at different DA, AA or UA concentrations, it was possible to note that for all the cases that the peak current varied linearly with the DA, AA or UA concentration, thus all these substances can be electrochemically quantified when they are not mixed. In agreement with the results obtained, it could be observed that the bare CPE is more sensitive (23.79 ± 0.04 μAmM^{-1}) toward the UA, as compared with the DA and AA, and that the lower detection limit (5.63 ± 0.01 μM) was also reached for UA.

Keywords: Dopamine; Uric Acid; Ascorbic Acid; Simultaneous quantification; DPV

1. INTRODUCTION

Dopamine (3,4-dihydroxy-fenil-ethyl amine), DA, is one of the basic neurotransmitters of the Central Nervous System, CNS; alteration of its normal concentration levels in the organism leads to illnesses such as Parkinson's disease or the development of schizophrenic disorders [1]. Considering the importance given to the determination of dopamine concentrations, our research group has developed various investigations [2-11] aiming to study the neurotransmitter both experimentally [2-4,7-11] and theoretically [5,6]. Furthermore, the effect that the media has on dopamine has been studied, namely that of the anionic surfactant, sodium dodecyl sulphate, SDS [2]. In this respect, it has been found that both species interact at such a level that electrochemical quantification of dopamine becomes viable even in the presence of ascorbic acid, AA, [3], which is considered the main natural anti-oxidant of the neurotransmitter and, at the same time, the principal interfering agent for this type of determinations alone with uric acid, UA, [8, 12-16]. However, considering that there are a number of important media where DA, AA, UA are not mixed, namely: medicines and vitamin complements, where reliable quantification media are still required (quality control purpose and in-situ determination for instance), in this research work we present an electrochemical study related with DA, AA and UA determination in aqueous solution using a simple carbon paste electrode, CPE.

2. EXPERIMENTAL

2.1 Reagents and Chemicals

The solutions were prepared with Merck analytic-grade reagents and type I deionized water, with a resistivity of 18.2 MΩ, from a US Filter PURE-LAB Plus. Also, the working solutions were freshly prepared before any experiments, nitrogen-bubbled for about 5 min mL^{-1} prior and during each determination and precluded from the incidence of light.

2.2 Electrochemical equipment

All determinations were carried out with the aid of an Autolab-PGSTAT 30 potentiostat-galvanostat coupled to a PC to allow for control and data acquisition. The carbon paste electrode, CPE, was prepared from graphite powder, just as described elsewhere [17]. A Pt wire served as counter electrode and a saturated Ag/AgCl as reference.

2.3 Procedure

The DA's, AA's and UA's electrochemical characterization was done by means of cyclic voltammetry at pH 7 in a typical three-electrode cell. The voltammograms were obtained within the -500 to 1200 mV potential range at different scan rates, namely from 20 to 1000 mVs^{-1}. From differential pulse voltammetry, DPV, recorded in the potential range 0 to 1000 mV at scan rates of 20 mVs^{-1} and different DA, AA and UA concentration values, the respective calibration curves were obtained.

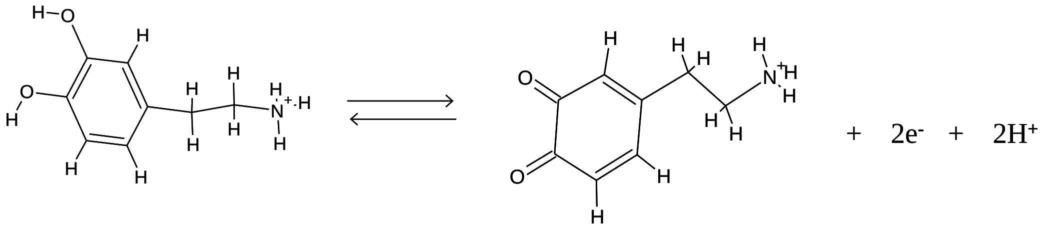
3. RESULTS AND DISCUSSION

3.1 Electrochemical study

3.1.1 Cyclic voltammetry

3.1.1.1 DA

Figure 1 shows a family of experimental cyclic voltammograms, CVs, recorded in the system CPE / 0.1 M NaCl, 0.1 mM DA at pH 7 at different scan rates, v. The analysis of both the anodic, i_{ap}, and cathodic, i_{cp}, peak´s current as a function of $v^{1/2}$ (see inset in Figure 1) reveals a linear trend for both cases, which indicates that DA electrooxidation (R1) and its subsequent electroreduction are both diffusion controlled processes. The equations supporting linearity are, for the anodic process i_{ap} /µA = (0.743 ± 0.001) µAmV^{-1} $v^{1/2}$ – (0.076 ± 0.022) µA, while for the cathodic process this is given as: i_{cp} /µA = (-0.541 ± 0.021) µAmV^{-1} $v^{½}$ + (1.511 ± 0.422) µA with a correlation coefficient of 0.99 and 0.98, respectively.



(R1)

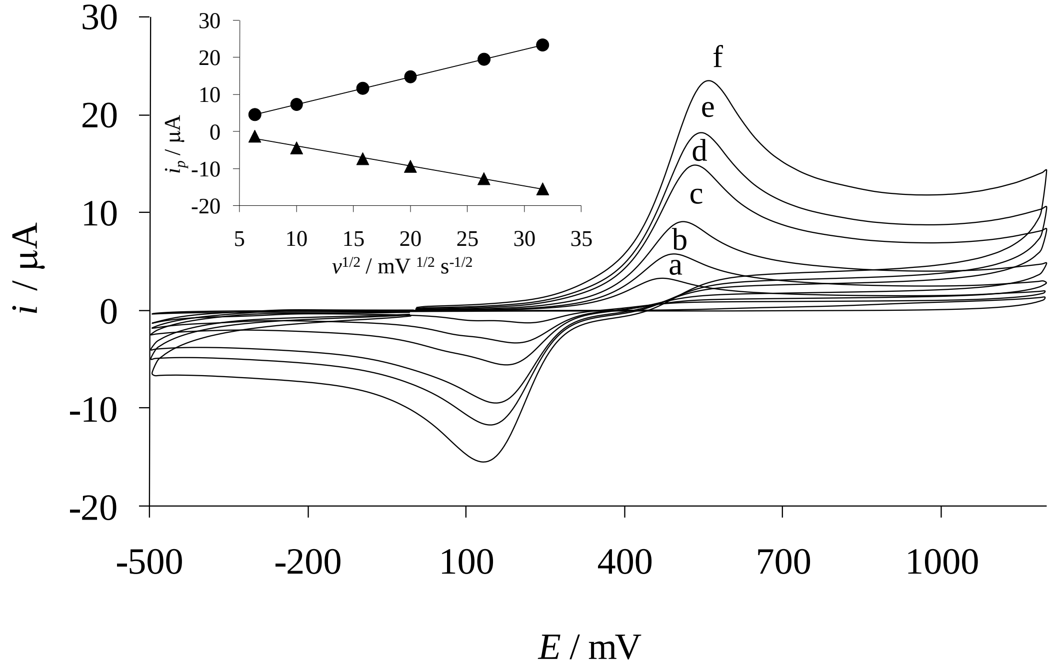


Figure 1. Experimental CVs recorded in the system CPE/0.1M NaCl, 0.1 mM DA at pH 7 at different scan rates, v, namely: (a) 40, (b) 100, (c) 250, (d) 400, (e) 700, (f) 1000 mVs^{-1}. The inset shows the variation of the peak current, i_p, as a function of $v^{1/2}$ for the anodic (●) and the cathodic (▲) peaks.

In order to determine the heterogeneous standard rate constant, k^0 and the number of electrons transferred during the DA's electrochemical reaction, we followed the methodology described in our previous work [2], therefore a plot of E_p as a function of ln v must be performed, see Figure 2A. The peaks' potentials depend on the linear relationship of ln v, as is described by equation (1) and (2) in Corona-Avendaño *et al.* [2]. With the value of the corresponding slope, and using the value of the DA diffusion coefficient of 5.40 x 10^{-6} cm^2 s^{-1} [18] the k^0 value was assessed as 0.009 and 0.007 cm^2s^{-1}, respectively. The average from both is 0.008 cm^2s^{-1}, which indicates that the DA's redox process can be termed quasireversible. From the experimental variation of the anodic or cathodic peak current, i_p, as a function of E-E^0, where $E^0 = (E_{cp}+E_{ap})/ 2$, see Figure 2B, and equation (5) in [18], it is possible to estimate the value of the energy transfer coefficient, α, which in our case was 0.45. Using this α value, equations (2) and (4) in [2] and the slope of lines in Figure 2B, the linear fittings were ln $i_{ap} = (21.158 \pm 0.130)V^{-1} (E_{ap}-E^o)-(15.434 \pm 0.707)$ and ln $i_{cp} = -(27.661 \pm 1.880)V^{-1} (E_{cp}-E^o)-(16.095 \pm 0.272)$, one can estimate the number of electrons involved during DA´s oxidation and reduction processes, as 0.94 and 0.96, respectively. From this result it is possible to conclude that DA oxidation occurs in this case through monoelectronic steps.

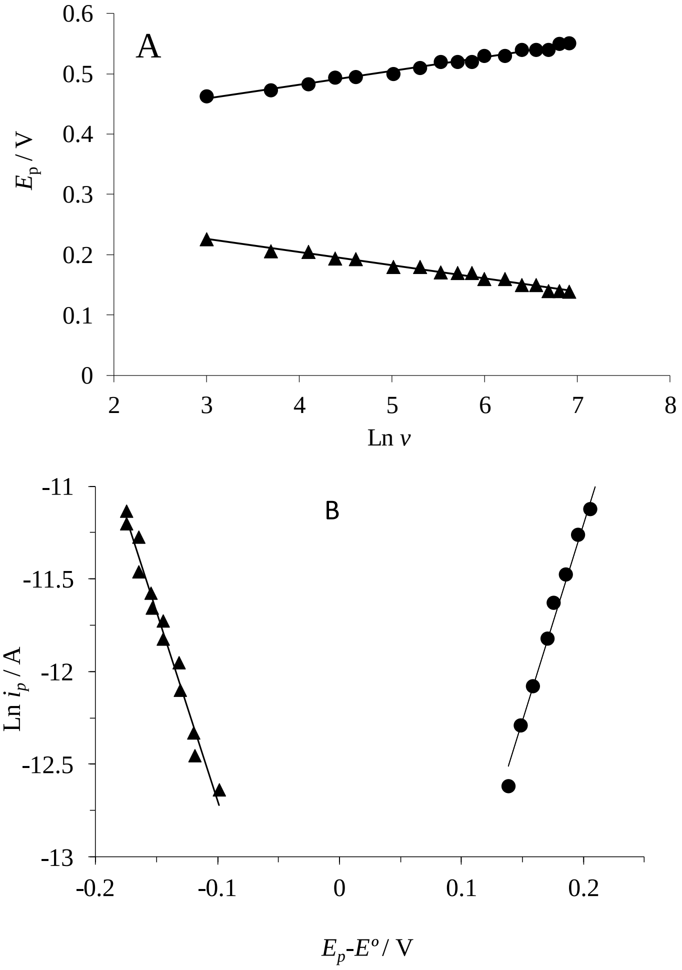
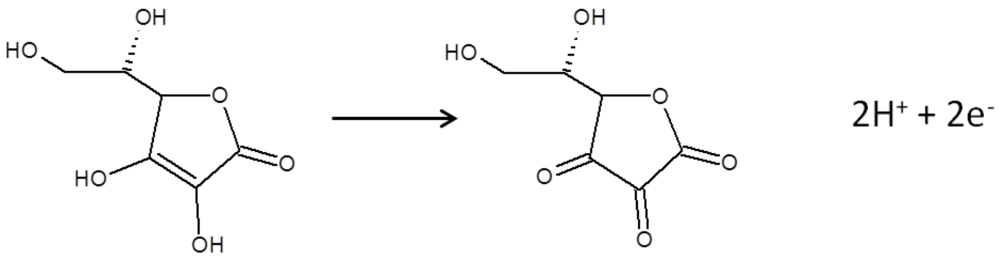
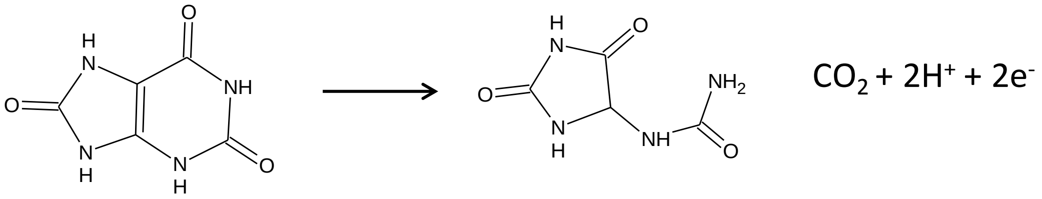


Figure 2. Experimental variation of A) the peaks' potential as a function of ln v, and B) ln i_p as a function of the difference E_p–E^o for the anodic (●) and cathodic (▲) processes. Obtained from the CVs shown in Figure 1.

3.1.1.2 AA and UA



(R2)



(R3)

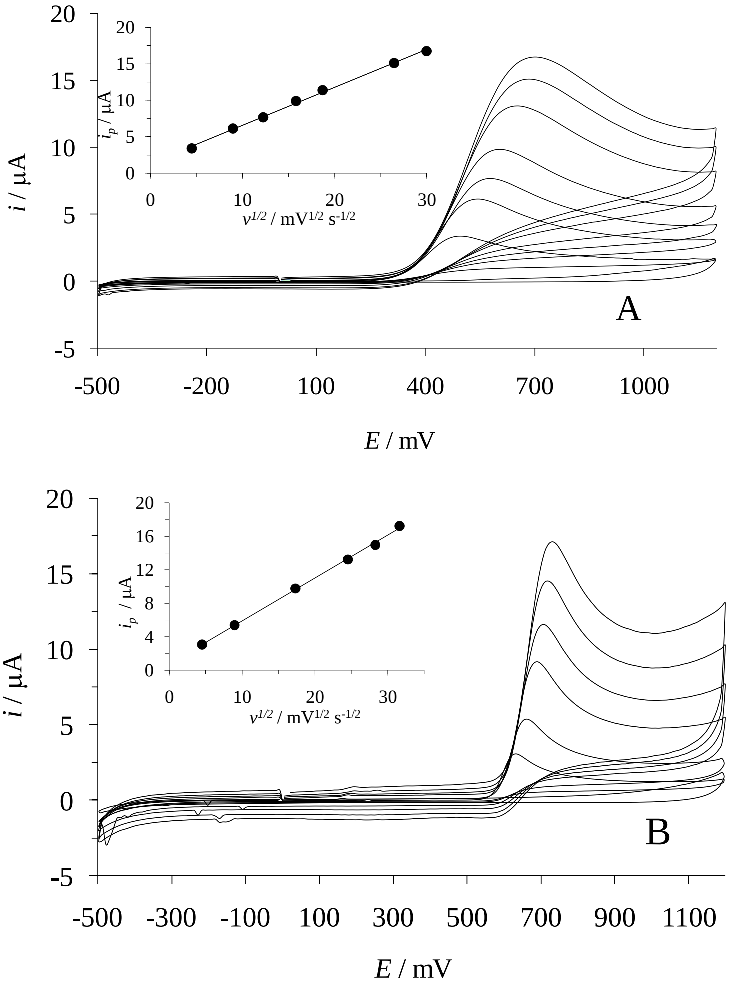
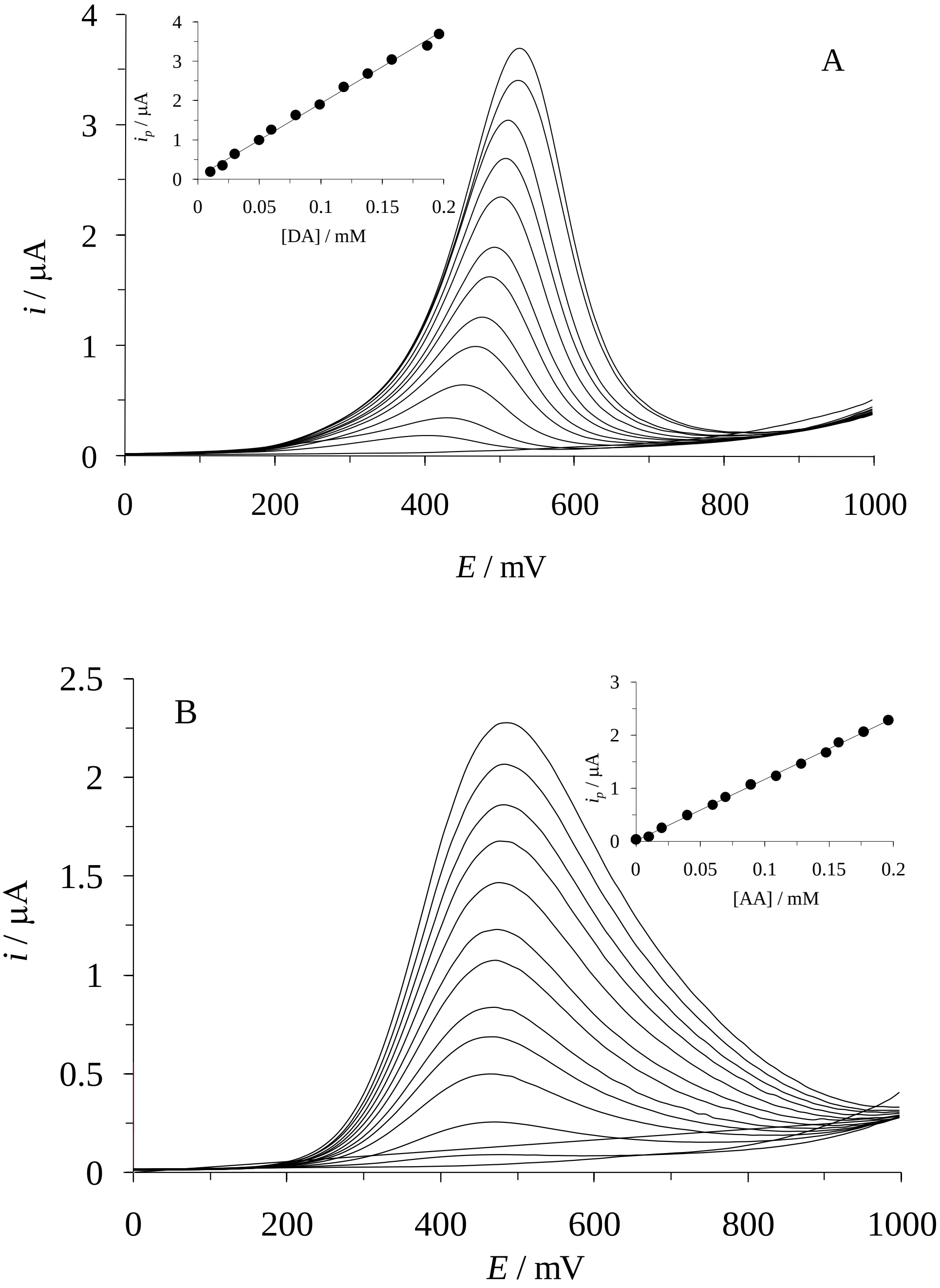


Figure 3. Family of CVs recorded in the systems A) CPE / 0.1M NaCl, 0.1 mM AA and B) CPE / 0.1M NaCl, 0.05 mM UA at pH 7 and different scan rates, from 20 to 1000 $\mathrm{mVs^{-1}}$. The insets show the respective variation of the peak current, i_p, as a function of $v^{1/2}$ for AA: i_p /μA = (1.374 ± 0.210)$\mu\mathrm{AmV^{-1}}\, v^{1/2}$ – (0.520 ± 0.011)μA and for UA: i_p /μA = (0.801 ± 0.186)$\mu\mathrm{AmV^{-1}}\, v^{½}$ + (0.512 ± 0.009) μA.

Figure 3 shows a set of CV plots recorded in the systems CPE / 0.1M NaCl, 0.1 mM AA, Figure 3A and CPE / 0.1M NaCl, 0.05 mM UA, Figure 3B, at pH 7 at different scan rates. In both cases, during the anodic potential sweep, voltammetric peaks were formed of which the peak current varies linearly as a function of $v^{1/2}$, see inset in Figures 3A and 3B, revealed that AA and UA electrochemical oxidation reactions, reactions (R2) and (R3) respectively, are diffusion-controlled processes. Moreover, also in both cases during the cathodic potential scan no significant currents were detected, thus both oxidation processes are irreversible.

3.1.2 Differential Pulse Voltammetry



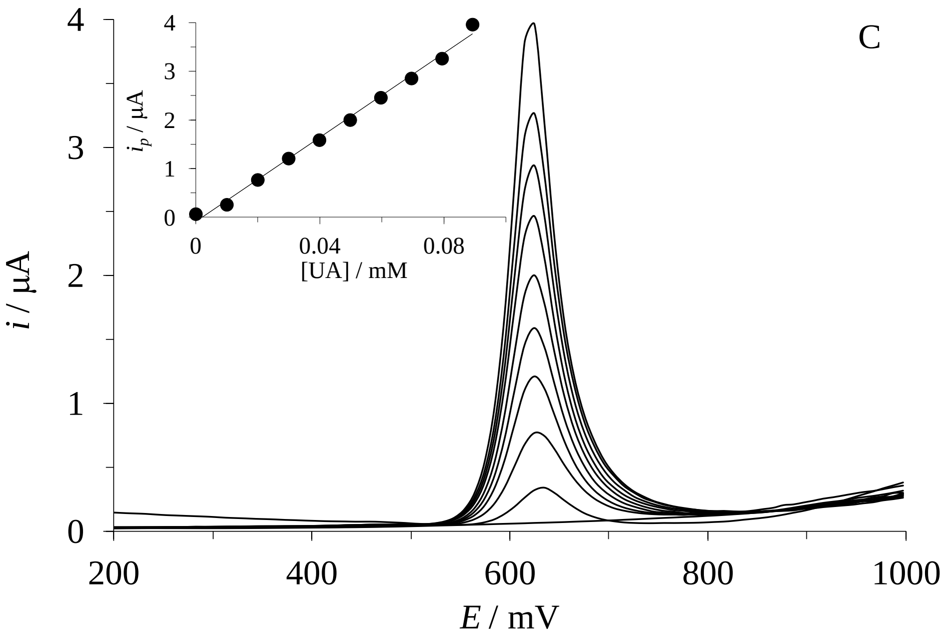


Figure 4. Family of DPVs recorded in the systems CPE / 0.1 M NaCl at pH 7, containing different concentrations (from 0 to 0.2 mM) of: A) DA, B) AA and C) UA. The insets show the respective calibration curves.

Figure 4 shows the DPVs plots recorded in the systems CPE / 0.1 M NaCl at pH 7 at different concentrations of DA (Figure 4A), AA (Figure 4B) and UA (Figure 4C). From the respective insets it is possible to note that for all cases the peak current varies linearly with DA, AA or UA concentration, thus all these substances could be electrochemically quantified when they are not mixed. The analytic parameters values namely: linearity range, sensitivity, detection (DL) and quantification limits (QL) are shown in Table 1. In agreement with the results obtained, it can be observed that the bare CPE is more sensitive toward the UA, as compared with the DA and the AA, and the lower detection limit is also reached for UA. Moreover, this CPE shows similar analytical features towards DA, AA and UA as those found using different electrodes, namely: vitreous carbon for AA [19], Triton X-100-modified CPE for DA [20] and Ni^{2+}-Prussian blue modified spectroscopic graphite for UA electrochemical quantification

Table 1. Analytic parameters obtained for the electrochemical quantification of DA, AA or UA from the respective calibration plots; see insets in Figure 4 using a bare CPE.

Sample	Linear Range / µM	Sensitivity /µA mM-1	DL / µM	QL / µM
DA	0 – 160	18.89 ± 0.07	11.34 ± 0.05	37.86 ± 0.08
AA	0 – 190	11.73 ± 0.02	7.66 ± 0.01	25.55 ± 0.05
UA	0 - 100	23.79 ± 0.04	5.63 ± 0.01	18.18 ± 0.05

4. CONCLUSIONS

This work shows that a simple CPE immersed in aqueous solution, at pH 7, of DA, AA, and UA is useful to determine these analytes with adequate sensitivity and detection limits for each of them in the μM range. Moreover, the results proved that DA, AA and UA oxidation were all diffusion-controlled processes. For DA, from CV experiments, the heterogeneous standard rate constant, k^0, and energy transfer coefficient, α, were evaluated as 0.008 cm^2s^{-1} and 0.45 respectively however, for AA and UA these parameters could not be measured because in both oxidation processes are irreversible.

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