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ORIGINAL PAPER

Homogeneous electrocatalytic oxidation of D-penicillamine with ferrocyanide at a carbon paste electrode: application to voltammetric determination

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Abstract The electrooxidation of D-penicillamine (D-PA) was studied in the presence of ferrocyanide as a homogeneous mediator at the surface of a carbon paste electrode in aqueous media using cyclic voltammetry (CV) and chronoamperometry. Under optimum pH in CV the oxidation of D-PA occurs at a potential about 380 mV less positive than that in the absence of ferrocyanide. The catalytic oxidation peak current was dependent on the D-PA concentration and a linear calibration curve was obtained in the ranges 4.0×10^{-5}–2.0×10^{-3} M and 8.0×10^{-6}–1.8×10^{-4} M of D-PA with CV and differential pulse voltammetry (DPV) methods, respectively. The detection limits (3σ) were determined as 1.9×10^{-5} and 3.2×10^{-6} M by CV and DPV methods. This method was also used for the determination of D-PA in pharmaceutical preparations by the standard addition method.

Keywords Ferrocyanide · Penicillamine · Homogeneous electrocatalysis · Carbon paste electrode · Differential pulse voltammetry · Cyclic voltammetry

1 Introduction

Thiols, R–SH are known to play many roles within physiological systems. Penicillamine (PA) is an unphysiological sulfur-containing amino acid that belongs to the aminothiols family. Penicillamine is a strong chelating agent and can react with the majority of heavy metal ions. The outstanding metal-binding capability is reflected in the pharmaceutical importance of PA [1]. Thus PA is the drug of choice in the treatment of hepatolenticular degeneration (Wilson's disease: a genetic disease that results in excessive copper deposits in the body tissues) and is also effective for the treatment of several disorders including rheumatoid arthritis, primary biliary cirrhosis, scleroderma, fibrotic lung disease, cystinuria, heavy element poisoning and progressive systemic sclerosis [2–4]. It exists in D- and L-enantiometric forms that show different biological and toxicological properties. The D-enantiomer is therapeutic and the L-enantiomer is highly toxic since it possesses the same configuration as the L-amino acids (which are constituents of proteins) and therefore interferes with the amino acid metabolism [5].

Different direct and indirect methods have been proposed for the determination of D-penicillamine including: high performance liquid chromatography with pre or post column derivatization [6–8], calorimetry [9], fluorometry [10], spectrophotometry [11–13], chemiluminescence [14], capillary electrophoresis [15, 16] and NMR spectrometry [17]. Electrochemical methods are an alternative for D-PA determination because they are cheap, simple, fast and sensitive. Mercury and mercury amalgam [18, 19] have been extensively used for thiol-compound determination; however, mercury has limitations due to its toxicity and the rapid deterioration of the electrode response [20]. Some chemically modified electrodes with various mediators such as cobalt phthalocyanine [21, 22], cobalt salophen [23], 4-*tert*-butylcatechol [24], dopamine [25] and tyrosinase [3] have been used for electrochemical determination of D-PA. Also the boron doped diamond thin film electrode has been applied for electrochemical analysis of D-PA in a flow injection system [26]. Also, many types of carbon-based electrodes such as glassy carbon [27, 28], carbon

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composites [29, 30] carbon nanotubes [31, 32] and carbon pastes [33–36] are used as modified electrodes.

Recently, we have demonstrated the suitability of ferrocyanide ion trapped in the poly (pyrrole) film prepared on the surface of carbon paste electrode as a mediator for the electrocatalytic oxidation of ascorbic acid and voltammetric determination of ascorbic acid and dopamine in the same sample [37, 38]. Also, we reported the homogeneous electrocatalysis of nitrite reduction by aqueous ferrocyanide at a carbon paste electrode [39]. This system due to the use of ferrocyanide and the inexpensive carbon paste electrode can provide a simple and low cost electrochemical sensor for catalytic oxidation detection of D-PA. In this work we investigated the suitability of ferrocyanide as a homogeneous mediator for electrocatalytic oxidation of D-PA at the surface of a carbon paste electrode in buffered aqueous media. Finally, in order to demonstrate the catalytic ability of this mediator in the electrooxidation of D-PA in real samples, we examined this method for the voltammetric determination of D-PA in pharmaceutical preparations.

2 Experimental

2.1 Reagents and materials

The solvent used for the electrochemical studies was bi-distilled water. Buffer solutions were prepared from orthophosphoric acid and its salts in the pH range 2.00–10.00. High viscosity paraffin (density = 0.88 g cm^{-3}) from Fluka was used as the pasting liquid for the carbon paste electrode. Graphite powder (particle diameter = 0.1 mm) from Merck was used as the working electrode (WE) substrate. Potassium chloride from Fluka was used as the supporting electrolyte. The potassium hexacyanoferrate and D-PA were from Fluka and were used as received. All other reagents were of analytical grade.

2.2 Working electrode

A 1:1 (w/w) mixture of graphite powder and paraffin was blended by hand mixing with a mortar and pestle for preparation of the carbon paste. Then the resulting paste was inserted in the bottom of a glass tube (internal radius 1.5 mm). The electrical connection was implemented by a copper wire lead fitted into the glass tube.

2.3 Instrumentation

The electrochemical experiments were carried out using a Potentiostat/Galvanostat (BHP 2061-Electrochemical Analysis system, Behpajooh, Iran) coupled with a Pentium III personal computer connected to a HP laser jet 6L printer. The experiments were performed in a three compartment cell. A platinum wire was used as the auxiliary electrode. A carbon paste electrode as the working electrode and a double junction Ag|AgCl|KCl_{sat} electrode as reference electrode were used. A pH-meter (Ion Analyzer 250, Corning) was used to read the pH of the buffered solution.

3 Results and discussion

3.1 Electrochemical of ferrocyanide in aqueous solutions

Previously, it has been demonstrated that electrochemical behavior of ferrocyanide at the usual solid electrodes is reversible [39]. But in this work, we studied the electrochemical behavior of ferrocyanide in 0.1 M phosphate buffered solution (pH = 7.00) with 0.1 M KCl as the supporting electrolyte at the surface of a carbon paste electrode (CPE) by cyclic voltammetry. The low cost, wide potential windows, low electrical resistance, chemical inertness and compatible with molecules and biological species are some advantages of the carbon paste electrode compared to other solid electrodes as working electrodes in electrochemical methods. Figure 1A shows the cyclic voltammogram of 1.0 mM of ferrocyanide at the various scan rates (υ = 5–1,000 mV s^{-1}) in the above mentioned condition. Anodic and cathodic peak potentials (E_{pa}, E_{pc}), half wave potential ($E_{1/2}$) and peak separation potential (ΔE_p) can be found 360, 140, 250 mV vs. Ag|AgCl|KCl_{sat} and 220 mV, respectively. ΔE_p is greater than $59/n$ mV ($n = 1$) as expected for a reversible system; which shows quasi-reversible behavior for the ferrocyanide/ferricyanide redox system. In addition, the plots of the anodic and cathodic peak currents were linearly depended on the square root of scan rate ($\upsilon^{1/2}$) at all scan rates (Fig. 1B). This behavior indicates that the redox process is diffusion-controlled.

3.2 Electrocatalytic ability of ferrocyanide at optimum pH

The effect of aqueous solution pH on the electrode process of D-PA (RSH in below) was investigated by cyclic voltammetry. Cyclic voltammograms of 1.5 mM D-PA in 0.1 M phosphate buffered solutions with various pH values were recorded at a scan rate of 10 mV s^{-1} at the surface of CPE (Fig. 2A). A potential—pH diagram was constructed by plotting the oxidation peak potential values of D-PA as a function of pH (Fig. 2B). This diagram comprises a linear segment with slope value equal to 63 mV per unit of pH in the range $5.00 < pH < 9.00$. According to the slope value,

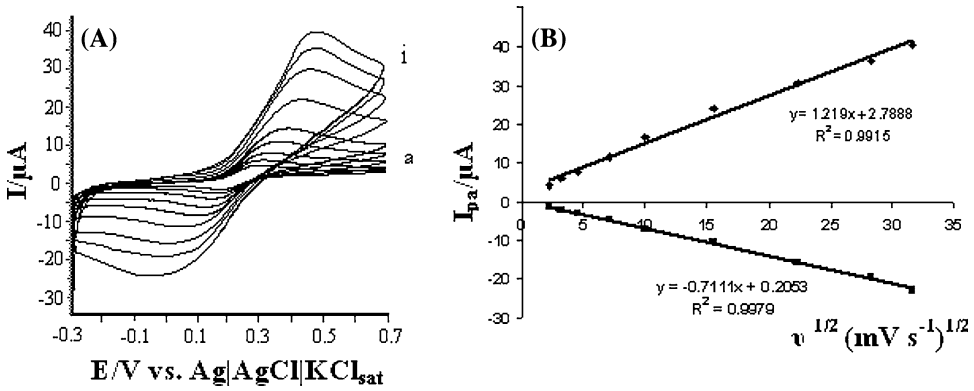


Fig. 1 **A** Cyclic voltammograms (CVs) of 0.5 mM ferrocyanide in 0.1 M phosphate buffer solution (pH 7.00) containing 0.1 M KCl as supporting electrolyte at the surface of CPE at various scan rates: (a) 5 (b) 10 (c) 20 (d) 50 (e) 100 (f) 250 (g) 500 (h) 800 (i) 1,000 mV s^{-1}. **B** Plots of anodic and cathodic peak currents of ferrocyanide vs. $\upsilon^{1/2}$ from CVs of (**a**)

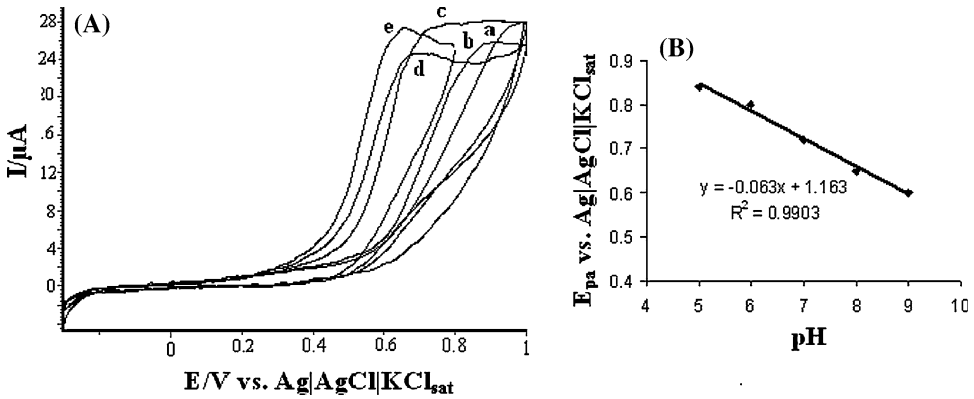


Fig. 2 **A** Cyclic voltammograms of 1.5 mM D-PA in phosphate buffer solution containing 0.1 M KCl as supporting electrolyte at the surface of CPE in various pHs: (a) 5.00 (b) 6.00 (c) 7.00 (d) 8.00 and (e) 9.00 at scan rate 10 mV s^{-1}. **B** Variation of the anodic peak current vs. pH

the reaction scheme probably involves sulfide radical formation via the following mechanistic steps [40]:

$$RSH \rightarrow RS^- + H^+ \quad (1)$$

$$RS^- \rightarrow RS^\bullet + e^- \quad (2)$$

$$2RS^\bullet \rightarrow RSSR \quad (3)$$

$$\text{Overall: } 2(RSH \text{ or } RS^-) \rightarrow RSSR + 2e^- \quad (4)$$

Therefore, the electrochemical behavior of D-PA and ferrocyanide are dependent on pH [23, 39]. Therefore, pH optimization of the solution is necessary in order to obtain the electrocatalytic oxidation of D-PA by ferrocyanide. Thus, we studied the electrochemical behavior of D-PA in 0.1 M phosphate buffered solutions with various pH values ($2.00 < pH < 10.00$) at the surface of CPE in the presence of ferrocyanide by cyclic voltammetry. Cyclic voltammograms of D-PA in strong acidic medium (such as pH 2.00) show that the oxidation of D-PA cannot be catalyzed by ferricyanide (Fig. 3A, curve a). However the oxidation of D-PA and ferrocyanide are pH-dependent and shift toward less positive potential with increasing solution pH. So, the thermodynamic driving force for the catalysis varies with pH, making the peak currents and the shapes of the cyclic voltammograms different at different pH values. Consequently, buffered solutions of pH ≥4.00 favor the catalyzed oxidation of D-PA which is initiated by ferricyanide produced from electrooxidation of ferrocyanide.

This was manifest as a gradual growth in the anodic peak current and a simultaneous decrease in the cathodic peak current of cyclic voltammogram of $Fe(CN)_6^{4-/3-}$ redox system in the presence of D-PA at the CPE (Fig. 3A, curves b–d). The variation of I_{pa} with pH is shown in Fig. 3B. The electrocatalytic current decreases at high pH values. Therefore, pH 7.00 was chosen as the optimum pH for the electrocatalysis of D-PA oxidation by $Fe(CN)_6^{3-}$ at the CPE. The anodic peak potential of D-PA was shifted to a less-positive potential with increasing pH in the presence of ferrocyanide at the surface of CPE (Fig. 3C).

Comparison of the cyclic voltammograms of 0.5 mM of ferrocyanide in the 0.1 M phosphate buffered solution (pH 7.00) in the absence (Fig. 4c) and presence of 1.5 mM of D-PA (Fig. 4d) with the cyclic voltammogram of 1.5 mM of D-PA (Fig. 4b) at the surface of CPE in the same pH, demonstrated that the electrooxidation of D-PA can be catalyzed by electrochemically generated $Fe(CN)_6^{3-}$. The reaction can be defined in Scheme 1, whereby the generation of $Fe(CN)_6^{3-}$ at the CPE surface catalyzes the oxidation of D-PA. Then, the $Fe(CN)_6^{3-}$ undergoes a catalytic reduction by D-PA back to $Fe(CN)_6^{4-}$, which can be re-oxidized electrochemically to produce an enhancement in the oxidation current. The kinetic mechanism of this electrocatalyzed reaction (EC′) process remains unexplained due to the oxidation

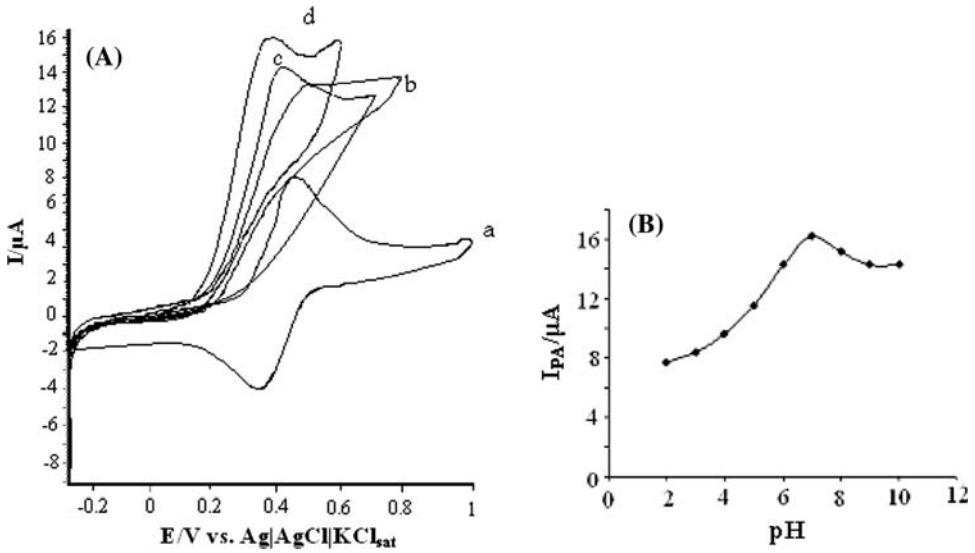


Fig. 3 **A** Cyclic voltammograms (CVs) of 0.5 mM ferrocyanide in the presence of 1.5 mM D-PA in 0.1 M phosphate buffer solution containing 0.1 M KCl as supporting electrolyte at the surface of CPE in various pHs: (a) 2 (b) 4 (c) 6 (d) 7 at scan rate 10 mV s^{-1}. **B** Variation of the anodic peak current vs. pH. **C** Variation of the anodic peak potential vs. pH

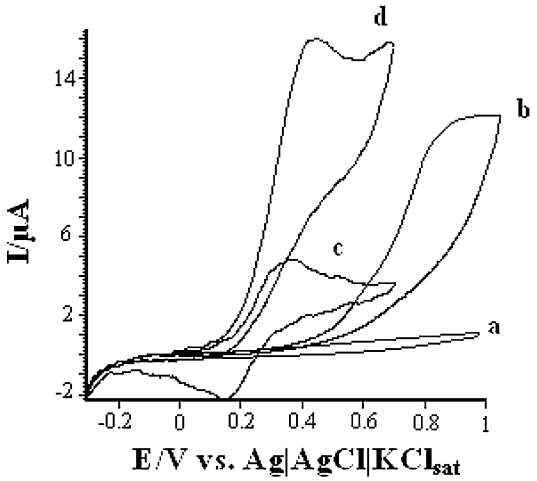
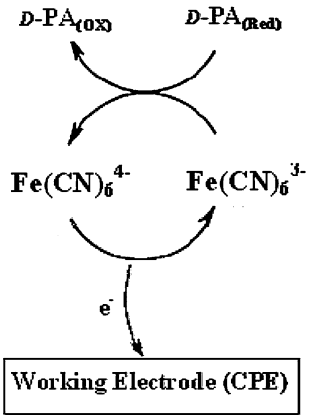


Fig. 4 Cyclic voltammograms of **a** CPE in 0.1 M phosphate buffer solution (pH 7.00) at scan rate of 10 mV s^{-1} and **b** as (**a**) in the presence of 1.5 mM D-PA, **c** as (**a**) and **d** as (**b**) in the presence of 0.5 mM ferrocyanide



Scheme 1 Homogeneous electrocatalytic oxidation of D-PA with ferrocyanide at CPE

processes of $Fe(CN)_6^{4-}$ and D-PA having similar voltages at CPE. Figure 3b shows that the oxidation of D-PA at the bare CPE occurs irreversibly with a peak potential of nearly 800 mV vs. Ag|AgCl|KCl_{sat}, whereas the cyclic voltammogram of supporting electrolyte at the CPE did not show any anodic and cathodic peaks (Fig. 4a). Comparison of Fig. 4b and d shows that the oxidation of D-PA in the presence of ferrocyanide at the surface of CPE occurs at a potential about 380 mV less positive than that in the absence of ferrocyanide. The electrocatalytic

Table 1 Comparison of the efficiency of some modified electrodes in the electrocatalytic oxidation of D-PA

Electrode	Modifier	pH	Peak potential shift (mV)	LDR (μM)	LOD (μm)	References
CP	Cobalt salophen	3.00	50	10–1,000[a]	1.00[a]	[23]
GC[c]	4-*tert*-Butylcatechol	7.00	420	0.02–80[b]	0.007[b]	[41]
CP	Ferrocene carboxylic acid	7.00	420	6.5–100[a]	6.15[a]	[42]
CP	Ferrocyanide	7.00	380	8–180[a]	3.20[a]	This work

[a] LDR and LOD were obtained using differential pulse voltammetry

[b] LDR and LOD were obtained using cyclic voltammetry

[c] GC is on the top of the rotating biosensor

oxidation of D-PA has been investigated at the surface of other chemically modified electrodes. Our value is comparable with other results (see Table 1) [23, 41, 42].

3.3 Double potential step chronoamperometry

Double potential step chronoamperometry, as well as other electrochemical methods, was employed for the investigation of electrochemical processes. Figure 5A shows the current–time curves of ferrocyanide by setting the working electrode potential at 0.40 V (first potential step) and 0.04 V (second potential step) vs. Ag|AgCl|KCl$_{sat}$ for various concentration of D-PA in buffered aqueous solutions (pH 7.00). There is no net cathodic current corresponding to the reduction of $Fe(CN)_6^{3-}$ to $Fe(CN)_6^{4-}$ in the presence of D-PA, when the second potential step is employed. The oxidation current increases with increasing D-PA concentration at the first potential step. While the forward and backward potential step chronoamperometry of $Fe(CN)_6^{3-}$ in the buffered solution in the absence of D-PA at the CPE show very symmetrical chronoamperograms with an equal charge consumed for the oxidation and reduction of $Fe(CN)_6^{4-}$and $Fe(CN)_6^{3-}$ (Fig. 5B, curve a′). However, in the presence of D-PA, the charge value associated with forward chronoamperometry is significantly greater than that observed for backward chronoamperometry (Fig. 5B, curve e′).

The rate constant for the chemical reaction can be evaluated by chronoamperometry according to the method described in [43]:

$$I_C/I_L = \pi^{1/2}\gamma^{1/2} = \pi^{1/2}(K_h C_b t)^{1/2} \quad (5)$$

where I_C is the catalytic current in the presence of D-PA and I_L is the limited current in the absence of D-PA, γ is the argument of the error function, C_b is the bulk concentration of D-PA, mol cm^{-3}, K_h and t are the catalytic rate constant (cm^3 mol^{-1} s^{-1}) and time elapsed (s). The above equation can be used to calculate the rate constant of the catalytic process, K_h. The value of K_h can be simply calculated for a given concentration of substrate from the slope of the I_C/I_L vs. $t^{1/2}$ plot. The calculated value of K_h is 4.33×10^2 cm^3 mol^{-1} s^{-1} using the slope of the $I_C/I_L - t^{1/2}$ plot (with linear equation $y = 1.4766x + 1.4147$, $R^2 = 0.994$). This value of K_h also explains the sharp feature of the catalytic peak observed for the oxidation of D-PA by $Fe(CN)_6^{3-}$.

3.4 Electrocatalytic determination of D-PA

The electrocatalytic peak current of D-PA oxidation by $Fe(CN)_6^{3-}$ at the CPE was used for determination of D-PA in solution. Cyclic voltammetry and differential pulse voltammetry experiments of 0.5 mM of ferrocyanide were performed in phosphate buffer solution containing various concentrations of D-PA (Fig. 6). The electrocatalytic peak

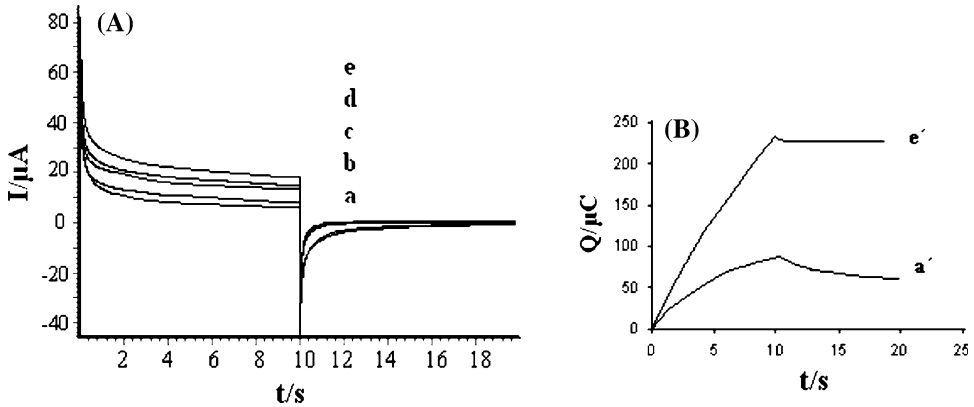


Fig. 5 **A** Double step potential chronoamperograms obtained for 0.5 mM ferrocyanide in the (a) absence and presence of (b) 0.3 (c) 1.0 (d) 1.2 (e) 1.6 mM of D-PA in 0.1 M phosphate buffer solution (pH 7.00). First and second potential steps were 0.40 and 0.04 V vs. Ag|AgCl|KCl$_{sat}$. **B** The charge–time curves: (a′) for curve (a) and (e′) for curve (e)

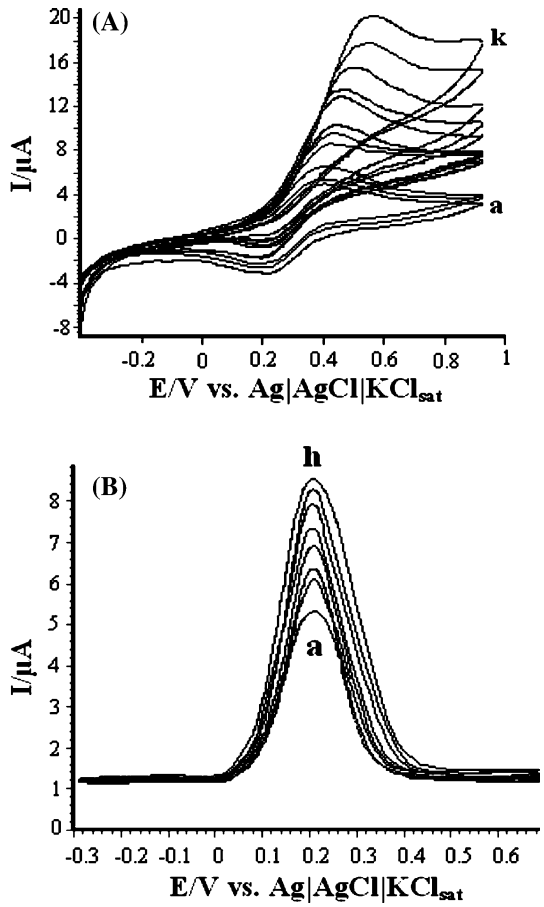


Fig. 6 **A** Cyclic voltammograms of 0.5 mM ferrocyanide in the presence of various D-PA concentration: (a) absence and (b) presence of 0.04 (c) 0.1 (d) 0.3 (e) 0.5 (f) 0.7 (g) 0.9 (h) 1.0 (i) 1.2 (j)1.5 and (k) 2.0 mM at a scan rate of 10 mV s^{-1}. **B** Differential pulse voltammograms of 0.5 mM ferrocyanide at the surface CPE in (a) absence and presence of (b) 0.008 (c) 0.020 (d) 0.040 (e) 0.080 (f) 0.110 (g) 0.160 and (h) 0.180 mM of D-PA in 0.1 M phosphate buffer solution (pH 7.00)

current of D-PA oxidation was linearly dependent on D-PA concentration. The calibration plot was linear in the range 4.0×10^{-5}–2.0×10^{-3} M (with linear equation $y = 8.0443\ x + 5.2807$, $R^2 = 0.998$) and 8.0×10^{-6}–1.8×10^{-4} M (with linear equation $y = 15.581\ x + 5.8418$, $R^2 = 0.990$) in the cyclic voltammetry and differential pulse voltammetry. The detection limits (3σ) were 1.9×10^{-5} and 3.2×10^{-6} M with CV and DPV, respectively. Thus, the catalytic oxidation of D-PA by $Fe(CN)_6^{3-}$ at the CPE can readily be applied for the determination of D-PA.

Also, we studied the influence of other compounds such as alanine, tryptophan, cysteine and glutathione on the electrocatalytic peak current of D-PA oxidation in 0.1 M phosphate buffer solution at the surface of CPE using CV. The presence of alanine, tryptophan and cysteine did not influence the determination of D-PA in the experimental conditions. But glutathione, in large concentration, did influence the determination of D-PA.

3.5 Determination of D-PA in pharmaceutical preparations

In order to demonstrate the electrocatalytic oxidation of D-PA in pharmaceutical preparation, we examined this ability in the voltammetric determination of D-PA in the D-PA capsules (containing 250 mg D-PA) purchased from local sources (Laboratories Rubio, S.A. Spain). The precision of the method was obtained on the basis of intra-assay using the standard addition method. The intra-assay data is summarised in Table 2. In the United States pharmacopoeia (USP) PA tablets are assayed by an ion-pairing HPLC method [12]. There is no significant difference between the labelled contents and those obtained by the proposed method with satisfactory recovery.

4 Conclusions

Ferrocyanide can act as a homogeneous mediator for the electrocatalytic oxidation of D-PA in buffered aqueous solution (pH 7.00) at the surface of a CPE. Under optimum conditions the oxidation peak potential of D-PA is shifted by 380 mV to a less positive potential in the presence of ferrocyanide. Therefore, the electrocatalytic oxidation peak

Table 2 Determination of D-PA in D-PA capsule and recovery data obtained for D-PA added at specified concentrations to buffer solution (pH 7.00) at the surface of CPE using ferrocyanide as a homogeneous mediator

Amount added (mg mL^{-1})	Amount found (mg mL^{-1})	Mean recovery (%)		T_{exp}	F_{exp}
		Proposed-method[a]	USP-method[b]		
0.5 mg per tablet	0.504	100.8 ± 1.56	102.6 ± 0.6	2.40	6.76
0.93	0.980	105.3 ± 4.0			
1.05	1.098	104 ± 7.0			
1.50	1.480	98 ± 8.5			

[a] Result based on five replicate determinations per samples

[b] Result based on five replicate determinations per samples. Theoretical values for $t = 2.45$ and $F = 6.94$ ($P = 0.05$)

current of D-PA in the presence ferrocyanide was used for voltammetric determination of D-PA in aqueous solution. This method can be employed as a new and simple method for the voltammetric determination of D-PA in pharmaceutical preparations.

References

1. Chong CR, Auld DS (2000) Biochemistry 39:7580
2. Klein D, Lichtmannegger J, Heinzmann U, Summer KH (2000) J Hepatol 32:193
3. Preedy VR, Wassif WS, Baldwin D, Jones J, Falkous G, Marway JS, Mantle D, Scout DL (2001) Int J Biochem Cell Biol 33:1013
4. Committee of Chinese Pharmacopoeia (2005) Chinese pharmacopoeia (Part II). Chemical Industry Press, Beijing
5. Cervantes G, Moreno V, Molins E, Quiros M (1998) Polyhedron 17:3343
6. Russell J, McKeown JA, Hensman C, Smith WE, Reglinski J (1997) J Pharm Biomed Anal 15:1757
7. Beales D, Finch R, McLean AEM, Smith M, Wilson ID (1981) J Chromatogr 226:498
8. Bystryakov VP, Lanin SN, Arzamastsev AP (1991) Khim Farm Zh 25:81
9. Al-Majed AA (1999) J Pharm Biomed Anal 21:827
10. Al-Majed AA (2000) Anal Chim Acta 408:169
11. Besada A, Tadros NB, Gawargious YA (1989) Mikrochim Acta 3:143
12. Suliman FEO, Al-Lawati HAJ, Al-Kindy AMZ, Nour IEM, Salama SB (2003) Talanta 61:221
13. Corominas BGT, Pferzschner J, Icardo MC, Zamora LL, Calatayud JM (2005) J Pharma Biomed Anal 39:281
14. Zhang Z, Baeyens WRG, Zhano X, Weken GVD (1997) Anal Chim Acta 347:325
15. Wronski M (1996) J Chromatogr B 676:29
16. Zinellu A, Carru C, Sotgia S, Deiana L (2004) J Chromatogr B 803:299
17. Ibrahim SE, Al-Badr AA (1980) Spectrosc Lett 13:471
18. Rabenstein DL, Yamashita GT (1989) Anal Biochem 180:259
19. Yamashita GT, Rabenstein DL (1989) J Chromatogr 491:341
20. Zhang S, Sun W, Zhang W, Qi W, Jin L, Yamamoto K, Tao S, Jin J (1999) Anal Chim Acta 386:21
21. Favaro G, Fiorani M (1996) Anal Chim Acta 332:249
22. Martin RS, Gawron AJ, Fogarty BA, Regan FB, Dempsey E, Lunte SM (2001) Analyst 126:277
23. Shahrokhian S, Sauri A, Khajehsharifi H (2004) J Electroanal Chem 565:95
24. Torriero AAJ, Salinas E, Marchevsky EJ, Raba J, Silber JJ (2006) Anal Chim Acta 580:136
25. Shahrokhian S, Bozorgzadeh S (2006) Electrochim Acta 51:4271
26. Wangfuengkanagul N, Chailapakul O (2002) Talanta 58:1213
27. Hart JP, Norman MD, Tsang S (1995) Analyst 12:1059
28. Zen JM, Kumar AS, Chen JC (2001) Anal Chem 73:1169
29. Spãtaru N, Sarada BV, Popa E, Tryk DA, Fujishima A (2001) Anal Chem 73:514
30. Wang LH, Chen ZS (1997) Electroanalysis 9:1294
31. Zhao Q, Gan Z, Zhung Q (2002) Electroanalysis 14:1609
32. Martin CR, Mitchell DT (1998) Anal Chem 70:332
33. Shahrokhian S, Amini MK, Mohammadpoor-Baltork I, Tangestaninejad S (2000) Electroanalysis 12:863
34. Ojani R, Raoof JB, Zamani S (2005) Electroanalysis 17:1740
35. Raoof JB, Ojani R, Ramine M (2006) Electroanalysis 18:1722
36. Raoof JB, Ojani R, Beitollahi H (2007) Electroanalysis 19:1822
37. Raoof JB, Ojani R, Nadimi SR (2004) Electrochim Acta 271:49
38. Raoof JB, Ojani R, Nadimi SR (2005) Electrochim Acta 50:4694
39. Ojani R, Raoof JB, Zarei E (2006) Electrochim Acta 52:753
40. Tan WT, Bond AM, Ngooi SW, Lim EB, Goh JK (2003) Electrochim Acta 491:181
41. Torriero AAJ, Piola HD, Martinez NA, Panini NV, Raba J, Silber JJ (2007) Talanta 71:1198
42. Raoof JB, Ojani R, Chekin F (2007) Electroanalysis 19:1883
43. Galus Z (1967) Fundamentals of electrochemical analysis. Ellis Horwood, New York