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Electroanalytical Determination of Captopril in Pharmaceutical Formulations Using Boron-Doped Diamond Electrodes

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Captopril lacks of an aromatic chromophore required for facile direct UV detection and also has two chiral centers; therefore its determination in pharmaceutical dosage forms is very challenging. Here, we developed an analytical methodology and quantified captopril in two samples of pharmaceutical formulations by square-wave voltammetry. The analytical signal response was obtained by electrochemical oxidation of the captopril drug at a boron-doped diamond electrode. The determination was carried out in 0.04 mol L^{-1} Britton-Robinson pH 9 buffer solution. Captopril oxidation reveals well-defined irreversible oxidation peaks. The analytical curve was obtained in the concentration range from 20 to 100 mg L^{-1} (r = 0.9986) with a detection limit of 36.0 µg L^{-1} (0.165 µmol L^{-1}). For one sample analyzed, recovery values were in the range 96.6–98.14%, while for the other sample they were within 97.6 and 98.5%, indicating no matrix interference effects on the analytical determination for both captopril commercial samples.

Keywords: Captopril, pharmaceuticals, electrochemical oxidation, square-wave voltammetry, boron-doped diamond electrode.

1. INTRODUCTION

Captopril (Figure 1) (2S)-3-mercapto-2-methyl-1-oxo-proptonyl]-L-proline [1], the first orally active and specific inhibitor of Angiotensin Converting Enzyme (ACE). It blocks the conversion of angiotensin I to angiotensin II by inhibiting the angiotensin converting enzyme and inactivates

bradykinin, a potent vasodilator. The hypotensive activity of captopril probably results both from inhibitory action on renin angiotensin system and simulating action on kallikerin-kinin system [2].

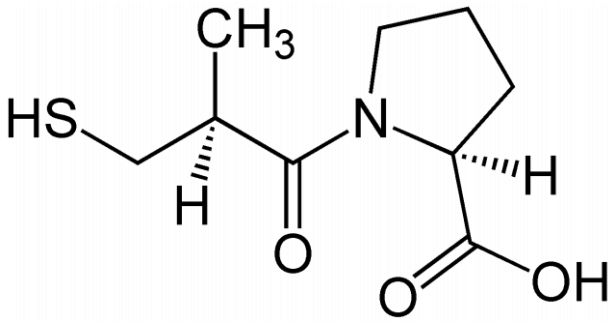

Figure 1. Chemical structure of captopril.

Various instrumental methods have been developed for the determination of captopril including high-performance liquid chromatography [3–5], colorimetry [6], fluorometry [7, 8], chemiluminescence [9, 10], capillary electrophoresis [11,12] spectrophotometry [13, 14] and mass spectrometry [15]. Chemical derivatization was applied in the majority of these methods, mainly to stabilize the sufhydryl group and prevent the formation of disulfide dimers, and to introduce a chromophoric or a fluorophoric group, thus enhancing detection sensitivity and selectivity. However, the direct determination of captopril is desirable to overcome the complexity, the increased time, and the cost of derivatization. Electrochemical techniques are useful alternative methods widely used in pharmaceutical applications. They are usually easy and rapid to perform and are less expensive than chromatographic methods. In addition, the sensitivity of electrochemical methods is often greater than that of spectrophotometric procedures.

There are several literature reports on chemically modified electrodes for captopril sensing based on various electron mediators such as cobalt-5-nitrolsalophen [16], nano-TiO_2/ferrocene carboxylic acid [17], multiwall carbon nanotubes [18–22], ferrocenedicarboxylic acid [23], chlorpromazine [24] and l-aminoacid oxidase biosensor [25].

The procedures in electroanalysis strongly depend on working-electrode materials, increasing the interest in the development of new electrode materials. Carbon materials such as pyrolytic graphite, glassy carbon, and boron-doped diamond (BDD) have been widely used for electrochemical applications [26–28]. It is well established that BDD electrodes have several advantages compared with other carbon surfaces. BDD electrodes have been extensively studied in recent years focusing in both their fundamental electrochemical properties [29–32] and from technological point of view [33, 34].

The outstanding electrochemical features of this material, including a wide potential window in aqueous solutions [35], very low background current [36], weak adsorption for most types of organic molecules [37], high stability of response [38] and good electroactivity toward certain organic species all of which deactivate the surface of other conventional electrodes [39]—make this new material promising for electroanalytical applications [40–44], electrosynthesis [39], and electrochemical

combustion [45–47], as well as for use as a supporting material in electrocatalysis [28,48–50]. Recent studies reported in the literature have shown that several inorganic, organic and biomolecules can be satisfactorily determined with the use of BDD electrodes [42, 51]. Siangproh et al. [52] used hydrodynamic voltammetry and flow injection analysis with amperometric detection to determine captopril in standard chemical form and in commercial available tablets on a BDD electrode.

The combination of square-wave voltammetry (SWV) and BDD electrodes is interesting and desirable alternative for the analytical determination of some organic molecules [43, 52]. So, in view of the lack of a simple and direct electroanalytical methodology for the determination of captopril, we developed an electrochemical method capable of directly quantifying captopril in commercial pharmaceutical preparations, using SWV with BDD as the working electrode.

2. EXPERIMENTAL

All reagents used were analytical grade and all solutions were prepared in ultrapure water purified by a Milli-Q® system from Millipore. Standard captopril (99.0 %) was supplied by Sigma Chemical (USA) and was used without further purification.

The stock solution of captopril reference substance was prepared by dissolving 50 mg of captopril in 100 mL of ultrapure water. To prepare the sample solutions, twenty tablets containing 50 mg of captopril were accurately weighed and crushed to a fine powder to obtain the average weight, respectively. Amounts of powdered tablets equivalent to 50 mg of captopril were transferred to a 250 mL volumetric flask. Then the mixture was ultrasonically shaken (15 min).

The BDD electrodes were prepared in the *Centre Suisse d'Electronique et de Microtechnique* SA (CSEM), Neuchâtel, Switzerland, using the hot filament chemical vapor deposition (HF-CVD) technique with filament temperatures in the range of 2440–2560 °C and a gaseous mixture containing methane, H_2, and trimethylboron, with a final boron content of the order of 800 ppm.

The electrochemical experiments were carried out in a one-compartment Pyrex® glass cell provided with three electrodes and degassing facilities for N_2 bubbling. The working electrode was glued onto a copper plate using a silver paste. The copper plate and the BDD edges were later isolated with Araldite® resin, leaving an exposed area of 0.090 cm^2. The reference electrode used was Ag/AgCl, where the all potentials are referred to this electrode. The auxiliary electrode was a 2.0 cm^2 Pt foil. The electrochemical experiments were also performed using an EMSTAT 1 electrochemical instrument controlled by a personal microcomputer through the PS.Lite 1.7.3 Software. All solutions were deoxygenated by bubbling N_2 for 10 min prior to measurements and the solutions were blanketed with the gas during measurements.

Analytical curves were obtained by the standard addition method. The measurements were performed without pre-treatment of the solutions but the pH was adjusted appropriately to the desired value in each case. Cyclic voltammetry (CV) and SWV were used as electroanalytical tools for the determination of captopril in aqueous solutions. The BDD electrodes were pre-treated at +3.0 and -3.0 (*vs.* HESS), 30 s each, in a 0.1 mol L^{-1} $HClO_4$ solution (cathodized BDD electrode).

For the quantitation of captopril in tablet dosage forms, the respective stock solutions were diluted to appropriate concentration, filtered, analyzed in triplicate and the percentage recoveries of the drug calculated.

3. RESULTS AND DISCUSSION

A cathodic polarization was necessary for conditioning the BDD surface prior to electroanalytical determinations. Such pretreatment improves the voltammetric response of BDD surfaces, resulting in very low quantification limits and high data reproducibility [30-32]. Afterwards, the initial cyclic voltammetric experiments were conducted using standard solutions of captopril in medium of Britton-Robinson (B-R) buffer solution (0.4 mol L^{-1}) in the pH range 2–10. In quantitative terms, the data on current response showed the best values to be those obtained using alkaline solutions. This finding led to the choice of Britton–Robinson buffer pH 9 as the electrolyte for the analytical determinations. The value found (pH 9) is very close to that reported in the literature [52] and it was chosen as optimal for the rest of the experiments. The voltammetric profile shown in Figure 2 reveals well-defined irreversible oxidation peaks for captopril on the BDD electrode with and without performing a cathodic pre-treatment (dashed curve and dotted curve, respectively).

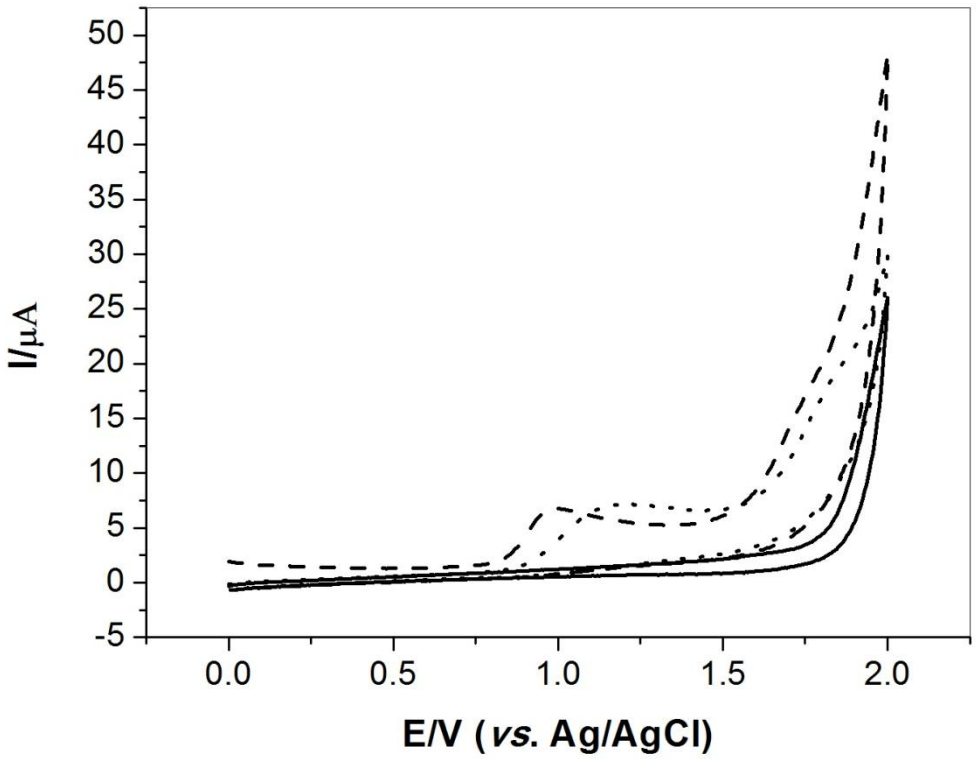

Figure 2. Cyclic voltammograms obtained at a BDD electrode at 0.1 V s^{-1}, in B-R buffer (pH 9) (solid line) and for captopril (3.8×10^{-4} mol L^{-1}) at the BDD electrode with (dashed line) and without cathodic pre-treatment (dotted line).

Captopril oxidation on BDD is characterized by the presence of two peaks at 1.0 and 1.8 V (*vs* Ag/AgCl). The peaks can be attributed to the thiol group that is electrooxidized to form disulfide, suggesting a dimerization mechanism [53]. No cathodic peak was observed on the reverse scan within the investigated potential range (0 to +1.5 V) because thiol oxidation is an electrochemically irreversible process [52]. The first peak of the oxidation of captopril on the BDD cathodically pre-treated shifted 0.2 V to more negative potential compared with the response at the BDD without cathodic pre-treatment (dotted line). Notably, the pretreated electrode showed peaks with better resolutions.

From the scan rate dependence study carried out varying the scan rate from 0.05 to 0.3 V s^{-1} we found a linear relation between Ip and $\nu^{1/2}$ for captopril with a correlation coefficient of approximately 0.99 (Figure 3). From the diagnostic criteria of cyclic voltammetry, this behavior is characteristic of diffusion-controlled processes [54].

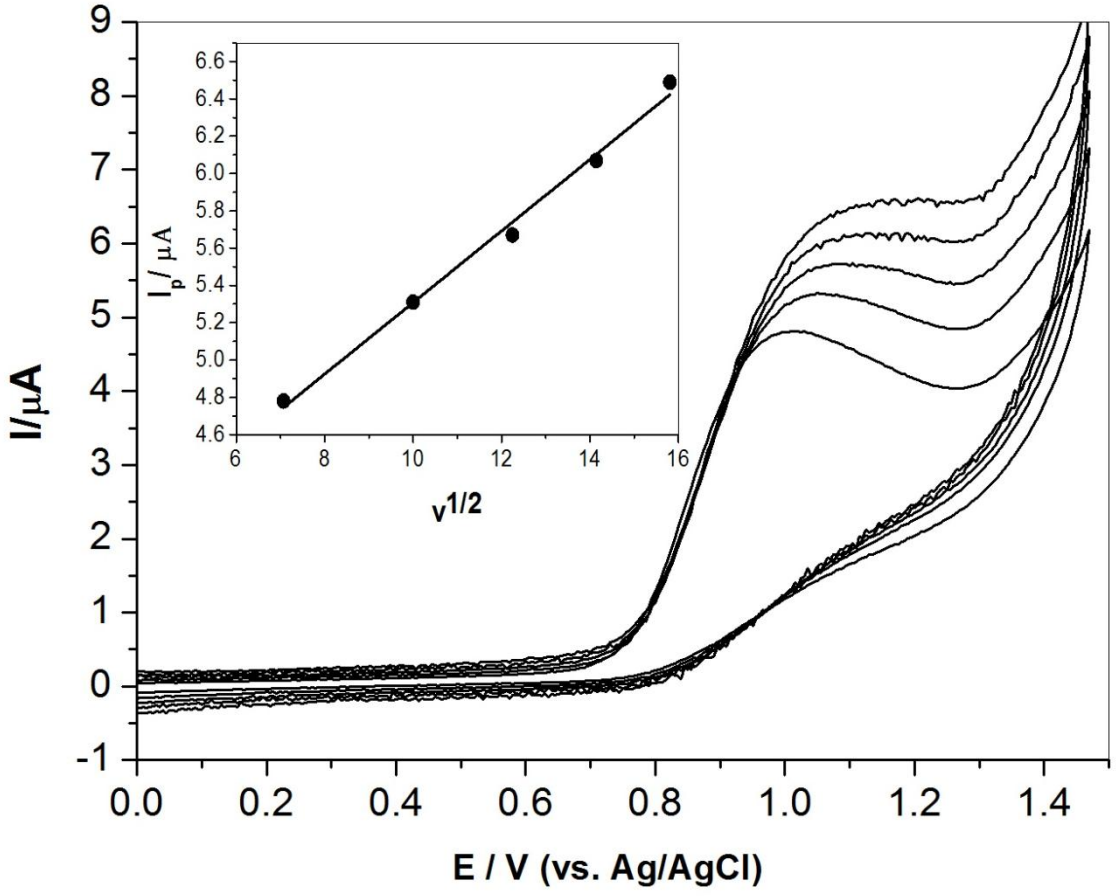

Figure 3. Cyclic voltammograms of the captopril electrochemical oxidation at a BDD electrode in B-R buffer (pH 9) containing 2.5 × 10^{-4} mol L^{-1} of captopril at different scan rates: 50, 100, 150, 200 and 250 mV s^{-1}. Inset: Linear relation between current peak *vs* $\nu^{1/2}$ observed in the same experimental conditions.

The response obtained by square-wave voltammetry is dependent on parameters such as frequency (*f*), pulse height (ΔEp) and scan increment (ΔEs), which have a combined influence on the

peak current. Hence, they were analyzed in order to optimize the experimental set-up for captopril determination. The square-wave parameters optimization was carried out in 1.0×10^{-4} mol L^{-1} captopril solutions in 0.04 mol L^{-1} B-R buffer, pH 8. The anodic current increased with the increase in the frequency at constant ΔEp and ΔEs. The frequency exhibits linear behavior when I_p does not exceed 50 Hz, whereas for values higher than 60 Hz no contribution can be observed in the electroanalytical response. At higher frequencies, a broadening and a distortion in the voltammograms were also observed. An excellent compromise between the voltammetric profile and sensitivity was obtained at the intersection point. Consequently, the frequency of 50 Hz was chosen and used in subsequent experiments. Finally, SWV amplitude was evaluated again at 50 Hz and 5 mV of frequency and scan increment, respectively. The I_p maximal value was also obtained at amplitude of ~40 mV. This ΔEp value was then used throughout the following experiments. The highest current density was observed, and then selected, for ΔEs of 5 mV. The optimized values were subsequently used to validate the proposed method, as well as for captopril determination in the two commercial samples analyzed.

With these voltammetric parameters optimized, an electroanalytical methodology was developed for the determination of captopril in pharmaceutical formulations. The square-wave voltammograms of the standard solutions as a function of captopril concentration in aqueous solution pH 9 (B-R buffer) are shown in Figure 4. The calibration plot yielded a straight line (r = 0.998, n = 3) (Inset of Figure 4)

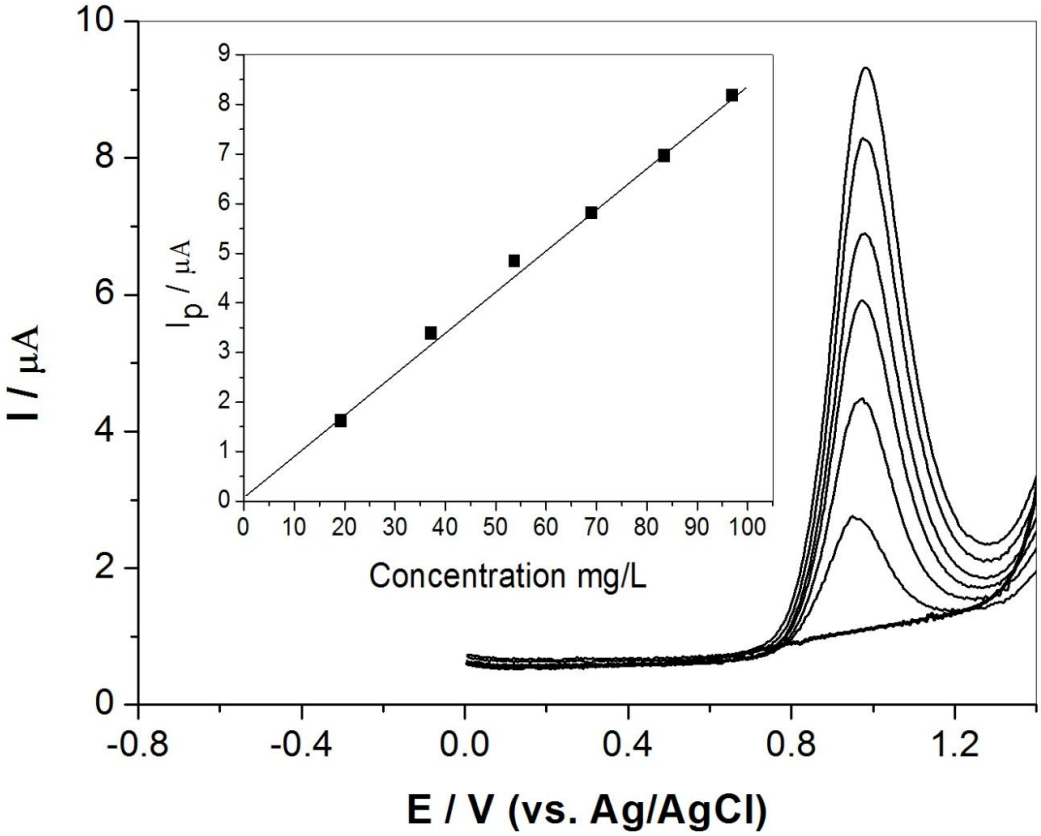

Figure 4. SWV responses taken at a BDD electrode for different captopril concentrations in B-R buffer, pH 9. Inset: Linear dependence of the peak current on the captopril concentrations. f = 40 Hz, E_{sw} = 50 mV, E_s = 5 mV

A linear relationship was found between Ip and the concentration of captopril in the range from 20 to 100 mg L^{-1}. The correlation coefficient was 0.9986 indicating excellent linearity.

The limits of detection and quantification (LOD and LOQ, respectively) for the captopril were obtained in different water samples using the procedure recommended by IUPAC. The standard deviation of blanks (*SB*) was used together with the slope (*b*) of the straight line of the analytical curves to determine the quantification and the detection limits (inset of Figure 4) using Equation 1.

$$LOQ = 10\ SB/b \quad \textbf{(1a)}$$

$$LOD = 3\ SB/b \quad \textbf{(1b)}$$

The detection and quantification limits were obtained for three determinations of in pure water using BDD electrodes and the SWV as electroanalytical technique. The values of LOD and LOQ were 36.0 µg L^{-1} and 121.95 µg L^{-1}, respectively, while the sensitivity was 0.082±0.003 µA / mg L^{-1} (0.0178 µA / µmol L^{-1}).

Table 1. Comparison of the efficiency of some voltammetric methods in the determination of captopril.

Electrode	Method	LOD (µmol L^{-1})	Reference
Fluorine-doped tin oxide	Cyclic voltammetry	84	[55]
BDD thin film	Cyclic voltammetry	25	[52]
Glassy carbon modified with chlorpromazine	Cyclic voltammetry	4.8	[24]
Modified Carbon paste electrode	Differential pulse voltammetry	1.1	[16]
Biosensor	Chronoamperometry	1.0	[25]
Pt	Cathodic stripping voltammetry	0.92	[53]
Multi-wall carbon nanotubes	Cyclic voltammetry	0.2	[18]
Carbon paste electrode biosensor	Chronoamperometric/Sequential injection analysis system	0.2	[56]
BDD	SWV	0.165	This work
Carbon paste electrode/multi-wall carbon nanotubes	Differential pulse voltammetry	0.150	[19]
Carbon paste	SWV	0.090	[23]
Manganese supported on organo-modified SiO_2/Al_2O_3 framework	Linear sweep voltammetry	0.09	[57]
graphene/ferrocene composite carbon paste	Differential pulse voltammetry	0.87	[58]
Carbon paste	Differential pulse voltammetry	0.070	[22]
N-NHPBMCNTPE[a]	Differential pulse voltammetry	0.034	[20]
p-APMCNTPE[b]	SWV	0.020	[21]

[a] N-(3,4-dihydroxyphenethyl)-3,5-dinitrobenzamide-modified carbon nanotubes paste electrode
[b] *p*-aminophenol-modified multiwall carbon nanotubes paste electrode

Table 1 compares the performance of the proposed SWV approach with several voltammetric electrochemical methods reported in the literature for captopril determination. The proposed approach is the most sensitive method that used a bare electrode; however, it is less sensitive only than the methodologies that used complex and modified electrodes. Despite their general satisfactory sensitivities, several methods listed in Table 1 used modified electrodes, and complex biosensors whose preparation are laborious, expensive, require skilled labor, and involve several steps. Therefore, the proposed approach using a bare electrode (BDD) is more advantageous than these previously reported electroanalytical methods.

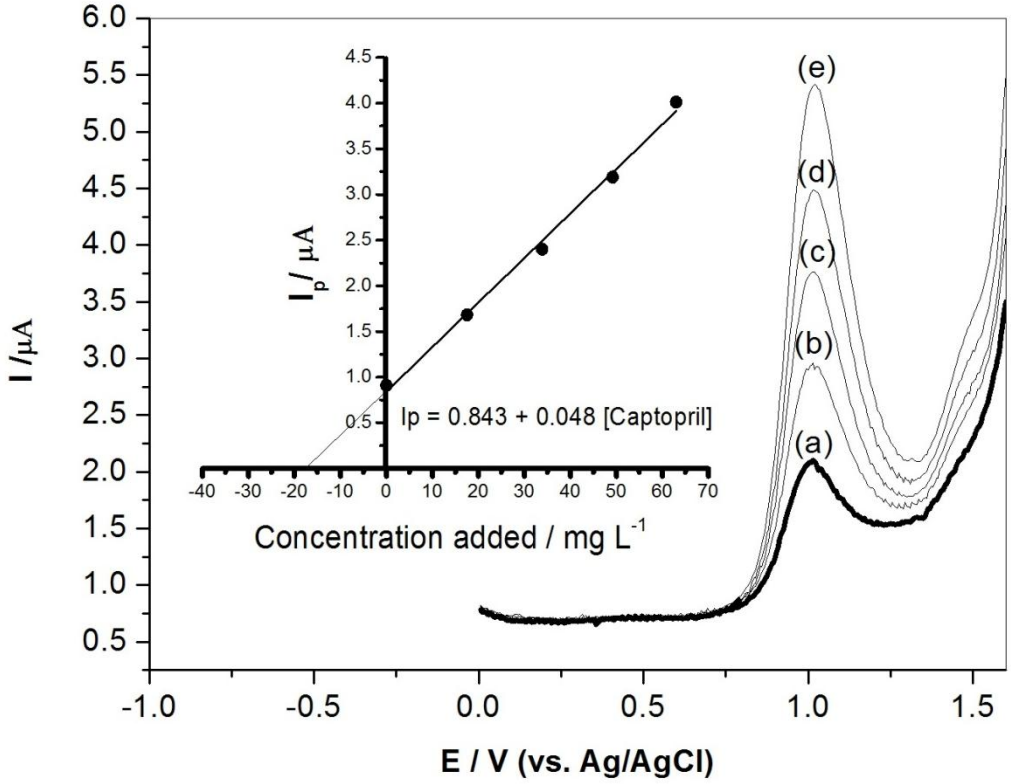

Figure 5. Recovery studies and analytical determination of captopril in 0.04 mol L^{-1} B-R buffer, pH 9, at a BDD electrode under optimized conditions for sample A. Concentration of captopril standard solution added: (a) sample, (b) 17.5 mg L^{-1}, (c) 3.9 mg L^{-1}, (d) 49.2 mg L^{-1}, (e) 63.0 mg L^{-1}.

The SWV method was applied to determine the captopril content in commercial pharmaceutical products. The determination of captopril content in the formulations was performed by using the standard addition method. No influence of others agents contained in commercial pharmaceutical products, such as starch, lactose monohydrate, microcrystalline cellulose, silicon dioxide and stearic acid, on the voltammetric response was thus observed in the studied potential range. Each sample of commercial pharmaceutical products was treated as described in experimental section. The recovery experiments were carried out by adding 500 μL of the captopril solution prepared from commercial products to the supporting electrolyte (5.0 mL) followed by standard additions of the stock solutions (200 μL) and plotting the resulting analytical curve (Figure 5). The recoveries of known amounts of captopril contained in pharmaceutical formulations (Table 2) ranged

from 96.6 to 98.5 %. Thus, these high recovery values offer the possibility of analytical captopril determinations for quality control of pharmaceutical formulations.

Table 2. Recoveries of captopril samples in commercial products using SWV experiments carried out using the following conditions: f = 40 Hz, E_{sw} = 50 mV, E_s = 5 mV (n = 3).

Sample	Content (mg)	Found (mg)	RDS (%)
Tablet of captopril	50.0	48.66±0.33	0.8
Tablet of captopril	50.0	48.81±0.39	1.0

4. CONCLUSION

In this investigation, captopril displayed two oxidation peaks when cyclic and square-wave voltammetry experiments were conducted using BDD electrodes. Based on these experiments, an electroanalytical methodology for the determination of captopril in water and commercial pharmaceutical products was developed. The electrochemical responses of pharmaceutical formulations were identical to those of standard captopril and no influence of others agents contained in commercial products on the voltammetric responses was observed. Captopril recovery values ranged from 96.6 to 98.5 % demonstrated the elevated efficiency of the developed methodology. Consequently, given it's easily of use, high sensitivity, and low analysis time, the proposed methodology can be successfully used to determine trace captopril in several commercial products.

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References

1. C. O. Wilson, O. Gisvold, J. H. Block, J. M. Beale, *Wilson and Gisvold's Text Book of Organic Medicinal and Pharmaceutical Chemistry*; J. B. Lippincott Company (2004)
2. G. K. Bertam. *Basis and Clinical Pharmacology*; Revised; Appleton and Lange (1998)
3. A. Khedr, H. El-Sherief, *Biomed. Chromatogr.*, 12 (1998) 57
4. M. Amini, A. Zarghi, H. Vatanpour, *Pharm. Acta Helv.*, 73 (1999) 303
5. T. Mirza, H. S. Tan, *J. Pharmaceu. Biomed.*, 25 (2001) 39
6. R. Li, H.-T. Yan, *Spectrosc. Spect. Anal*., 33 (2013) 1104
7. El-Didamony, A. M.; *J. Chin. Chem. Soc.*, 56 (2009) 755
8. L. Wang, X.-F. Yang, M. Zhao, *J. Fluoresc.*, 19 (2009) 593
9. X. Zheng, Z. Zhang, B. Li, *Electroanalysis*, 13 (2001) 1046
10. M. H. Sorouraddin, M. Iranifam, A. Imani-Nabiyyi, *J. Fluoresc.*, 19 (2009) 575
11. N. A. Lacher, K. E. Garrison, S. M. Lunte, *Electrophoresis*, 23 (2002) 1577
12. A. O. Alnajjar, M. E. El-Zaria, *Eur. J. Med. Chem.*, 43 (2008) 357
13. P. D. Tzanavaras, D. G. Themelis, A. Economou, G. Theodoridis, *Microchim. Acta*, 142 (2003) 55

14. M. Skowron, W. Ciesielski, *J. Anal. Chem.*, 66 (2011) 714
15. E. Dias, B. Hachey, C. McNaughton, H. Nian, C. Yu, B. Straka, N. J. Brown, R. M. Caprioli, *J. Chromatogr. B*, 937 (2013) 44
16. S. Shahrokhian, M. Karimi, H. Khajehsharifi, *Sensor. Actuat. B-Chem.*, 109 (2005) 278
17. J. B. Raoof, R. Ojani, M. Baghayeri, *Chinese J. Catal.*, 32 (2011) 1685
18. B. Rezaei, S. Damiri, *Sensor. Actuat. B-Chem*., 134 (2008) 324
19. M. Fouladgar, *Int. J. Electrochem. Sci.* 6 (2011) 705
20. A. A. Ensafi, H. Karimi-Maleh, S. Mallakpour, B. Rezaei, *Colloid. Surface. B*, 87 (2011) 480
21. A. A. Ensafi, B. Rezaei, Z. Mirahmadi-Zare, H. Karimi-Maleh, *J. Braz. Chem. Soc.*, 22 (2011) 1315
22. M. Mazloum-Ardakani, M. A. Sheikh-Mohseni, B.-F. Mirjalili, L. Zamani, *J. Electroanal. Chem.*, 686 (2012) 12
23. H. Karimi-Maleh, A. A. Ensafi, A. R. Allafchian, *J. Solid State Electr.*, 14 (2009) 9
24. A. A. Ensafi, A. Arabzadeh, *J. Anal. Chem.*, 67 (2012) 486
25. R.-I. Stefan, C. Bala, H. Y. Aboul-Enein, *Sensor. Actuat. B-Chem.*, 92 (2003) 228
26. H. B. Suffredini, S. A. S. Machado, L. A. Avaca, *J. Braz. Chem. Soc.*, 15 (2004) 16
27. J. S. Foord, C. H. Goeting, *Diam. Relat. Mater.*, 13 (2004) 1054
28. G. R. Salazar-Banda, K. I. B. Eguiluz, A. E. de Carvalho, L. A. Avaca, *J. Braz. Chem. Soc.*, 24 (2013) 1206
29. I. Duo, C. Levy-Clement, A. Fujishima, C. Comninellis, *J. Appl. Electrochem.*, 34 (2004) 935
30. H. B. Suffredini, V. A. Pedrosa, L. Codognoto, S. A. S. Machado, R. C. Rocha-Filho, L. A. Avaca, *Electrochim. Acta*, 49 (2004) 4021
31. G. R. Salazar-Banda, L. S. Andrade, P. A. P. Nascente, P. S. Pizani, R. C. Rocha-Filho, L. A. Avaca, *Electrochim. Acta*, 51 (2006) 4612
32. G. R. Salazar-Banda, A. E. de Carvalho, L. S. Andrade, R. C. Rocha-Filho, L. A. Avaca, *J. Appl. Electrochem.*, 40 (2010) 1817
33. M. S. Saha, T. Furuta, Y. Nishiki, *Electrochem. Commun.*, 6 (2004) 201
34. D. Ghernaout, M.W. Naceur, A. Aouabed, *Desalination*, 270 (2011) 9
35. M. Hupert, A. Muck, J. Wang, J. Stotter, Z. Cvackova, S. Haymond, Y. Show, G. M. Swain, *Diam. Relat. Mater.*, 12 (2003) 1940
36. T. Yano, D. A. Tryk, K. Hashimoto, A. Fujishima, *J. Electrochem. Soc.*, 145 (1998) 1870
37. N. Vinokur, B. Miller, Y. Avyigal, R. Kalish, *J. Electrochem. Soc.*, 143 (1996) L238
38. T. N. Rao, I. Yagi, T. Miwa, D. A. Tryk, A. Fujishima, *Anal. Chem.*, 71 (1999) 2506
39. J. Iniesta, P. A. Michaud, M. Panizza, G. Cerisola, A. Aldaz, C. Comninellis, *Electrochim. Acta*, 46 (2001) 3573
40. V. A. Pedrosa, L. Codognoto, S. A. S. Machado, L. A. Avaca, *J. Electroanal. Chem.*, 573 (2004) 11
41. V. A. Pedrosa, H. B. Suffredini, L. Codognoto, S. T. Tanimoto, S. A. S. Machado, L. A. Avaca, *Anal. Lett.*, 38 (2005) 1115
42. R. T. S. Oliveira, G. R. Salazar-Banda, V. S. Ferreira, S. C. Oliveira, L. A. Avaca, *Electroanalysis*, 19 (2007) 1189
43. R. T. S. Oliveira, G. R. Salazar-Banda, S. A. S. Machado, L. A. Avaca, *Electroanalysis*, 20 (2008) 396
44. J. H. T. Luong, K. B. Male, J. D. Glennon, *Analyst*, 134 (2009) 1965
45. J.-F. Zhi, H.-B. Wang, T. Nakashima, T. N. Rao, A. Fujishima, *J. Phys. Chem. B*, 107 (2003) 13389
46. R. T. S. Oliveira, G. R. Salazar-Banda, M. C. Santos, M. L. Calegaro, D. W. Miwa, S. A. S. Machado, L. A. Avaca, *Chemosphere*, 66 (2007) 2152
47. C. A. Martínez-Huitle, E. Brillas, *Appl. Catal. B-Environ.*, 87 (2009) 105
48. F. Montilla, E. Morallón, I. Duo, C. Comninellis, J. L. Vázquez, *Electrochim. Acta*, 48 (2003) 3891

49. G. R. Salazar-Banda, H. B. Suffredini, L. A. Avaca, *J. Braz. Chem. Soc.*, 16 (2005) 903
50. H. B. Suffredini, G. R. Salazar-Banda, S. T. Tanimoto, M. L. Calegaro, S. A. S. Machado, L. A. Avaca, *J. Braz. Chem. Soc.*, 17 (2006) 257
51. E. T. G. Cavalheiro, C. M. A. Brett, A. M. Oliveira-Brett, O. Fatibello-Filho, *Bioanal. Rev.*, 4 (2012) 31
52. W. Siangproh, P. Ngamukot, O. Chailapakul, *Sensor. Actuat. B-Chem.*, 91 (2003) 60
53. G. K. Ziyatdinova, G. K. Budnikov, V. I. Pogorel'tsev, *J. Anal. Chem.*, 61 (2006) 798
54. D. Pletcher, *Instrumental Methods in Electrochemistry*, Wiley, New York (1985)
55. F. Armijo, I. Torres, R. Tapia, L. Molero, M. Antilén, R. del Río, M. A. del Valle, G. Ramírez, *Electroanalysis*, 22 (2010) 2269
56. R. I. Stefan, J. F. van Staden, H. Y. Aboul-Enein, *Biosens. Bioelectron.*, 15 (2000) 1
57. D. Habibi, A. R. Faraji, A. Gil, *Sensor. Actuat. B-Chem.*, 182 (2013) 80
58. M. B. Gholivand, M. Khodadadian, *Electroanalysis*, 25(2013) 1263