http://dx.doi.org/10.5935/0103-5053.20140005

J. Braz. Chem. Soc., Vol. 25, No. 3, 478-483, 2014.
Printed in Brazil - ©2014 Sociedade Brasileira de Química
0103 - 5053 $6.00+0.00

Article

Simultaneous Determination of Paracetamol and Ibuprofen in Pharmaceutical Samples by Differential Pulse Voltammetry Using a Boron-Doped Diamond Electrode

Amanda B. Lima,[a] Lívia M. F. C. Torres,[b] Carlos F. R. C. Guimarães,[a] Rodrigo M. Verly,[a] Leonardo M. da Silva,[a] Álvaro D. Carvalho Júnior[b] and Wallans T. P. dos Santos[*,b]*

[a]Departamento de Química and [b]Departamento de Farmácia, Universidade Federal dos Vales do Jequitinhonha e Mucuri, 39100-000 Diamantina-MG, Brazil

O presente trabalho apresenta uma metodologia simples, rápida e de baixo custo para determinação simultânea de paracetamol (PC) e ibuprofeno (IB) em formulações farmacêuticas por voltametria de pulso diferencial usando eletrodo de diamante dopado com boro (BDD). Os analitos apresentaram picos de oxidação definidos em 0,85 V para o PC e 1,72 V para o IB (*vs.* Ag/AgCl) sobre o eletrodo de trabalho de BDD em meio de uma solução de H_2SO_4 0,1 mol L^{-1} com 10% (v/v) de etanol. As curvas de calibração mostraram uma resposta linear para determinação simultânea dos analitos entre 20 a 400 μmol L^{-1} (r^2 = 0,999) e os limites de detecção obtidos pelas regressões foram de 7,1 μmol L^{-1} e 3,8 μmol L^{-1} para PC e IB, respectivamente. Os estudos de adição e recuperação nas amostras ficaram próximos de 100% e os resultados foram validados por métodos cromatográficos.

This work presents a simple, fast and low-cost methodology for the simultaneous determination of paracetamol (PC) and ibuprofen (IB) in pharmaceutical formulations by differential pulse voltammetry using a boron-doped diamond (BDD) electrode. A well-defined oxidation peak was observed using the BDD electrode for each analyte (0.85 V for PC and 1.72 V for IB (*vs.* Ag/AgCl)) in 0.1 mol L^{-1} H_2SO_4 solution containing 10% (v/v) of ethanol. Calibration curves for the simultaneous determination of PC and IB showed a linear response for both drugs in a concentration range of 20 to 400 μmol L^{-1} (r^2 = 0.999), with a detection limit of 7.1 μmol L^{-1} for PC and 3.8 μmol L^{-1} for IB. The addition-recovery studies in samples were about 100% and the results were validated by chromatographic methods.

Keywords: simultaneous analysis, differential pulse voltammetry, ibuprofen, paracetamol

Introduction

Paracetamol (PC), or acetaminophen (*N*-acetyl-*p*-aminophenol, 4-acetamidophenol), is an analgesic and antipyretic drug widely used for pain relief and fever reduction. Ibuprofen (IB), denoted chemically as (*R,S*)-α-methyl-4-(2-methylpropyl) benzeneacetic acid, is also an analgesic and antipyretic drug with anti-inflammatory effects and it is used for the treatment of pain or inflammation caused by conditions such as rheumatoid arthritis, degenerative joint diseases and menstrual cramps.[1] The combination of PC and IB is found in pharmaceutical formulations for the treatment of moderate rheumatic pain.

The development of efficient analytical methods for drug-quality control is extremely important in the health area. According the United States Pharmacopoeia,[2] when two or more active ingredients are present in a specific formulation their quantifications are made by high-performance liquid chromatography (HPLC) with ultraviolet detection (UV), e.g., for PC and IB determinations in pharmaceutical samples. However, HPLC-UV methods are more expensive and usually require a sample pretreatment, generating a great amount of residue in comparison with other analytical methods.

There are few references cited in the literature for simultaneous determination of PC and IB, being some of them based on HPLC-UV[3] or spectrophotometric methods using multivariate calibration.[4] Despite this, the electroanalytical methods present interesting characteristics for the drug-quality control, such as high selectivity and sensibility, low-cost, simplicity and a higher analytical frequency when compared with most of the aforementioned

*e-mail: wallanst@ufvjm.edu.br

methods. There were published several electroanalytical methods for the detection of PC[5] and some specific methods for IB.[6] However, up to now there are no reports in the literature regarding the simultaneous determination of these compounds in pharmaceutical samples using electrochemical techniques.

Various types of working electrodes have been used for the electrochemical detection of drugs in pharmaceutical formulations.[7] Among these electrodes, the boron-doped diamond (BDD) stands out due to its high reproducibility, broad potential window and low background current.[8] Compared to other conventional electrodes, the BDD also offers advantages such as low noise and resistance to passivation.[9] Considering the potentiality of electroanalytical methods for the drug analysis, the present work deals with the possibility of simultaneous determination of PC and IB in pharmaceutical formulations by differential pulse voltammetry (DPV) using a BDD electrode.

Experimental

Reagents and solutions

All reagents used were of analytical grade and the solutions were prepared in deionized water (Milli-Q Plus, Millipore®), with a resistivity of no less than 18 MΩ cm. PC and IB standards were obtained from Sigma-Aldrich (St. Louis, MO, USA) with a purity of > 98%. Stock solutions of PC and IB were freshly prepared immediately prior to the experiments in ethanol for electrochemical detection or in acetonitrile for HPLC-UV detection, both reagents being obtained from Sigma-Aldrich (St. Louis, MO, USA). In the investigations of the analytes by voltammetric detection, the following 0.1 mol L^{-1} electrolyte solutions containing 10% (v/v) of ethanol were used: phosphoric acid (85% m/v) from Reagen (Rio de Janeiro, Brazil), boric acid from QM (Cotia, Brazil), glacial acetic acid from Carlo Erba (Milan, Italy), sulfuric acid from Synth (Diadema, Brazil), sodium hydroxide from Dinamica (Diadema, Brazil). A Britton-Robinson buffer solution containing 10% (v/v) of ethanol was composed of a mixture of 0.04 mol L^{-1} acetic acid, boric acid and phosphoric acid, and its different pH values were adjusted with sodium hydroxide. The electrochemical responses to PC and IB were studied in a large range of pH using Britton-Robinson buffer and other electrolytes. The best voltammetric response was obtained in 0.1 mol L^{-1} H_2SO_4 solution containing 10% (v/v) of ethanol.

Pharmaceutical formulations (capsules) were obtained from local drug stores. For each analysis, ten capsules were powdered in a mortar and a weight corresponding to one capsule was dissolved in ethanol using an ultrasonic bath for 30 min for the voltammetric detection or in acetonitrile for the HPLC-UV detection. After filtration, the respective working solutions and samples were prepared through dilution of the stock solution in the supporting electrolytes or in the mobile phase used in the HPLC-UV analysis, which was used for comparison with the present proposed method.

Instrumentation

All electrochemical measurements were carried out using a model PGSTAT 128N potentiostat from Autolab (Netherlands) and a three-electrode cell (10.0 mL volume). A miniaturized Ag/AgCl/saturated KCl[10] and a platinum wire were used as reference and auxiliary electrodes, respectively. The working electrode was a thin film (ca. 1.2 mm) of boron-doped diamond (approximately 8000 ppm doping level) supported on a polycrystalline silicon wafer (Adamant Technologies SA, La Chaux-de-Fonds, Switzerland). Background current correction was carried out using the GPS software from Autolab. Prior to the measurements, the BDD electrode (active area: 0.13 cm^2) was anodically pretreated in a 0.5 mol L^{-1} H_2SO_4 by applying 0.01 A during 60 s. The cathodic pretreatment was carried out by applying –0.01 A during 120 s using the same solution.[11] The BDD electrode was pretreated only once, prior to the measurements.

The electrochemical studies using the BDD electrode for the electroactive species (PC and IB) in the different supporting electrolytes were carried out using cyclic voltammetry ($\nu = 50$ mV s^{-1}) in a potential window located between the hydrogen and oxygen evolution reactions. The DPV technique was selected for simultaneous determinations of PC and IB due its better performance in comparison to the square-wave voltammetry. The optimized DPV parameters were 50 mV of amplitude, 500 ms of pulse time, 10 mV of pulse width, and 20 mV s^{-1} of scan rate. The proposed DPV method was applied for simultaneous determination of PC and IB in two pharmaceutical formulations and the results were compared with a reference method using statistical tests. Recovery tests were carried out for the pharmaceutical samples. All electrochemical measurements were carried out at room temperature, in the presence of dissolved oxygen.

The analytical method based on the HPLC-UV technique was used for comparison with the proposed method according to the United States Pharmacopoeia.[2] However, there is not an official methodology using chromatography for the analysis of a mixture of new drugs as IB and PC. Therefore, the experimental conditions for

the chromatographic study were optimized in the present study. The chromatographic analysis was carried out using a model Pro Star 315 chromatograph from Varian. The separation of the analytes was done using a C18 column (a Vydac model measuring 250 mm × 4.6 mm) and a mobile phase composed of water/acetonitrile (40:60) with retention times of 3.7 min and 5.9 min for PC and IB, respectively. UV detection was carried out at a fixed wavelength of 219 nm.

Results and Discussion

Methodology optimization

The best selectivity and sensitivity conditions for the simultaneous detection of PC and IB using the BDD electrode were obtained in the electrolyte composed of 0.1 mol L^{-1} sulfuric acid with 10% (v/v) ethanol. The addition of ethanol in the acidic solution was due to the low solubility of IB in water. The voltammograms of these studies and the chemical structures of the analytes are presented in Figure 1. The cyclic voltammograms in Figure 1 presented two oxidation peaks, i.e., 0.85 V for PC and 1.72 V for IB. The electrochemical treatments (cathodic or anodic) applied to the BDD electrode did not change significantly the oxidation processes observed for the analytes. However, the anodic treatment was chosen because of its better definition of the oxidation peaks observed for PC and IB. Therefore, the BDD electrode after an anodic treatment was chosen for the further studies comprising the DPV technique.

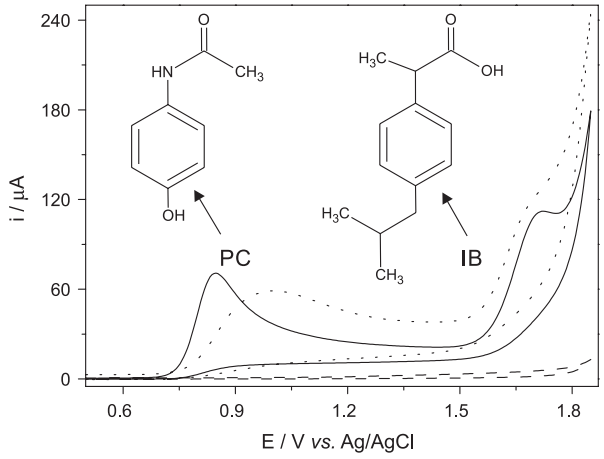

Figure 1. Cyclic voltammograms of the supporting electrolyte 0.1 mol L^{-1} H_2SO_4 with 10% (v/v) ethanol (---) plus the addition of 1.0 mmol L^{-1} PC and IB 1.0 mmol L^{-1} at the BDD working electrode after anodic (—) and cathodic (…) pretreatment. Scan rate: 50 mV s^{-1}. The chemical structures of PC and IB are shown in the inset.

The behavior of the voltammograms observed for the present experimental conditions is in agreement with electrochemical behavior exhibited by these analytes in the previous literature for the BDD electrode.[6,12] The electrochemical behavior of PC is well known.[13] PC can be oxidized to *N*-acetyl-*p*-benzoquinoneimine with a two-electron and two-proton transfer, which can be subsequently reduced at more negative potentials (reversible or quasi-reversible behavior).[14] Under this condition, optimized in Figure 1, PC has presented one peak for the cathodic current at a more negative potential of –0.15 V (data not shown). The electrochemical behavior exhibited by PC in this work (quasi-reversible behavior) might be occurred due to the use of hydroethanolic solution as the electrolyte with 10% ethanol. This was confirmed in previous studies by Pereira and co-authors,[15] who observed an irreversible electrochemical behavior for PC when using the same working electrode and electrolyte solution, but with 30% ethanol. The electrochemical oxidation mechanism of IB is not well known from the literature. Recently, Lima and co-authors[6] suggested that the electrochemical behavior of IB is similar to the one verified for naproxen,[16] which is not affected by pH, and its mechanism possibly involves a single-electron transfer via radical cation formation, followed by decarboxylation.[17] The choice for the acidic medium (0.1 mol L^{-1} H_2SO_4 solution containing 10% (v/v) of ethanol) was based on the wider potential window verified at low pH, which improved the electrochemical response for IB. The plot of the current for the oxidation peak of PC (0.85 V) and IB (1.72 V) as a function of the root of the scan rate (10 to 100 mV s^{-1}) was linear, thus supporting that the oxidation processes are controlled by diffusion.

Thus, these conditions made possible the simultaneous determination of the analytes using the DPV technique with a BBD working electrode. DPV parameters were evaluated in order to obtain the highest sensitivity and, primarily, to achieve greater selectivity for the simultaneous analysis of the electroactive analytes. The optimized parameters were 50 mV of amplitude and 20 mV s^{-1} of scan rate. Figure 2 presents ten repeated DPV measurements carried out in 0.1 mmol L^{-1} for PC and IB (the repeatability study).

The repeatability studies showed relevant results (Figure 2), indicating that the BDD electrode does not undergo passivation or contamination, which have been a recurrent problem for the electroanalytical methods making use of other electrodes. The relative standard deviation (RSD) obtained for ten measurements of the analyte solutions was calculated to be 2.6% for PC and 1.9% for IB. The reproducibility obtained for different surfaces of BDD in 10 measurements (considering that a new surface is obtained after electrochemical activation) was not so high, presenting an RSD of 10% for both analytes. The interference

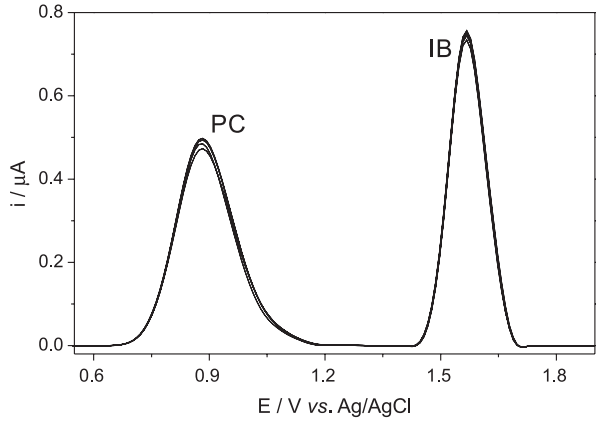

Figure 2. Differential-pulse voltammograms at BDD working electrode of the supporting electrolyte plus 0.1 mmol L^{-1} PC and IB. DPV conditions: amplitude: 50 mV; pulse time: 500 ms; pulse width: 10 mV; scan rate: 20 mV s^{-1}.

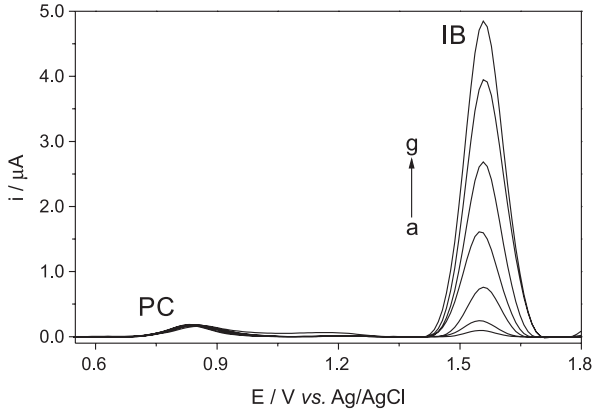

Figure 4. DPV over BDD in 0.1 mol L^{-1} H_2SO_4. PC with constant concentration at 50 µmol L^{-1} and changing IB concentration of 20 (a) up to 800 (g) µmol L^{-1}. DPV conditions: amplitude: 50 mV; pulse time: 500 ms; pulse width: 10 mV; scan rate: 20 mV s^{-1}.

of each analyte in the simultaneous analysis of its pairs was performed by changing one analyte concentration and keeping the other unchanged. Firstly, the PC concentration was changed from 20 to 800 µmol L^{-1}, while the concentration of IB was maintained at 50 µmol L^{-1}. Subsequently, the IB concentration was changed from 20 to 800 µmol L^{-1} and the concentration of PC was kept at 50 µmol L^{-1}. The results are presented in Figures 3 and 4.

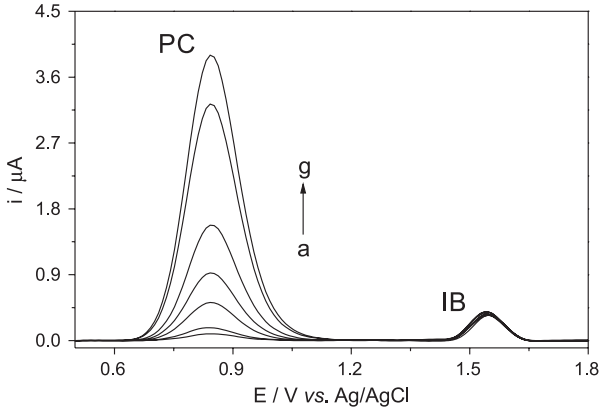

Figure 3. DPV over BDD in 0.1 mol L^{-1} H_2SO_4. IB with constant concentration at 50 µmol L^{-1} and changing PC concentration of 20 (a) up to 800 (g) µmol L^{-1}. DPV conditions: amplitude: 50 mV; pulse time: 500 ms; pulse width: 10 mV; scan rate: 20 mV s^{-1}.

As seen in Figure 3 PC does not interfere to a significant extent in the electrochemical response obtained for IB. The IB signal varies less than 4.3% when the PC concentration increases up to 16 times greater than IB. Likewise, the change in IB does not interfere in PC analysis (Figure 4). The PC signal varies less than 4% when the IB concentration increases up to 16 times greater than PC. It is worth noting that in the pharmaceutical market, these drugs are usually combined in the proportion of 200:325 mg of IB and PC, respectively. Therefore, since the PC:IB molar ratio presented in formulations is 2.22, neither PC nor IB would interfere in the simultaneous analysis using the proposed method.

Analytical parameters

Linearity studies were carried out for the analysis of drugs in pharmaceutical formulations. Figure 5 depicts the DPV measurements of PC and IB at different concentrations. The corresponding analytical curve is presented in the inset of Figure 5. The working linear range was from 20 to 400 µmol L^{-1} for PC and IB. The linear correlation coefficient for both curves was 0.999. The equations obtained from the linear regressions for PC and IB were I (µA) = 0.01134 + 0.00339 [PC] (µmol L^{-1}) and I (µA) = –0.07715 + 0.00694 [IB] (µmol L^{-1}), respectively. The limits of detection for PC and IB were obtained by multiplying the baseline noise standard deviation (SD) by three and dividing this value by the sensitivity (angular coefficient) of each curve. The obtained values were 7.1×10^{-6} mol L^{-1} for PC and 3.8×10^{-6} mol L^{-1} for IB. The LOD was compared with simultaneous determinations of PC and IB. LOD values for the simultaneous analysis of these analytes are higher than the ones reported in the literature for other methods, which is about 100 to 10 times smaller than the values obtained in the present study.[3,4] Nevertheless, the LOD values obtained in the present work are sufficient to carry out the analysis of PC and IB in pharmaceutical formulations. The addition-recovery studies were carried out for the commercial samples using the calibration curves presented in Figure 5. The results of the recoveries obtained by the proposed method for both analytes were approximately 100%, indicating the absence of sample-matrix effects. As can be verified, the proposed method presents a good working linear range and a low limit

Table 1. PC and IB simultaneous determination by HPLC-UV (official method) and by the proposed method (DPV). The values after ± are the SD of three measurements (n = 3)

Sample	Ingredient	Labeled / mg	DPV / (mg *per* capsule)	HPLC-UV / (mg *per* capsule)
1	PC	325	325 ± 4	328 ± 3
	IB	200	213 ± 3	211 ± 2
2	PC	325	326 ± 4	325 ± 3
	IB	200	220 ± 2	218 ± 2

of detection for analysis in pharmaceutical formulations. Therefore, the proposed method for the simultaneous determination of PC and IB could be an advantageous alternative for the well-established methods.

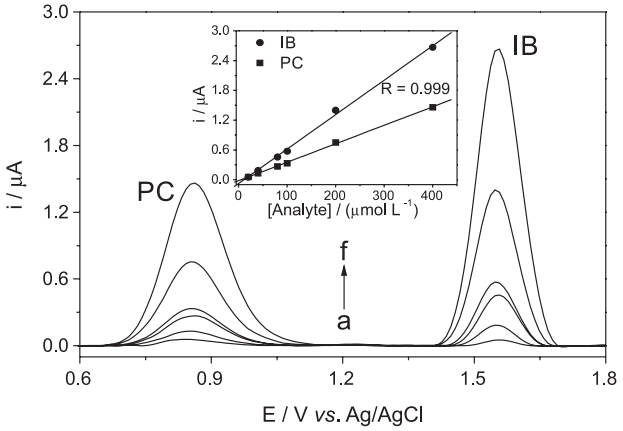

Figure 5. DPVs in 0.1 mol L^{-1} H_2SO_4 over a BDD electrode containing PC and IB in the following concentrations (μmol L^{-1}): 20 (a); 40 (b); 80 (c); 100 (d); 200 (e); and 400 (f). The respective calibration curves, including the correlation coefficient, are shown in the inset. DPV conditions: amplitude: 50 mV; pulse time: 500 ms; pulse width: 10 mV; scan rate: 20 mV s^{-1}.

Comparison with the chromatographic method (HPLC-UV)

Table 1 presents the experimental findings for the simultaneous determination of PC and IB in pharmaceutical formulations using the HPLC-UV method and the proposed method (DPV). In addition, Table 1 shows the nominal content of the analytes and the average of three determinations for each sample, as well as the corresponding standard deviation. The results obtained by the two methods were evaluated with the support of statistical tests (*F* and *t*), where it was verified that the two methods present similar results with a confidence level of 95%.[18]

Conclusions

We present for the first time a methodology using electroanalytical methods for the simultaneous determination of PC and IB in pharmaceutical formulations. The DPV technique using the BDD electrode showed a good resolution for the oxidation peaks exhibited by the different drugs (PC and IB) and a high stability for the electrode performance. Moreover, the proposed method presents several advantages, including simplicity of application, lower waste generation, greater speed, and lower cost in comparison with the standard method (HPLC-UV) recommended by the United States Pharmacopoeia. The accuracy of the proposed method was confirmed by comparative determinations using the standard method and by recovery tests. Therefore, the proposed voltammetric detection for PC and IB offers a good alternative, both economically and environmentally, for the quality control of pharmaceutical formulations containing PC and IB. In addition, the proposed method offers a promising alternative for the analysis of other formulations containing electrochemically active drugs.

Acknowledgements

The authors are grateful to CNPq, FAPEMIG (CEX-APQ-01874-12) and CAPES for financial support. This work is a collaboration research project of members of the Rede Mineira de Química (RQ-MG) supported by FAPEMIG.

References

1. Brunton, L. L.; Lazo, J. S.; Parker, K. L.; *Goodman & Gilman's The Pharmacological Basis of Therapeutics*; 11th ed.; McGraw Hill: New York, USA, 2006.
2. The United States Pharmacopoeia, USP 25 rev., The United States Pharmacopoeia Convention: Rockville, 2002.
3. Battu, P. R.; Reddy, M. S.; *Asian J. Research Chem.* **2009**, *2*, 70; Dubey, N.; Jain, D. K.; Jadhawani, S.; *JPC-J. Planar Chromat.* **2012**, *25*, 162.
4. Sena, M. M.; Freitas, C. B.; Silva, L. C.; Pérez, C. N.; de Paula, Y. O.; *Quim. Nova* **2007**, *30*, 75; Khoshayanda, M. R.; Abdollahib, H.; Shariatpanahia, M.; Saadatfarda, A.; Mohammadi, A.; *Spectrochim. Acta, Part A* **2008**, *70*, 491.
5. Bosch, M. E.; Sanchez, A. J. R.; Rojas, F. S.; Ojeda, C. B.; *J. Pharm. Biomed. Anal.* **2006**, *42*, 291.

6. Lima, A. B.; Faria, E. O.; Montes, R. H. O.; Cunha, R. R.; Richter, E. M.; Munoz, R. A. A.; dos Santos, W. T. P.; *Electroanalysis* **2013**, *25*, 1585.
7. Gupta, V. K.; Jain, R.; Radhapyari, K.; Jadon, N.; Agarwal, S.; *Anal. Biochem.* **2011**, *408*, 179.
8. Lopes, A. C. V.; Luz, R. C. S.; Damos, F. S.; dos Santos, A. S.; Franco, D. L.; dos Santos W. T. P.; *J. Braz. Chem. Soc.* **2012,** *23,* 1800; Sartori, E. R.; Medeiros, R. A.; Rocha-Filho, R. C.; Fatibello-Filho, O.; *J. Braz. Chem. Soc.* **2009,** *20,* 360; Ribeiro, F. W. P.; Cardoso, A. S.; Portela, R. R.; Lima, J. E. S.; Machado, S. A. S.; De Lima, P.; De Souza, D.; Correia, A. N.; *Electroanalysis* **2008**, *20*, 2031; Lima, A. B.; Chaves, S. C.; da Silva, L. M.; Pereira, P. F.; Richter, E. M.; dos Santos, W. T. P.; *Quim. Nova,* **2013**, *36*, 1296; Sartori, E. R.; Trench, A. B.; Rocha-Filho, R. C.; Fatibello-Filho, O.; *J. Braz. Chem. Soc.* **2013,** *24*, 1504.
9. de Barros, R. C. M.; Ribeiro, M. C.; An-Sumodjo, P. T.; Julião, M. S. S.; Serrano, S. H. P.; Ferreira, N. G.; *Quim. Nova* **2005**, *28*, 317; Pleskov, Y. V.; *J. Anal. Chem.* **2000**, *55*, 1045; Suffredini, H. B.; Pedrosa, V. A.; Codognoto, L.; Machado, S. A. S.; Rocha-Filho, R. C.; Avaca, L. A.; *Electrochim. Acta* **2004**, *49*, 4021; Swain, G. M. In *Electroanalytical Chemistry*; Bard, A. J.; Rubinstein, I., eds.; Marcel Dekker: New York, 2004, ch. 22.
10. Pedrotti, J. J.; Angnes, L.; Gutz, I. G. R.; *Electroanalysis* **1996**, *8*, 673.
11. Salazar-Banda, G. R.; de Carvalho, A. E.; Andrade, L. S.; Rocha-Filho, R. C.; Avaca, L. A.; *J. Appl. Electrochem.* **2010**, *40*, 1817.
12. Lourenção, B. C.; Medeiros, R. A.; Rocha-Filho, R. C.; Mazo, L. H.; Fatibello-Filho, O.; *Talanta* **2009**, *78*, 748.
13. Sanghavi, B. J.; Srivastava, A. K.; *Electrochim. Acta* **2010**, *55*, 8638; Miner, D. J.; Rice, J. R.; Riggin, R. M.; Kissinger, P. T.; *Anal. Chem.* **1981**, *53*, 2258.
14. Saciloto, T. R.; Cervini, P.; Cavalheiro, E. T. G.; *J. Braz. Chem. Soc.* **2013**, *24*, 1461; dos Santos, W. T. P.; de Almeida, E. G. N.; Ferreira, H. E. A.; Gimenes, D. T.; Richter, E. M.; *Electroanalysis* **2008**, *20*, 1878; dos Santos, W. T. P.; Gimenes, D. T.; de Almeida, E. G. N.; Eiras, S. D.; Albuquerque, Y. D. T.; Richter, E. M.; *J. Braz. Chem. Soc.* **2009**, *20,* 1249; Wangfuengkanagul, N.; Chailapakul, O.; *J. Pharm. Biomed. Anal.* **2002**, *28*, 841.
15. Pereira, P. F.; Marra, M. C.; Lima, A. B.; dos Santos, W. T. P.; Munoz, R. A. A.; Richter, E. M.; *Diamond Relat. Mater.* **2013**, *39*, 41.
16. Stefano, J. S.; Lima, A. P.; Montes, R. H. O.; Richter, E. M.; Munoz, R. A. A.; *J. Braz. Chem. Soc.* **2012**, *23*, 1834.
17. Bosca, F.; Martinez-Martinez, R.; Miranda, M. A.; Primo, J.; Soto, J.; Vano, L.; *J. Pharm. Sci.* **1992**, *81*, 479.
18. Skoog, D. A.; Holler, F. J.; Nieman, T. A.; *Principles of Instrumental Analysis,* 5th ed.; Saunders College Publishing: Philadelphia, USA, 1998.

Submitted: September 27, 2013
Published online: January 10, 2014