Talanta 90 (2012) 99–102

Contents lists available at SciVerse ScienceDirect

Talanta

journal homepage: www.elsevier.com/locate/talanta

Fast batch injection analysis system for on-site determination of ethanol in gasohol and fuel ethanol

Polyana F. Pereira, Mariana C. Marra, Rodrigo A.A. Munoz, Eduardo M. Richter*

Instituto de Química – Universidade Federal de Uberlândia, Av. João Naves de Ávila, 2121 Uberlândia, MG, Brazil

ARTICLE INFO

Article history:
Received 17 November 2011
Received in revised form
30 December 2011
Accepted 3 January 2012
Available online 8 January 2012

Keywords:
Batch injection analysis (BIA)
On-site analysis
Fuel ethanol
Gasohol
Fuel adulteration

ABSTRACT

A simple, accurate and fast (180 injections h^{-1}) batch injection analysis (BIA) system with multiple-pulse amperometric detection has been developed for selective determination of ethanol in gasohol and fuel ethanol. A sample aliquot (100 μL) was directly injected onto a gold electrode immersed in 0.5 mol L^{-1} NaOH solution (unique reagent). The proposed BIA method requires minimal sample manipulation and can be easily used for on-site analysis. The results obtained with the BIA method were compared to those obtained by gas-chromatography and similar results were obtained (at 95% of confidence level).

Published by Elsevier B.V.

1. Introduction

Ethanol (bioethanol) has been an alternative energy source widely produced and used in Brazil since 1975, when the Brazilian government stimulated its production (fermentation of sugarcane) and its consumption as a fuel for automotive vehicles in order to become more independent on petroleum-based fuels [1,2]. The Brazilian fuel ethanol is used either in the hydrated form (94%, v/v ethanol) as a car fuel or in the anhydrous form, mixed with gasoline and then resulting in gasohol [1–3]. Ethanol acts as an antiknock agent for gasoline and can be considered an environmental-friendly substitute for alkyllead and manganese additives, highly toxic and environmental pollutants [3,4]. The National Brazilian Agency (ANP), responsible for the control of commercialization and of production of biofuels and petroleum-based fuels, established the upper limit of 25% (v/v) for ethanol in gasohol. Higher concentrations of ethanol can damage rubber seals and diaphragms of gasoline engines [3]. Besides the limited content of ethanol, gasohol may be adulterated by the addition of diesel oil, kerosene and petrochemical raffinates, due to the low cost of these solvents in comparison to gasoline [5–7]. Methanol is not a common adulterant found in gasohol but it is added in the Brazilian fuel ethanol, once again due to its low cost and to their similar physical-chemical properties [8,9]. Additionally, methanol is not detected by the ABNT (Associação Brasileira de Normas Técnicas – Brazilian Association of Technical Standards) analytical method, which is based on the volume increase of the aqueous phase after the extraction with water [10].

Gas chromatography (GC) is the analytical technique recommended by the American Society for Testing and Materials (ASTM D 4815-03) for the determination of volatile ethers and alcohols (including ethanol) in gasoline [11]. This technique can also be applied for the analysis of fuel ethanol [9]. Data from distillation curve profiles [5], from Fourier transform near infrared spectroscopy [7–9] and from gas chromatography–mass spectrometry [6] were associated to chemometric data treatment in order identify adulteration of gasoline and fuel ethanol. A simple spectrophotometric method was described for the determination of ethanol in gasohol after aqueous extraction [12]. Electrochemical detectors have been proposed for the determination of ethanol in gasoline using contactless impedance [13,14] and amperometry [3]. The amperometric sensor for ethanol was based on its electrocatalytic oxidation at copper electrodes in alkaline media [3,15]. However, the sensor was not free of interference from methanol which was also oxidized at the electrode [3].

Gold electrodes have been described to present electrocatalytic properties toward oxidation of ethanol and other short-chain alcohols in alkaline media [16–20]. However, the oxidation process is accompanied by passivation of the electrode surface due to the adsorption of oxidation products and, consequently, the current signal does not follow a linear behavior with increasing concentrations of ethanol [19]. In order to obtain a constant clean and reactive

---

* Corresponding author. Tel.: +55 34 3239 4143x206; fax: +55 34 3239 4208.
E-mail address: emrichter@iqufu.ufu.br (E.M. Richter).

0039-9140/$ – see front matter. Published by Elsevier B.V.
doi:10.1016/j.talanta.2012.01.004

gold surface and to avoid electrode passivation, a triple-pulse amperometric detection technique has been proposed for accurate ethanol determination [19]. Similarly, multiple-pulse amperometric (MPA) detection was required for the accurate determination of tert-butylhydroquinone (phenolic antioxidant) in biodiesel samples at a bare glassy-carbon electrode without any electrode passivation [21]. MPA was also applied to introduce an internal standard [22] in flow injection analysis (FIA) and for simultaneous determinations in FIA [23–27] and batch injection analysis (BIA) systems [28]. Batch injection analysis (BIA) is a non-flow injection technique introduced by Wang and Taha [29]. This approach renders several desirable characteristics, such as the need of small sample volumes (typically 1–100 μL) and the possibility of high speed and easy to use analysis. Also, it can be easily used in on-site analysis, besides its low cost [29–31].

In this work, we propose the determination of ethanol in gasohol and fuel ethanol samples using BIA with MPA detection at a gold electrode under basic media. This method is free of interference from methanol as well as from other solvents that can be used as adulterant in gasohol and fuel ethanol.

2. Experimental

2.1. Reagents and samples

All solutions were prepared with deionized water (Millipore Direct-Q3) with a resistivity no less than 18 MΩ-cm. All reagents were of analytical grade and used without further purification. Sodium hydroxide was obtained from Dinâmica (Diadema, Brazil) and ethanol and methanol from Synth (Diadema, Brazil). Fuel ethanol samples were analyzed after appropriate dilution in 0.5 mol L^{-1} NaOH. Gasohol samples could be analyzed after simple manual liquid/liquid extraction after manual agitation (10 mL of each—1:1 water/sample) in a closed small flask and subsequent dilution of an aliquot from the aqueous solution containing ethanol in 0.5 mol L^{-1} NaOH. The extraction procedure is similar to the one used by the Brazilian Association of Technical Standards for the determination of anhydrous ethanol content in gasohol samples [10].

2.2. Instruments and apparatus

Electrochemical measurements were performed with a three-electrode BIA cell system employing a μ-Autolab Type III potentiostat (Metrohm Autolab B.V.). A mini Ag/AgCl/KClsat [32], platinum and gold ($\varnothing$ = 3 mm; Metrohm) were employed as reference, auxiliary and working electrodes, respectively.

BIA measurements were carried out using a cylindrical acrylic cell ($\varnothing_I$ = 7 cm; height = 5 cm; volume≈200 mL) similar to that previously described [33]. Fig. 1 presents a schematic diagram of the batch injection cell used in the study.

A micro DC-motor (3–24 V; used in hair dryer or electric toys) was used for solution stirring. Only, a Teflon rod was adapted on the motor shaft. Therefore, a common battery could be used as a power supply of the micro DC-motor and the proposed stirring arrangement could be easily employed in outside analysis, as proposed in this work. The stirring rate could be easily changed by varying the battery voltage. All studies were performed at a constant stirring rate of 280 ± 10 rpm (with the application of 4.5 V). Many micro DC-motors commercially available can be used for this purpose.

Injections solutions were performed with a motorized electronic micropipette (Eppendorf Multipette® stream) with a constant distance from the working electrode to Multipette® combitip® (≈2 mm), as recommended in a previous work [30].

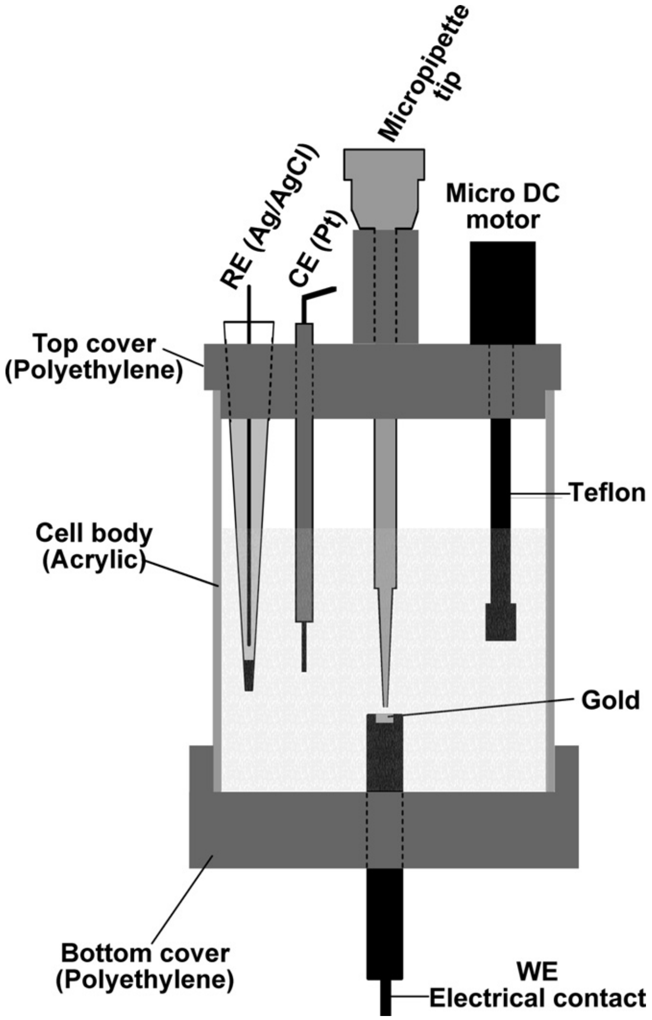

Fig. 1. Schematic diagram of the batch injection cell.

Results for the ethanol determination in gasohol and fuel ethanol were compared to those obtained by using gas chromatography (GC). A Shimadzu GC-2014 chromatographer with a flame ionization detector (FID) and carbowax column (30 m × 0.25 mm × 0.25 μm) was used.

3. Results and discussion

Fig. 2 shows cyclic voltammograms obtained at a gold electrode in 0.5 mol L^{-1} NaOH before (—) and after addition of ethanol (- - -) or methanol (·····).

Under this condition, only ethanol is oxidized to the corresponding aldehyde at about 0.18 V, which is in agreement with previous report [19]. These results clearly demonstrate that this system (gold electrode in alkaline medium) can be used for selective determination of ethanol in the presence of methanol.

Fig. 3 presents the results obtained for successive injections (n = 10) of a solution containing 0.1% (a) and 0.5% (b) of ethanol using the BIA system with amperometric detection.

When the conventional amperometry (Fig. 3A) was employed (constant potential at 0.18 V vs Ag/AgCl), the response decreases run-to-run for a solution containing 0.1% of ethanol (a) and decreases dramatically for a solution containing 0.5% of ethanol (b). As previously described [19], the ethanol oxidation product (the corresponding aldehyde) strongly adsorbs on the gold surface and its accumulation leads to the loss of electrode activity.

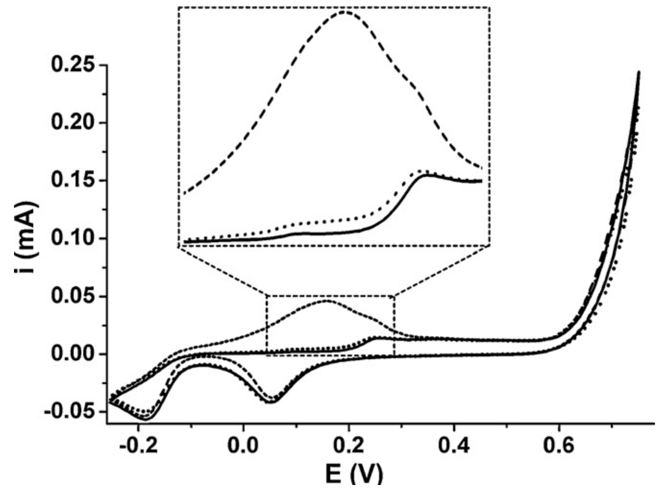

Fig. 2. Cyclic voltammograms of gold electrode in NaOH 0.5 mol L^{-1} before (—) and after addition of 0.3% (v/v) of ethanol (- - -) or methanol (· · ·· · ·). Scan rate = 50 mV s^{-1}. Step potential = 5 mV.

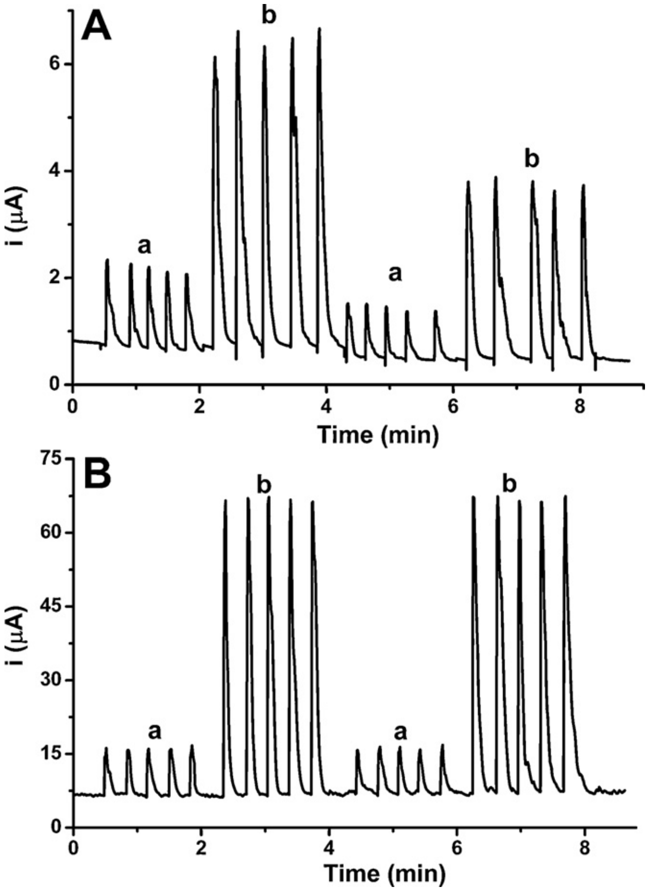

Fig. 3. Comparison between the results obtained by BIA with (A) conventional amperometric and (B) pulsed amperometric detection for successive injections of solutions containing (a) 0.1 and (b) 0.5% of ethanol. Applied potentials: (A) only 0.18 V; (B) +0.18 V/100 ms, +0.70 V/300 ms and −0.25 V/300 ms; electrolyte: 0.5 mol L^{-1} NaOH; flow rate: 4 mL min^{-1}; injection volume: 100 μL.

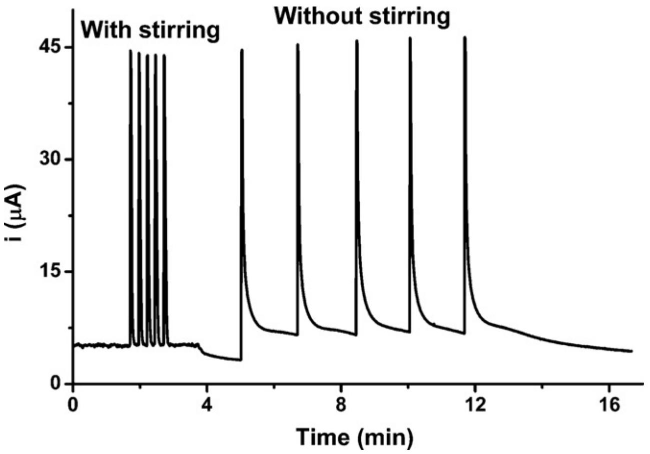

Fig. 4. Comparison between the results obtained by BIA with pulsed amperometric detection with and without the solution stirring. Injection solution: 0.5% ethanol; other conditions see Fig. 3.

However, if pulsed amperometry is used (Fig. 3B), a second potential pulse (0.7 V) can also periodically be applied and the adsorbed species are oxidized to carbon dioxide, simultaneously with the formation of gold oxide. In addition, a third potential pulse (negative potential region) can also be applied to reduce the gold oxide (cleaning procedure). Then, further experiments were carried out employing pulsed amperometry with the application of three sequential potential pulses using gold as the working electrode and NaOH solution as the electrolyte: (+0.18 V/100 ms) oxidation of ethanol and adsorption of the oxidation product at the electrode surface; (+0.70 V/300 ms) oxidation of the adsorbed species (cleaning procedure) and formation of gold oxide; (−0.25 V/300 ms) removal of the oxide layer (reactivation procedure). After the implementation of the triple-pulse waveform, the system started to show high reproducibility on peak currents (Fig. 3B), with an RSD value of 1.6% and 0.6% for solutions containing 0.1 and 0.5% of ethanol, respectively.

BIA experiments can be carried out with and without solution stirring. However, if pulsed amperometry detection and gold working electrode in alkaline medium are used, the peak current is considerably influenced by the solution with and without stirring which can be clearly observed in the results presented in Fig. 4.

Under solution stirring, the peak current quickly returns to baseline (fast current decrease) and one injection can be carried out every 20 s (180 injections h^{-1}). However, if the solution is maintained without stirring, the current slowly decreases and one injection can be carried out each 120 s (30 injections h^{-1}). Probably, this occurs because the periodical cleaning and activation procedure are most effective if the solution is stirred constantly. In this case, the products generated during the cleaning step are quickly removed from the working electrode surface. It is important to emphasize that the stirring procedure proposed in this work (using a micro DC-motor) can be easily used in outside analysis. The precision of the BIA system is slightly better under stirred solution than under static solution (RSD = 0.4 and 1.4%, respectively; $n = 5$).

Fig. 5 presents the amperogram obtained for injections of 100 μL of standard solutions (in triplicate) containing increasing concentrations of ethanol (a–e: 0.1–0.5%) and fuel ethanol (A–C) and gasohol (D–F) samples adequately diluted. The sample E is gasoline adulterated with methanol.

The calibration curve showed good linearity in the investigated concentration range with the following calibration equation:

$$I\ \ (\mu\text{A}) = -3.632 + 96.964\,c\ \ (\%) \qquad r = 0.998$$

The limits of detection and quantification for ethanol were found to be 1.1×10^{-3} and 3.63×10^{-3}%, respectively. The sampling frequency was calculated at approximately 180 and 30 injections h^{-1} with and without stirring, respectively. The proposed BIA method was used to determine ethanol in three fuel ethanol samples, one gasohol sample (containing 20–25% ethanol, according to Brazilian legislation) and two gasoline samples after the addition of

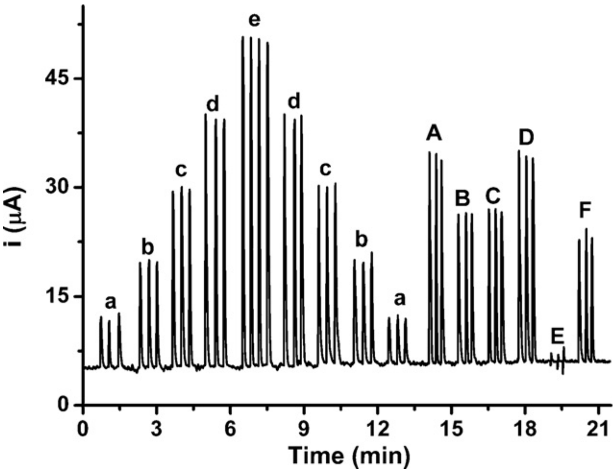

Fig. 5. BIA-MPA amperogram obtained by the injections of five ethanol standard solutions (a–e: 0.1–0.5%), fuel ethanol (A–C) and gasohol (D–F) samples diluted appropriately in 0.5 mol L^{-1} NaOH; other conditions see Fig. 3.

Table 1
Comparison of results obtained for ethanol determination using BIA versus GC methods ($n = 3$).

Samples	Added	BIA (%)	GC (%)
Fuel ethanol	–	89 ± 1	91 ± 2
Fuel ethanol	20% H_2O	65 ± 2	59 ± 10
Fuel ethanol	20% MetOH	67 ± 1	69 ± 2
Gasohol	–	22 ± 1	23 ± 6
Gasoline	30% MetOH	<LD	<LD
Gasoline	15% EtOH + 15% MetOH	16 ± 2	13 ± 3

MetOH: methanol; EtOH: ethanol.

methanol or ethanol. The results obtained through the proposed BIA method were also compared to those obtained by the GC method. Table 1 shows the results for the analysis of these samples with their respective standard deviations ($n = 3$).

No significant differences between the two methods (BIA and GC) were observed, which indicates the absence of systematic errors. The statistical *t*-test at 95% confidence intervals shows reasonable agreement between the results for ethanol concentrations obtained by the proposed BIA and GC methods ($t_{\text{calculated}} < t_{\text{table}} = 2.78$; $n = 3$).

4. Conclusions

In this work, we report for the first time the determination of ethanol by BIA with multiple pulse amperometric detection using gold as working electrode and 0.5 mol L^{-1} NaOH as unique reagent. The proposed BIA method is simple, accurate, rapid (180 injections h^{-1}) and can be easily used in outside (on-site) analysis. The sample manipulation requires only a simply dilution (fuel ethanol) or a manual extraction and further dilution (gasohol) which can also be easily performed outside of the laboratory. The proposed electrochemical method detects only ethanol, what can be considered an advantage in relation to previous published studies [3,13,14] and the ABNT NBR 13992:1997 method [10] in which methanol (more toxic alcohol) is considered as a potential chemical interfering molecule.

Acknowledgements

The authors are grateful to CNPq (476269/2010-5 and 305227/2010-6), FAPEMIG (CEX-APQ-02276-09) and CAPES for financial support.

References

[1] R.A.A. Munoz, L. Angnes, Microchem. J. 77 (2004) 157–162.
[2] R.A.A. Munoz, E.M. Richter, D.P. de Jesus, C.L. do Lago, L. Angnes, J. Braz. Chem. Soc. 15 (2004) 523–526.
[3] T.R.L.C. Paixao, J.L. Cardoso, M. Bertotti, Fuel 86 (2007) 1181–1185.
[4] R.A.A. Munoz, C.E. Banks, T.J. Davies, L. Angnes, R.G. Compton, Electroanalysis 18 (2006) 621–626.
[5] F.S. Oliveira, L.S.G. Teixeira, M.C.U. Araujo, M. Korn, Fuel 83 (2004) 917–923.
[6] V.L. Skrobot, E.V.R. Castro, R.C.C. Pereira, V.M.D. Pasa, I.C.P. Fortes, Energy Fuels 19 (2005) 2350–2356.
[7] R.C.C. Pereira, V.L. Skrobot, E.V.R. Castro, I.C.P. Fortes, V.M.D. Pasa, Energy Fuels 20 (2006) 1097–1102.
[8] H.S.P. Carneiro, A.R.B. Medeiros, F.C.C. Oliveira, G.H.M. Aguiar, J.C. Rubim, P.A.Z. Suarez, Energy Fuels 22 (2008) 2767–2770.
[9] H.L. Fernandes, I.M. Raimundo Jr., C. Pasquini, J.J.R. Rohwedder, Talanta 75 (2008) 804–810.
[10] Brazilian Association Technical Standard (ABNT) 1997; NBR:13992.
[11] Standard test method for determination of MTBE, ETBE, DIPE, tertiary-amyl alcohol and C1 to C4 alcohols in gasoline by gas chromatography, American Society of Testing and Materials, D 4815-03, West Conshohocken, PA, USA; 2003.
[12] S. Muncharoen, J. Sitanurak, W. Tiyapongpattana, N. Choengchan, N. Ratanawimarnwong, S. Motomizu, P. Wilairat, D. Nacapricha, Microchim. Acta 164 (2009) 203–210.
[13] M.S. Rocha, J.R. Simões-Moreira, Fuel 84 (2005) 447–452.
[14] F. Opekar, R. Cabala, T. Kadlecova, Anal. Chim. Acta 694 (2011) 57–60.
[15] T.R.L.C. Paixao, D. Corbo, M. Bertotti, Anal. Chim. Acta 472 (2002) 123–131.
[16] Y. Kwon, S.C.S. Lai, P. Rodriguez, M.T.M. Koper, J. Am. Chem. Soc. 133 (2011) 6914–6917.
[17] R.B. Lima, H. Varela, Gold Bul. 41 (2008) 15–22.
[18] G. Tremiliosi-Filho, E.R. Gonzalez, A.J. Motheo, E.M. Belgsir, J.M. Leger, C. Lamy, J. Electroanal. Chem. 444 (1998) 31–39.
[19] G. Schiavon, N. Comisso, R. Toniolo, G. Bontempelli, Electroanalysis 8 (1996) 544–548.
[20] A.M.O. Brett, F.M. Matysik, M.T. Vieira, Electroanalysis 9 (1997) 209–212.
[21] T.F. Tormin, D.T. Gimenes, L.G. Silva, R. Ruggiero, V.S. Ferreira, E.M. Richter, R.A.A. Munoz, Talanta 82 (2010) 1599–1603.
[22] D.T. Gimenes, W.T.P. dos Santos, R.A.A. Munoz, E.M. Richter, Electrochem. Commun. 12 (2010) 216–218.
[23] W.T.P. Santos, D.T. Gimenes, E.G.N. de Almeida, S.D. Eiras, Y.D.T. Albuquerque, E.M. Richter, J. Braz. Chem. Soc. 20 (2009) 1249–1255.
[24] W.T.P. Santos, E.G.N. de Almeida, H.E.A. Ferreira, D.T. Gimenes, E.M. Richter, Electroanalysis 20 (2008) 1878–1883.
[25] D.T. Gimenes, W.T.P. dos Santos, T.F. Tormin, R.A.A. Munoz, E.M. Richter, Electroanalysis 22 (2010) 74–78.
[26] R.A. Medeiros, B.C. Lourencao, R.C. Rocha, O. Fatibello, Anal. Chem. 82 (2011) 8658–8663.
[27] W.C. Silva, P.F. Pereira, M.C. Marra, D.T. Gimenes, R.R. Cunha, R.A.B. Silva, R.A.A. Munoz, E.M. Richter, Electroanalysis 23 (2011) 2764–2770.
[28] R.A.B. Silva, D.T. Gimenes, T.F. Tormin, R.A.A. Munoz, E.M. Richter, Anal. Met. 3 (2011) 2804–2808.
[29] J. Wang, Z. Taha, Anal. Chem. 63 (1991) 1053–1056.
[30] C.M.A. Brett, A.M.O. Brett, L.C. Mitoseriu, Anal. Chem. 66 (1994) 3145–3150.
[31] M.S.M. Quintino, L. Angnes, Electroanalysis 16 (2004) 513–523.
[32] J.J. Pedrotti, L. Angnes, I.G.R. Gutz, Electroanalysis 8 (1996) 673–675.
[33] T.F. Tormin, D.T. Gimenes, E.M. Richter, R.A.A. Munoz, Talanta 85 (2011) 1274–1278.