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**Organic-resistant screen-printed graphitic electrodes:
Application to on-site monitoring of liquid fuels**

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Abstract

This work presents the potential application of organic-resistant screen-printed graphitic electrodes (SPGEs) for fuel analysis. The required analysis of the antioxidant 2,6-di-*tert*-butylphenol (2,6-DTBP) in biodiesel and jet fuel is demonstrated as a proof-of-concept. The screen-printing of graphite, Ag/AgCl and insulator inks on a polyester substrate (250 μm thickness) resulted in SPGEs highly compatible with liquid fuels. SPGEs were placed on a batch-injection analysis (BIA) cell, which was filled with a hydroethanolic solution containing 99% v/v ethanol and 0.1 mol L⁻¹ HClO₄ (electrolyte). An electronic micropipette was connected to the cell to perform injections (100 μL) of sample or standard solutions. Over 200 injections can be injected continuously without replacing electrolyte and SPGE strip. Amperometric detection (+1.1 V vs. Ag/AgCl) of 2,6-DTBP provided fast (around 8 s) and precise (RSD = 0.7%, n = 12) determinations using an external calibration curve. The method was applied for the analysis of biodiesel and aviation jet fuel samples and comparable results with liquid and gas chromatographic analyses, typically required for biodiesel and jet fuel samples, were obtained. Hence, these SPGE strips are completely compatible with organic samples and their combination with the BIA cell shows great promise for routine and portable analysis of fuels and other organic liquid samples without requiring sophisticated sample treatments.

Keywords: Antioxidant; Batch-injection analysis; Biofuel; Fossil Fuel; Portable; Screen-printed electrode.

1. Introduction

Currently there is a replacement scenario of fossil fuels by renewable sources of fuel. Countries such as Brazil and USA have established goals to replace 20 and 30% of fossil fuels, respectively, over the next 5-10 years. However, this substitution will take a long period. For this reason, both fossil fuels and biofuels need a quality control for marketing and market acceptance [1]. Such a quality control is not just restricted to contaminants (organic and inorganic) but also is required to evaluate the presence of additives responsible to maintain the fuel characteristics during transport, storage and final consumption. Antioxidant additives are widely used in fossil fuels and biofuels in order to avoid deterioration processes via oxidation mechanisms/processes. Antioxidants with phenolic structures are the most commonly used in biodiesels [2] and in aviation jet fuels [3].

The addition of antioxidants in jet fuel is regulated by the standard ASTM-D1655. These compounds have been determined in aviation fuels by gas chromatography with mass spectrometry (GC-MS), [4-7] high-performance liquid chromatography (HPLC) with electrochemical [3, 8] and spectrophotometric detection in the UV region, [9,10] and differential-pulse voltammetry [11]. The determination of antioxidants in biodiesel by electroanalytical techniques is highlighted in a recent review [2] giving emphasis on the pioneering work of Tormin *et al.* [12], in which the amperometric determination of the antioxidant *tert*-butylhydroquinone in biodiesel was accomplished after large sample dilution in a hydroethanolic electrolyte solution. Another approach was reported for the determination of the antioxidant pyrogallol in biodiesel using differential-pulse voltammetry [13]. Both methods employed conventional glassy-carbon disc working electrodes.

The development of portable analytical systems for on-site monitoring of the quality control of fuels is mandatory. Electroanalysis attends this demand especially when associated with screen-printed electrodes (SPEs), which are disposable and easy-to-use sensors that can be operated by portable mini-potentiostats connected to laptops. SPEs can be applied for a large variety of analytes, as highlighted in recent reviews [14, 15]. However, few applications of SPEs involved fuel analysis. Caramit *et al.* reported the use of multi-walled carbon nanotube modified SPEs for the determination of antioxidants in biodiesel, but samples were 200-fold diluted in aqueous electrolyte containing a surfactant [16]. Our research group proposed the use of screen-printed gold electrode for metal determination in fuel bioethanol after sample dilution in aqueous electrolyte in such a way that the final ethanol concentration was 25% (v/v) [17]. Similarly, Saciloto *et al.* presented a SPE sensor using a graphite-polyurethane composite for metal determination in fuel ethanol after sample dilution to result in a final ethanol concentration in 20% (v/v) [18]. Therefore, these previous works on fuel analysis using SPEs revealed that samples are required to be diluted in aqueous electrolyte in order to perform accurate electrochemical measurements. The presence of organic solvents, especially non-polar solvents, in electrolyte affects electrochemical measurements due to their low constant dielectric, but also because inks used to construct SPEs may be dissolved by such solvents. This effect explains the high dilution ratios required for biodiesel analysis reported in the literature [13,16]. The application of SPEs for the quantification of fuel dyes in fossil fuel samples such as gasoline and kerosene required prior sample preparation involving solid-phase extraction due to the incompatibility of SPEs with such complex samples [19,20].

This work demonstrates the application of organic-resistant screen-printed graphitic electrodes (SPGEs) for the determination of the antioxidant 2,6-di-*tert*-

butylphenol (2,6-DTBP) in biodiesel and aviation jet fuels. Screen printing on a polyester substrate revealed to SPGEs highly compatible with organic solvents. This is the first report of a SPE sensor applied for measurements in a highly organic medium (99% v/v ethanol), which is a strong demand for fuel analysis especially when on-site analysis is required. SPGEs were placed on a portable batch-injection analysis (BIA) system for the amperometric detection of 2,6-DTBP. The BIA system is an analogue of flow-injection analysis (FIA); however, an electronic micropipette replaces the pump and valves used in FIA systems and the micropipette tip is placed close to the working electrode, which is immersed in blank electrolyte solution [21].

2. Experimental

2.1. Reagents, stock solutions and samples

High-purity deionized water ($R \geq 18 \text{ M}\Omega \text{ cm}$) obtained from a Milli Q water purification system (Millipore, Bedford, MA, USA) was used for preparing all aqueous solutions. Concentrated perchloric acid (70%, m/v) and ethanol (99.9%, v/v) were obtained from Vetec (Rio de Janeiro, Brazil). The antioxidant 2,6-*tert*-butylphenol (2,6-DTBP), ferrocene (99%) and tetrabutylammonium perchlorate (TBAClO₄, for electrochemical analysis) were obtained from Aldrich (USA). Working standard solutions were prepared immediately before use by appropriate dilution of the stock solution. A standard stock solution containing 2,6-DTBP ($1 \times 10^{-2} \text{ mol L}^{-1}$) was prepared in ethanol containing $0.1 \text{ mol L}^{-1} \text{ HClO}_4$. All reagents were used without further purification (analytical grade). Samples of aviation jet fuel were donated by the Radio Patrol Air Battalion (Brazilian Air Force), located at Uberlândia Minas Gerais, Brazil.

Biodiesel samples were produced in laboratory from fat pork, coconut oil (*Cocos nucifera*) and Macauba oil (*Acrocomia aculeate*) through alkaline transesterification.

2.2. Instrumentation, electrochemical cell and electrodes

Amperometry measurements were performed using a μ -Autolab Type III potentiostat (Metrohm Autolab B. V., Utrecht, The Netherlands). A PC with Nova 1.10 software for Windows 8® was used to control the instrument.

SPGEs were fabricated in-house on polyester flexible substrates (Autostat, 250 μm thickness). Each SPGE was designed in a three-electrode configuration printed on the same planar platform consisting of a graphite disc-shaped working electrode ($\text{\O} = 2.8 \text{ mm}$), a graphite counter electrode, and a silver pseudo-reference electrode as previously described [22]. Briefly, the carbon-graphite ink (Gwent Electronic Materials Ltd, UK) was printed on the substrate and cured at 60°C for 30 min. Similar consecutive steps of printing and curing (same temperature and time) were executed to print the Ag/AgCl paste (Gwent Electronic Materials Ltd, UK) and finally a dielectric paste (insulator) on the same substrate.

The BIA cell (with internal volume of 100 mL) adapted for screen-printed electrodes was fabricated in-house as described previously [21]. Additionally, a commercial version of this cell was recently introduced by Dropsens (Oviedo, Spain). Briefly, this cell was constructed in polypropylene and the SPGE is inserted at the bottom side using a rubber O-ring to prevent leaks and to limit the region over the three electrodes. The cover of the cell permits the insertion of an electronic micropipette that firmly fits over the cell in order to provide reproducible injections. The micropipette tip was placed at around 2 mm from the working electrode of the SPGE.

2.3. Electrochemical measurements

Injections of standard solutions or diluted samples were carried out using an Eppendorf electronic micropipette (Multipette® stream), which permits injections from 10 to 200 μL (using a 200 μL Combitip® tip) at a programmable dispensing rate (from 7 to 53 $\mu\text{L s}^{-1}$).

Standard solutions 2,6-DTBP used to construct analytical curves were prepared in a hydroethanolic solution containing 99% (v/v) ethanol and HClO_4 0.1 mol L^{-1} (optimized supporting electrolyte concentration). Fuel and biofuel samples were analyzed after a 5-, 10- or 20-fold dilution in electrolyte before injection by the electronic micropipette according to the concentration of the analyte. The same hydroethanolic electrolyte ($v = 80$ mL) was added to the BIA cell.

All electrochemical measurements were carried out in the presence of dissolved oxygen and at room temperature. The external calibration curve method was used for the quantification of 2,6-DTBP in all samples.

2.4. GC analysis

The measurements were performed on a Shimadzu GC-2014 gas chromatograph, equipped with a capillary column of 5 % diphenyl and 95 % dimethylpolysiloxane (HP-5, 30 m x 0.32 mm, and 0.25 mm film thickness), injection volume of 1 μL , injector temperature at 250 $^{\circ}\text{C}$, oven with the following temperature program: at 45 $^{\circ}\text{C}$ for 1 min; 10 $^{\circ}\text{C min}^{-1}$ to 260 $^{\circ}\text{C}$; 260 $^{\circ}\text{C}$ for 1 min; 40 $^{\circ}\text{C min}^{-1}$ to 280 $^{\circ}\text{C}$; and 280 $^{\circ}\text{C}$ for 2 min, flame ionization detector (FID) at 290 $^{\circ}\text{C}$, with a flow rate of the carrier gas (He) at 1.23 mL min^{-1} and 1:100 split. The obtained calibration curve was in the range of 25–

1000 mg L⁻¹ [23]. GC analyses of jet fuel were performed after 4-fold dilution of the samples in ethyl acetate.

2.5. HPLC analysis

The HPLC measurements were performed using a Shimadzu LC-10VP chromatograph equipped with UV/Visible detector (SPD-10AV), LC column (100 Lychrispher C18, 250 x 4.6 mm, 5 μm), column oven (CTO-20A), degasser (DGU-20A5), auto-sampler and pump (LC-10AD VP). The mobile phase consisted of methanol and water with 1% v/v HClO₄ (75:25 v/v), flow rate 1.0 mL min⁻¹ and injection volume of 20 μL. The detector wavelength was set at 275 nm. The calibration curve was obtained in the range of 2.2–26.3 mg L⁻¹. The samples were 30-fold diluted in the mobile phase just before the injections [24].

3. Results and Discussion

3.1. Optimization of the method

As the objective of this work was to demonstrate the potential application of organic-resistant SPGEs, the electrochemical activity of these sensors was first investigated towards the electrochemical detection of ferrocene and for the analyte (2,6-DTBP) in organic media; ferrocene is used as a standard probe in organic media. Figure 1A presents the cyclic voltammetry of 3 mmol L⁻¹ ferrocene and 5 mmol L⁻¹ 2,6-DTBP in 99% (v/v) ethanol (1% v/v water) containing 0.1 mol L⁻¹ HClO₄ and Figure 1B

presents the cyclic voltammetry of the same compounds at the same concentration in 0.1 mol L⁻¹ TBAClO₄ in pure ethanol.

INSERT FIGURE 1

Ferrocene was selected for the initial experiments because its electrochemical behavior is well-known characterized using a range of different electrodes [25]. The electrochemical oxidation of ferrocene is an electrochemically reversible process and the ΔE value ($E_{p_{\text{oxi}}} - E_{p_{\text{red}}}$) is typically expected to be close to 59 mV (considering the transfer of one electron for the electrochemical oxidation to ferrocinium); however, the ΔE values were found to be 500 and 400 mV in 0.1 mol L⁻¹ HClO₄ and TBAClO₄, respectively, as shown in Figure 1. These results indicate that the kinetics of the electron transfer on the SPGE working electrode is not as fast as it is on a glassy-carbon electrode and also likely due to solution resistance [25]. On the other hand, these experiments demonstrate that the SPGEs can be successfully applied for electrochemical measurements in such a complex medium that does not contain water (or contains trace amounts of water) in electrolyte. The electrochemical oxidation of 2,6-DTBP which exhibits an oxidation process starting at +0.5 V in both electrolyte solutions with the voltammetric peak current values found to be similar. Note that the use of 0.1 mol L⁻¹ HClO₄ was preferred due to the low cost of this reagent. The selection of ethanol to perform the initial measurements and for fuel analysis was due to its lower toxicity than methanol and other organic solvents typically used for electrochemical measurements in non-aqueous media.

Next, a hydrodynamic voltammogram of 2,6-DTBP was obtained by plotting the average current value obtained after triplicate injections of 2,6-DTBP using constant

potential amperometry in the BIA system. The potential values from +0.1 to +1.2 V were evaluated using 0.2 mol L⁻¹ BR buffer pH = 2 and 0.1 mol L⁻¹ HClO₄ both containing 50% v/v ethanol. The highest analytical response (higher current and lower standard deviation) was obtained in 0.1 mol L⁻¹ HClO₄ especially in the potential region higher than +0.9 V. The potential of +1.1 V was selected for further amperometric experiments because at this potential value the highest analytical signal was obtained.

After selecting the electrolyte and the oxidation potential, the stirring speed of the electrolyte solution inside the BIA cell during amperometric measurements for triplicate injections of the analyte was studied in the range between 0 and 2200 rpm in increments of 440 ppm (increment values specified by the stirrer fabricant). Stirring was used to decrease the response time of each transient peak as demonstrated in previous works since the injected sample plug is quickly dispersed to the bulk electrolyte solution [26,27]. Superior results were obtained using 1320 rpm based on the current responses, analytical frequency (faster responses) and lower standard deviation, especially when compared with injections without stirring (Figure 2 A/B). The increase in current obtained for triplicate injections of 2,6-DTBP for stirred solutions was also observed in previous works [26,27]. The injection rate of 53 μL s⁻¹ provided higher currents and low standard deviation for the triplicate injections (Figure 2 C/D), which is explained by the increased mass transfer of 2,6-DTBP that promotes a proportional increase in current [28]. This value was selected for further experiments and the injected volume was varied from 25 to 200 μL. The largest volume (200 μL) is defined by the maximum volume of the micropipette tip. The current increased until injections of 100 μL (no additional increase in current was verified for 150 and 200 μL) and lower standard deviation value was obtained for this value, which was selected for further measurements (Figure 2 E/F). The injection of lower volumes generates rapid

dispersion of the analyte resulting in great deviations and amperometric distorted peaks. This profile of current in function of injection volume in BIA systems was shown in previous works [29-31].

INSERT FIGURE 2

The concentration of HClO_4 in electrolyte was studied in the range from 0.05 to 0.20 mol L^{-1} and slightly higher currents were obtained for 0.10 mol L^{-1} HClO_4 , which was selected for further measurements. Next, the ethanol content in electrolyte was evaluated especially due to the main purpose of this work, which is the analysis of jet fuel and biodiesel samples, that is, a mixture of hydrocarbons and esters of fatty acids, respectively. Both samples are insoluble in a totally aqueous electrolyte, as well as the antioxidant 2,6-DTBP. Previous studies have already demonstrated the need for organic solvents in the electrolyte, mainly mixed with aqueous electrolytes, to afford the analytical signal in direct analyses of fuels using conventional disc electrodes [12, 24, 32, 33]. The ethanol content in hydroethanolic solutions was studied in the percentage proportions of 25; 50; 74; and 99% (v/v), keeping constant the concentration of HClO_4 in 0.1 mol L^{-1} . The percentage of ethanol that resulted in a better current signal was 99% (v/v) (Figure 3 A/B). The electrolyte containing higher ethanol content also showed better solubilization of the sample (clearly visualized by the clean solution of the stock solution in 99% ethanol), which can explain the higher current responses under this electrolyte. On the other hand, previous studies using SPEs showed opposite results, in which the higher content of organic solvents in electrolyte provided lower currents for the determination of inorganic and organic analytes, which was attributed to the increase in the content of solvents of low dielectric constant in electrolyte [16-18]. Nevertheless, the interaction of the inks within organic solvents has to be considered

because the longtime contact between the screen-printed electrodes and solvents may result in the partial solubilization of the inks. The influence of different organic solvents on the response of SPGEs needs additional investigation. It is noteworthy to mention that the organic-resistant SPGE shows great promising for (bio)fuel analysis due to these characteristics, especially if the SPGEs are connected to a BIA system which is a robust system for portable analysis of such inaccessible samples. Table 1 summarizes the studied conditions and the optimized values for the amperometric determination of 2,6-DTBP using the BIA system.

INSERT FIGURE 3

INSERT TABLE 1

3.2. Application of the proposed method in the analysis of the target analyte within real samples

Following the optimized conditions, an analytical curve was obtained from 4.0 to 25 mg L⁻¹ 2,6-DTBP, $I (\mu\text{A}) = 0.147 [2,6\text{-DTBP}] - 0.140$. The limits of detection (LOD) and quantification (LOQ) were found to be 290 $\mu\text{g L}^{-1}$ and 870 $\mu\text{g L}^{-1}$, calculated as 3xSD/S and 10xSD/S, respectively, in which SD is the standard deviation of blank samples (n = 10) and S the slope (sensitivity) of the analytical curve.

Next, a repeatability study was performed. Fifteen injections of 20.0 mg L⁻¹ 2,6-DTBP were made and a relative standard deviation (RSD) of 2.5% was obtained. The inter-day precision was also calculated for a concentration of 8.3 mg L⁻¹ of the antioxidant and a RSD of 2.9% was found for measurements performed in four different days. The average response time was 8.2 s, which results in a sample throughput of around 440 h⁻¹. However, considering the time for changing and refilling the

micropipette tip micropipette between injections, a sample throughput of around 240 h⁻¹ was obtained, which can be considered a high value when comparing with previous works using flow methods coupled with amperometric detection [28-32] and especially with GC or HPLC analyses. Table 2 summarizes the analytical characteristics of the method including linear range of proposed method under optimized conditions.

INSERT TABLE 2

After obtaining the analytical characteristics, the proposed method was applied for the determination of 2,6-DTBP in jet fuel (three samples) and biodiesel (two samples). The accuracy of proposed method was evaluated by recovery tests for spiked fuel and biofuel samples. Table 3 and 4 presents the concentration of 2,6-DTBP found in jet fuel and biodiesel samples, respectively, and recovery values for the same samples spiked with known concentrations of the antioxidant. The results are expressed as the mean of 3 independent determinations of each sample, with their deviations at 95% confidence level. Samples I, II and III are aviation fuels and the samples IV and V are biodiesels. Additionally, the values of the antioxidant in jet fuel and biodiesel samples were compared to the analytical techniques used for the analysis of each type of fuel sample, GC and HPLC, respectively. The concentration of 2,6-DTBP in jet fuels were in the range between the LOD (30 mg L⁻¹) and LOQ (100 mg L⁻¹) values, therefore, GC analysis could not reveal accurately the concentrations of the antioxidant. The concentration of 2,6-DTBP in biodiesel was expected to be found below the LOD value (15 mg L⁻¹) by HPLC analysis because the samples were produced in the laboratory and no further addition of antioxidants was performed. Therefore, the comparative analyses were applied for the determination of the antioxidant in spiked samples used for

recovery tests. As shown in Tables 3 and 4, the values were statistically in agreement for the analysis of both samples (according to *t*-test values).

INSERT TABLE 3

INSERT TABLE 4

All samples showed acceptable results for accuracy (compared with GC and HPLC results) and recovery values. The amperometric response obtained for the analysis of spiked biodiesel samples is presented in Figure 4. The external calibration curve method was applied for the quantification of 2,6-DTBP in fuel and biofuel samples as illustrated in Figure 4. According to ASTM D910-11, the antioxidant 2,6-DTBP can be added to the aviation fuel in a total concentration that does not exceed 12 mg L⁻¹ of fuel [34]. The concentration of 2,6-DTBP found in the jet fuel samples highly exceeded this upper limit (from 33 to 56 mg L⁻¹, data in Table 3) and also in comparison with the data from previous works [3,9]. The presence of other antioxidants in the fuel that undergo electrochemical oxidation in the same potential region would contribute to the obtaining of a higher concentration of 2,6-DTBP. However, GC measurements revealed no other phenolic antioxidant in the samples.

INSERT FIGURE 4

The amperometric response obtained for the injection of standard solutions with increasing concentrations of 2,6-DTBP (increasing and decreasing orders) and two spiked biodiesel samples is presented in Figure 4A. The external calibration curve

method was applied for the quantification of 2,6-DTBP in fuel and biofuel samples as illustrated in Figure 4B. The slopes obtained in both calibration curves (increasing and decreasing orders) showed similar values (0.203 and 0.204 $\mu\text{A L mg}^{-1}$), which indicates the absence of electrode fouling during the amperometric measurement even after injections of biodiesel samples.

An advantage of such SPGEs to be emphasized is related to electrode activation. These SPGEs did not require any electrochemical or chemical pretreatment before measurement while other screen-printed electrodes did [10,35-37].

Considering the sample throughput of 240 injections per hour, the SPGE coupled to the BIA system can be used continuously without replacement for 1 h; however, the electrolyte solution inside the BIA cell containing the added sample and standard solutions after 1 h (~ 24 mL in addition to the 80 mL of electrolyte) needs to be replaced due to volumetric capacity of the cell. Nevertheless, the same SPGE strip can be maintained in the cell for new measurements using the replaced electrolyte solution due to the high compatibility of these SPGEs with organic solvents. The SPGEs were also compatible for measurements in a waterless electrolyte (70:30 ethanol / methanol supported with LiCl) for the continuous monitoring of the radical 2,2-diphenyl-1-picrylhydrazyl, which is insoluble in molecule used for measuring the total antioxidant capacity of samples (results not shown). Moreover, commercial SPGEs, which typically employ ceramic substrates for the screen-printing of conductive inks to produce the electrodes, were evaluated for measurements in solutions containing 99% (v/v) ethanol and no success was obtained due to the low compatibility of such SPGEs with organic solvents. A previous work reported the use of similar screen-printed electrodes for bioethanol analysis (after 4-fold dilution of the sample) and the lifetime of such electrodes was 85 min in a hydroethanolic solution containing 25% (v/v) ethanol [10].

Other papers that performed the determination of fuel dyes in gasoline required the use of an external Ag/AgCl (3 mol L⁻¹ KCl) reference electrode due to the incompatibility of the pseudo-reference electrode of the SPE strip with the complex sample matrix [19]. The resistance to organic solvents of such SPGEs may be related to the substrate and the interaction of the inks with the substrate. A previous work described the fabrication of microfluidic devices by the thermal deposition of a toner (mainly composed by carbon powder and iron oxide) thin layer on polyester substrate (similar thickness of the one used in this work) and such devices were compatible with methanol and acetonitrile (even after 48 h of exposure) [38]. Further investigation is necessary to understand the high resistance to organic solvents of these polyester-printed sensors.

4. Conclusions

This work has demonstrated the first application of organic-resistant SPGEs for the analysis of fuel and biofuel in a medium containing 99% (v/v) ethanol. The polyester-based electrochemical sensor is highly compatible with these samples as well as with organic solvents. The association of SPGEs with BIA for 2,6-DTBP determination resulted in a highly precise, accurate (confirmed by recovery tests and chromatographic analyses), sensitive, and fast analytical method. The successful application of SPGEs for the analysis of jet fuel and biodiesel provides great promises for the development of a portable fuel analyzer capable of performing the quality control of automotive (bio)fuels at gas stations. Additionally, the SPGEs can be applied for the analysis of other organic samples such as food and edible oils.

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FIGURE CAPTIONS

Figure 1. Cyclic voltamograms of 5 mmol L⁻¹ 2,6-DTBP (—), 3 mmol L⁻¹ ferrocene (- - -) and (- - -) blank in a hydroethanolic solution containing 99% (v/v) ethanol and 0.1 mol L⁻¹ HClO₄ (A) and in pure ethanol containing 0.1 mol L⁻¹ TBAClO₄ (B). Scan rate of 50 mV s⁻¹.

Figure 2. Optimization of the BIA parameters for 2,6-DTBP determination on a SPGE. (A-B) Stirring Speed; (C-D) Injection rate; and (E-F) Injection volume. Conditions in (A-B): E_{ox} = 1.1 V; dispensing rate = 53 μL s⁻¹, injection volume = 50 μL and 0.1 mol L⁻¹ HClO₄ in 50% v/v ethanol; in (C-D and E-F) similar conditions to (A-B) except to the stirring speed = 1320 rpm.

Figure 3. Evaluation of the ethanol content in electrolyte. Conditions E_{ox} = 1.1 V; stirring speed = 1320 rpm, dispensing rate = 53 μL s⁻¹, injection volume = 100 μL and HClO₄ concentration = 0.1 mol L⁻¹.

Figure 4. (A) Amperometric response obtained after injections (n=4) of standard solutions containing 2,6-DTBP (a–e: 2.5–25 mg L⁻¹, increasing increments), samples after 20-fold dilution in electrolyte (IV and V, corresponding to samples in Table 4), and standard solutions of 2,6-DTBP (e'– a', decreasing increments). (B) Calibration curves for 2,6-DTBP: increasing (■ R = 0.9972) and decreasing concentrations (● R = 0.9953). Conditions in Table 1.