Analytical Methods

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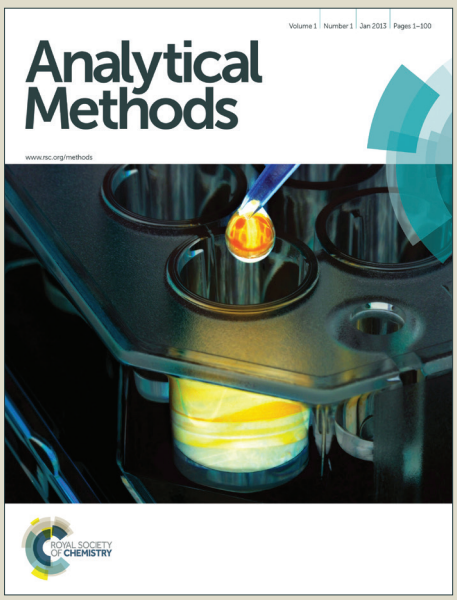

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PAPER

Carbon-nanotube–modified screen-printed electrodes, cationic surfactant, and peak deconvolution procedure: alternatives to provide satisfactory simultaneous determination of three synthetic antioxidants in complex samples

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The development of electroanalytical methods for determining three or more analytes simultaneously in a complex sample is highly desirable. Unfortunately, this is not an easy task in electrochemical studies of organic compounds, and alternative methods to achieve this goal have been increasingly sought in recent years. To this end, the present investigation employed a combination of screen-printed electrodes (SPEs), cetyltrimethylammonium bromide (CTAB), and a peak deconvolution procedure as an alternative approach to improve sensitivity and selectivity in the simultaneous determination of three antioxidants in samples of biodiesel and cosmetic oils. Use of CTAB also prevents the occurrence of SPE fouling by matrix constituents, being essential in the simultaneous detection of the antioxidants tert-butylhydroquinone (TBHQ), propyl gallate (PG), and butylhydroxyanisole (BHA). Under optimized conditions, the limit of detection proved satisfactory, with relative standard deviations of 0.99% for TBHQ, 2.1% for PG, and 0.61% for BHA, indicating that the method has satisfactory repeatability. The approach was successfully applied to determine the target antioxidants in biodiesel samples at different concentrations after simple, rapid dilution, yielding recovery rates of 98-106% for TBHQ, 98-103% for PG, and 92-101% for BHA. In the analysis of cosmetic oils, a deconvolution procedure was applied to achieve separation of the oxidation peak potentials, with recovery rates of 94% for PG and 101% for BHA using the standard addition method. The results were satisfactory compared with those obtained using high-performance liquid chromatography.

Introduction

Synthetic antioxidants are a group of chemical compounds extensively used in food, [1-3] cosmetics [4,5] and biodiesel industries [6-8] as additives to improve the stability of commercial products by preventing oxidative rancidity. [9,10] Tert-butylhydroquinone (TBHQ), butylhydroxyanisole (BHA), propyl gallate (PG), and hydroxytoluene (BHT) are among the primary phenolic antioxidants added to cosmetics and biodiesel for this purpose. However, the use of antioxidants is limited in a number of countries for posing serious health risks. Antioxidants are added to cosmetics to inhibit the degradation caused by lipid oxidation and also as preservatives. However, if used in large amounts, phenolic antioxidants can have detrimental effects on health. [11,12]

Several studies have compared the effects of single synthetic antioxidants on biodiesel oxidative stability and NO_x emission, revealing that TBHQ, BHA, and PG enhance oxidative stability and decrease NO_x emission. [9,10,13] Moreover, PG has been widely employed as a biodiesel additive, contributing towards complexation with metals present in this fuel. [14,15] The development of fast, straightforward analytical methods for monitoring the presence of antioxidants in commercial samples is currently in great demand.

Analytical methods have been developed for the simultaneous determination of different synthetic antioxidants. Several methods for antioxidant detection in samples of cosmetic oils and biodiesel rely on techniques such as high-performance liquid chromatography (HPLC) coupled with a diode array detector, [6] micellar electrokinetic capillary chromatography with electrochemical detection [4] and voltammetric measurements. [1-3,7,8,16-20] We have recently reported an electroanalytical method for simultaneous determination of TBHQ and BHA in biodiesel samples using linear sweep voltammetry and a cationic surfactant, in addition to multi-walled carbon nanotube SPEs. [18] Because other antioxidants, such as PG, are being used in the cosmetics and biodiesel industries, new methods for selective simultaneous determination of the antioxidant concentrations in commercial samples are currently required. Furthermore, some samples can alter oxidation peak potentials, interfering with their simultaneous

determination. Thus, a deconvolution procedure, previously described elsewhere [21], can be used to separate overlapped peaks satisfactorily, so as to overcome this limitation.

SPEs can serve as powerful tools for simultaneous determination of compounds, with advantages such as smaller size, low cost, high sensitivity, high reproducibility, and ease of use, in addition to being rapid and suitable for on-site analyses. [22-24] In addition, carbon nanotubes (CNTs) have drawn interest in the field of nanotechnology because of their structural features, electronic conduction, significant mechanical strength, high chemical stability, and chemical properties, all of which have made them widely used in the development of chemically modified electrodes. CNTs can also promote electron transfer reactions and improve sensitivity in electrochemistry. Furthermore, modification of the electrode surface with single- or multi-walled CNTs for applications in electroanalysis and sensing has enabled low detection limits, high sensitivity, and stability, while enhancing signal-to-noise ratios, decreasing overpotentials, and promoting resistance to surface fouling. [25-29]

Advancements in electroanalytical determination have also occurred in the use of surfactants, [18,30-34] amphiphilic molecules capable of increasing the solubility of phenolic compounds in aqueous phase and changing oxidation peak potentials, electron-transfer rates, and diffusion transfer coefficients, in addition to increasing the sensitivity and selectivity for analytes. [30-32] For instance, Dos Reis et al., [33] observed separation between peak potentials along with an increase in peak currents in the oxidation of ascorbic acid and dopamine in the presence of the cationic surfactant cetylpyridinium chloride. Furthermore, the use of surfactants can contribute to the stability of electrochemical signals and intermediate species, minimizing electrode surface passivation. [30-33]

In the present study, the anti-fouling ability of CTAB was combined with a deconvolution procedure plus use of multi-walled-carbon-nanotube–modified screen-printed electrodes (MWCNT-SPEs), affording a suitable alternative approach to improve selectivity in the simultaneous electroanalytical determination of TBHQ, PG, and BHA in biodiesel and cosmetic oil samples.

Experimental

Chemicals, reagents, and standard solutions

TBHQ (97.0%), PG (98.0%), and BHA (96.0%) were purchased from Acros Organics (USA). All reagents were used without further purification. Standard stock solutions were prepared by dissolving suitable amounts in ethanol (99.6%, Dinâmica, Brazil). Standard working solutions of the target antioxidants were prepared in ethanol by diluting the standard stock solutions (4.0×10^{-3} mol L^{-1}).

Britton–Robinson (BR) buffer, used as the supporting electrolyte, was prepared by mixing 0.04 mol L^{-1} acetic acid (99.7%, Acros Organics, USA), 0.04 mol L^{-1} boric acid (99.9%, Acros Organics, USA), and 0.04 mol L^{-1} orthophosphoric acid (85%, Acros Organics, USA). For pH adjustments, appropriate volumes of 0.5 mol L^{-1} sodium hydroxide (Acros Organics, USA) were used.

Solutions of the anionic surfactant sodium dodecyl sulfate (SDS) (95.0%, Sigma, USA), the cationic surfactant cetyltrimethylammonium bromide (CTAB) (SERVA, Germany), and the non-ionic surfactant Triton X-100 (Acros Organics, USA) were prepared in ultrapure water ($R \geq 18.2$ MΩ cm).

Methanol (HPLC grade, J.T. Baker, USA) and ultrapure water were used for chromatographic analysis. Glacial acetic acid (Suprapure, Vetec, USA) at 0.5% (v/v) was employed for acidification of the aqueous mobile phase.

Apparatuses and electrodes

All voltammetric measurements were performed using a μ-Autolab Type II potentiostat/galvanostat (Eco Chemie, Metrohm Autolab B.V.) interfaced to a microcomputer and controlled by GPES 4.9.007 software. The working electrode consisted of a device with a carboxyl-functionalized MWCNT-SPE, a carbon screen-printed electrode (C-SPE) or a carboxyl-functionalized single-walled-carbon-nanotube screen-printed electrode (SWCNT-SPE), all with surface areas of 12.6 mm^2. These systems included a printed carbon counter-electrode and a silver pseudo-reference electrode (DropSens, Oviedo, Spain).

The HPLC system (Shimadzu) consisted of LC 20AT multichannel pumps, an SIL 20A autosampler, a DGU 20A5 degasser, and a DAD SPD 20A diode array detector. Separation of antioxidants was performed using a C-18 reversed-phase column (150 mm × 4.6 mm i.d., 5 μm, Agilent HP).

Adjustment of pH was made using a combined glass electrode (BlueLine, Shott) connected to a digital MPA-20 pH-meter (Tecnopon) and deionized water purified using a Purelab classic system (Elga, United Kingdom). A USC 1400 ultrasonic cleaner (Unique) was employed for dissolution of the reagents and sample preparation. A micropipette (Labmate) was used during solution preparation and also to transfer the reactant solution to the electrochemical cell. A model II centrifuge (Certomat) was used to prepare the stock solutions as well as the biodiesel and cosmetic oil samples before analysis.

Voltammetric analysis

The supporting electrolyte solution (BR buffer, 0.04 mol L^{-1}) was transferred to the electrochemical cell (maximum volume: 10 mL) and stirred with pure nitrogen for approximately 30 s, and left to rest for 15 s before the background voltammetric curve was recorded. An aliquot of surfactant at the desired concentration was subsequently added to the cell under stirring for 30 s and, after a 15 s rest period, cyclic or linear sweep voltammograms were recorded. For antioxidant determination, aliquots of stock solution were transferred to the cell, and voltammograms were again recorded using the same SPE. Although the SPEs were described by the manufacturer as disposable, it was possible to reuse the same electrode for at least 50 measurements. To this end, the SPE surface was cleaned with ethanol (99.6%, Dinâmica, Brazil) and left to rest for approximately 5.0 min between measurements. This cleaning method did not lead to peak current loss over time.

Deconvolution procedure

To analyze the cosmetic oil sample (a commercial mixture of kukui nut and date oils) containing TBHQ and PG, a mathematical deconvolution procedure [21] using Microcal Origin® software (version 6.0) was applied to achieve satisfactory simultaneous determination of the target antioxidants. The

baselines of all voltammograms were adjusted and the "analysis-Gaussian" tool was employed to select the number of peaks, peak widths at half-height ($W_{1/2}$, fixed at 95 mV), and peak potentials. The deconvolution procedure ensured satisfactory separation of TBHQ and PG peaks and quantification of these compounds in the cosmetic oil sample.

Preparation and analysis of biodiesel samples

Commercial samples of antioxidant-free soybean biodiesel (collected by the Laboratório de Combustíveis de Mato Grosso do Sul) were spiked with TBHQ, PG, and BHA at different ratios (Table 2), vigorously agitated, and diluted in ethanol using calibrated flasks to attain a final concentration of 10.0% (biodiesel : ethanol, v/v). A 50.0 µL aliquot of the resulting solution was transferred to the electrochemical cell containing 10.0 mL of supporting electrolyte solution. The resulting solution was directly analyzed by linear sweep voltammetry (LSV). The standard addition method was applied to determine TBHQ, PG, and BHA concentrations in the biodiesel samples.

Preparation, extraction, and analysis of cosmetic oil samples

Samples of the kukui and date oils mixture containing TBHQ were spiked with PG and BHA at different ratios (see Table 2). Aliquots of 5.0 g of the oil mixture were placed into a centrifuge tube with 10 mL of ethanol and gently stirred for 15 min. The mixture was sonicated for 10 min and centrifuged at 3000 rpm for another 15 min. A 25.0 µL aliquot of the resulting supernatant solution was transferred to an electrochemical cell containing 10 mL of supporting electrolyte and voltammograms were then recorded. The target antioxidants were quantified using the standard addition method.

Chromatographic conditions

For determination of TBHQ, PG, and BHA, optimal chromatographic conditions were achieved by adapting the methodology developed by Caramit et. al. [18] To this end, HPLC was performed in gradient mode using methanol as the organic phase and 1.0% acetic acid as the aqueous phase, at a flow rate of 1.00 mL min^{-1} (25 ºC). The detector was set at 280 nm. For operating in gradient mode, elution started at 55.0% methanol (from 0 to 3.00 min), followed by 55.0-100% methanol (from 3.00 to 6.00 min), and 100% methanol thereafter, up to 12.0 min. The methanol percentage was returned to 55.0% (from 12.0 to 13.0 min), remaining as this level until 23.0 min. Retention times were 4.5 min for TBHQ, 2.9 min for PG, and 9.7 for BHA.

Results and discussion

Voltammetric behavior of TBHQ, PG, and BHA at a MWCNT-SPE

Voltammetric measurements were performed with different types of SPEs. Figure 1 shows cyclic voltammograms obtained in the absence and presence of TBHQ, PG**,** and BHA in buffer solution without organic solvents. In Figure 1, voltammogram **A** depicts the voltammetric behavior of these antioxidants for a C-SPE. Note the presence of only two oxidation peaks, indicating that this electrode failed to detect all three antioxidants simultaneously. In contrast, well-defined oxidation peak currents were detected by the MWCNT-SPE at –0.05, 0.11, and 0.25 V, corresponding to oxidation of TBHQ, PG, and BHA, respectively (Figure 1C). [20] The TBHQ oxidation peak current detected by the SWCNT-SPE, however, was very small (Figure 1B). The higher oxidation peak current observed using the MWCNT-SPE can be attributed to the fact that electron transfer from the antioxidant is facilitated by the structural features of MWCNTs, as reported in earlier studies. [18,25,27] The separation of TBHQ, PG, and BHA peak potentials, together with increased oxidation peak currents, suggests that MWCNT-SPEs are promising devices for the development of a novel electroanalytical method for the simultaneous determination of target antioxidants.

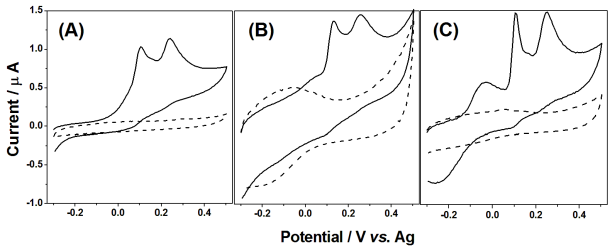

Figure 1. Cyclic voltammograms obtained on different screen-printed electrode surfaces. Blank: Britton–Robinson buffer (0.04 mol L^{-1}, pH 4.0) and a mixture of TBHQ, PG, and BHA, each at 1.0×10^{-5} mol L^{-1}, detected by (*A*) C-SPE, (*B*) SWCNT-SPE, and (*C*) MWCNT-SPE. Scan rate: 70 mV s^{-1}.

The separation of anodic peak potentials and the intensity of the peak current were investigated by comparing differential pulse voltammetry (DPV, Figure 2a), linear sweep voltammetry (LSV, Figure 2b), and square-wave voltammetry (SWV, Figure 2c) readings on the surface of a MWCNT-SPE under the same experimental conditions. DPV and SWV revealed lower anodic peak currents and ensured separation between PG and BHA, while LSV yielded better separation of all three antioxidants. Given the high antioxidant concentrations expected in biodiesel samples (250 mg L^{-1}), [9,10,13] highly sensitive techniques such as DPV or SWV are not required. LSV was therefore the technique selected for further studies, for which several parameters related to this approach were optimized.

The influence of LSV scan rate on the oxidation peak current was also evaluated. The increase in oxidation peak currents for all three antioxidants was proportional to the increase in scan rates. However, at a scan rate above 70 mV s^{-1}, deformation of the oxidation peak current was observed for PG. A scan rate of 70 mV s^{-1} was therefore selected for further measurements.

Choice of surfactants

Selectivity and sensitivity for separation of peak currents was monitored by recording LSV readings of the antioxidants in the presence of cationic (CTAB), anionic (SDS), or nonionic (Triton X-100) surfactants. In all three cases, none of the background voltammograms exhibited peaks in the potential range scanned. Use of anionic surfactant (2.0×10^{-4} mol L^{-1}, Figure 3c) and non-ionic surfactant (2.0×10^{-4} mol L^{-1}, Figure 3b) did not significantly change the electroanalytical response to the point of interfering with the simultaneous detection of the antioxidants. However, presence of the cationic surfactant (2.0×10^{-4} mol L^{-1}, Figure 3d) shifted the oxidation peak potentials and increased peak

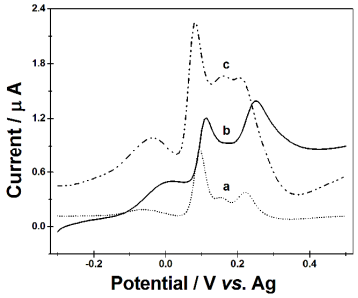

Figure 2. (a) DPV, (b) LSV, and (c) SWV readings obtained using a MWCNT-SPE in BR buffer (0.04 mol L^{-1}, pH 4.0) in a mixture of TBHQ, PG and BHA, each at 1.0×10^{-5} mol L^{-1}. E_{step}: 6 mV; frequency: 10 Hz; amplitude: 5 mV (SWV). E_{step}: 6 mV; scan rate: 70 mV s^{-1} (LSV). E_{step}: 6 mV; modulation time: 0.07 s; interval time: 0.5 s; modulation amplitude: 0.02 V (DPV).

potentials and increased peak currents, proving a more favorable condition for simultaneous detection of antioxidants.

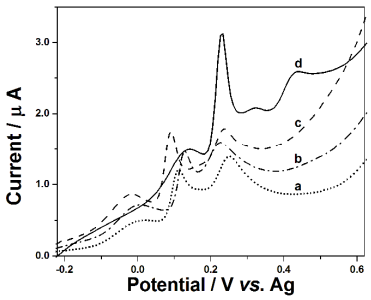

Figure 3. Linear sweep voltammograms obtained using a MWCNT-SPE in BR buffer (0.04 mol L^{-1}, pH 4.0) ***(a)*** in the presence of 1.0×10^{-5} mol L^{-1} TBHQ, PG, and BHA in the absence of surfactant; ***(b)*** in the presence of 2.0×10^{-4} mol L^{-1} Triton X-100 surfactant; ***(c)*** in the presence of 2.0×10^{-4} mol L^{-1} SDS surfactant; ***(d)*** in the presence of 2.0×10^{-4} mol L^{-1} CTAB surfactant. Scan rate: 70 mV s^{-1}.

This effect was observed while the cationic surfactant concentration remained below the critical micelle concentration (CMC), due to adsorption of the monomeric surfactant species onto the electrode surface, leading to formation of a positively charged film capable of altering the electron transfer rate and electrode overvoltage, as well as attracting the organic molecules via electrostatic interaction and solubility of the generated products, avoiding passivation of the electrode surface. [30,32,33,35] Cationic surfactants can be more easily adsorbed onto the electrode hydrophilic surface than other surfactants, [35] a feature that facilitates antioxidant accumulation on the electrode surface by way of the adsorbed CTAB layer.

Figure 4 shows the linear sweep voltammograms obtained on a MWCNT-SPE surface for the electrochemical oxidation of TBHQ, PG, and BHA (1.0×10^{-5} mol L^{-1} each) in BR buffer (pH 4.0) in the presence of CTAB (2.0×10^{-4} mol L^{-1}). TBHQ, PG, and BHA exhibited oxidation peaks at 0.12 V (Figure 4b), 0.23 V (Figure 4c), and 0.43 V (Figure 4d), respectively. The first peak, at 0.12 V (for TBHQ), corresponded to oxidation of the hydroquinone group to quinone. [2] The second peak, at 0.23 V, and a broad peak at 0.32 V (for PG) were attributed to oxidation of the hydroxyl group to quinone. [3,20] The fourth peak, at 0.43 V (for BHA), corresponded to oxidation of the hydroxyanisole group to quinone.[2] The mechanisms of TBHQ, PG, and BHA electrochemical oxidation involve a two-electron process. [1-3]

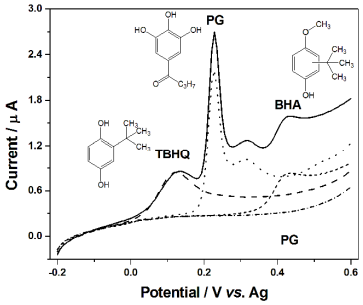

Figure 4. Linear sweep voltammograms obtained on a MWCNT-SPE for (*a*) blank: BR buffer (0.04 mol L^{-1} , pH 4.0); (*b*) 1.0×10^{-5} mol L^{-1} TBHQ; (*c*) 1.0×10^{-5} mol L^{-1} PG; (*d*) 1.0×10^{-5} mol L^{-1} BHA; (*d*) a mixture of TBHQ, PG, and BHA, each at 1.0×10^{-5} mol L^{-1}. Scan rate: 70 mV s^{-1}.

Effect of pH

The effect of BR buffer (pH 2.0-10.0) on the separation of the peak potentials (E_p) of TBHQ, PG, and BHA was investigated in the presence and absence of CTAB using a MWCNT-SPE to record LSV readings at a scan rate of 70 mV s^{-1}. E_p shifted towards more negative values when pH was increased, indicating that the process is influenced by protonation reactions facilitated at lower pH values. [36]

In the presence of CTAB, the E_p *vs*. pH plot shows linear anodic shifts for TBHQ, PG, and BHA in the pH range of 2.0 to 10.0, with slopes of –64.7 mV pH^{-1} (r = –0.991), –61.8 mV pH^{-1} (r = –0.997), and –56.3 mV pH^{-1} (r = –0.997), respectively. Absence of CTAB did not change these slope values significantly, indicating that this surfactant does not interfere with the oxidation mechanism of the antioxidants. The slopes suggest that the oxidation process involves the same number of protons and electrons. The theoretical value of 59 mV pH^{-1} indicates the involvement of two electrons and two protons in all three electrochemical processes.

The influence of pH variation on the peak currents (I_p) of oxidation is shown in Figure 5. Within the pH range investigated, current values were satisfactory at pH 4.0 for BHA and PG oxidation. For TBHQ, the anodic peak current remained constant.

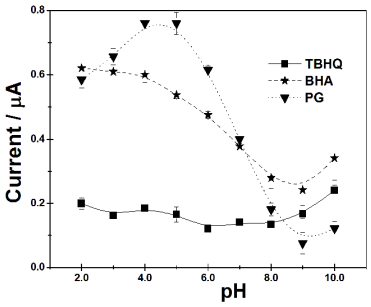

Figure 5. Influence of pH on the oxidation peak current (I_p) for (■) 1.0×10^{-5} mol L^{-1} TBHQ, (▼) 1.0×10^{-5} mol L^{-1} PG, and (★) 1.0×10^{-5} mol L^{-1} BHA. Scan rate: 70 mV s^{-1}.

Anodic peak currents and separation of peak potentials indicated that the best experimental conditions to detect TBHQ, PG, and BHA were provided using 0.04 mol L^{-1} BR buffer at pH 4.0.

Optimization of CTAB concentration

The influence of CTAB concentration on simultaneous oxidation was investigated by monitoring the voltammetric behavior of TBHQ (1.0×10^{-6} mol L^{-1}), PG (1.0×10^{-6} mol L^{-1}), and BHA (1.0×10^{-6} mol L^{-1}) at CTAB concentrations ranging from 0 to 1.1×10^{-3} mol L^{-1}. For each of these, an increase was observed in the anodic peak currents at a concentration of 2.0×10^{-4} mol L^{-1}. Higher CTAB concentrations led to lower peak currents, possibly due to formation of micellar aggregates. [31] The 2.0×10^{-4} mol L^{-1} concentration was therefore selected as the most favorable for simultaneous TBHQ, PG, and BHA detection.

Analytical curve and repeatability

Once the optimal experimental conditions for simultaneous electroanalytical detection of TBHQ, PG, and BHA were identified, voltammograms were obtained in BR buffer (pH 4.0) and 2.0×10^{-4} mol L^{-1} CTAB before and after addition of TBHQ, PG, and BHA at concentrations in the 1.0-10.7 μmol L^{-1} range using a MWCNT-SPE (Figure 6). The insets to Figure 6 reveal suitable linearity of the analytical curves in the concentration range investigated.

The limits of detection (LODs) were calculated from the statistical relations 3 *sd*/*m* and 10 *sd*/*m*, where *sd* is the standard deviation of the peak current for the blank and *m* is the slope of the analytical curve. The LOD values shown in Table 1 reveal the high sensitivity of the proposed method. No published studies, however, were found on the simultaneous determination of TBHQ, PG, and BHA in biodiesel by electrochemical methods. Thus, the values obtained for the proposed method were satisfactory, relative to those obtained by HPLC and found in the literature. [37] The precision of the method (repeatability) was investigated by monitoring the voltammetric behavior of TBHQ, PG, and BHA (1.0×10^{-6} mol L^{-1} each) over the course of 11 successive scans. Relative standard deviations (RSDs) were 0.99% for TBHQ, 2.1% for PG, and 0.61% for BHA, indicating acceptable repeatability.

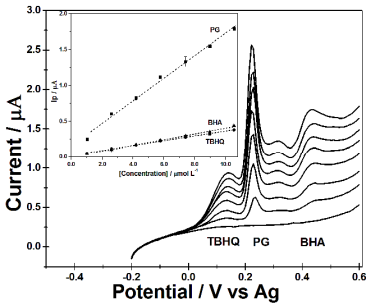

Figure 6. Linear sweep voltammograms recorded using a MWCNT-SPE at a scan rate of 70 mV s^{-1} for TBHQ, PG, and BHA concentrations of 1.00×10^{-6} to 1.07×10^{-5} mol L^{-1} in 0.04 mol L^{-1} BR buffer at pH 4.0 with 2.00×10^{-4} mol L^{-1} CTAB. Inset: Analytical calibration for the dependence of oxidation peak currents on TBHQ, PG, and BHA concentrations.

Analytical application

Using the optimal experimental conditions of the proposed method, a MWCNT-SPE was employed to determine TBHQ, PG, and BHA in commercial biodiesel samples. No oxidation signals for the selected antioxidants were initially found in the samples (Figure 7, curve *a*). The biodiesel samples were then spiked with different TBHQ, PG, and BHA concentrations. [9,10,13] Figure 6 shows the LSV readings for antioxidant detection after applying the standard addition method (Figure 7, curves *b*-*e*).

The proposed method successfully detected these antioxidants in the biodiesel samples using simple, rapid dilution steps, and the results were not compromised by matrix effects. The average recovery rates of TBHQ, PG, and BHA from the biodiesel samples are reported in Table 2 and the results reveal the method's satisfactory accuracy for simultaneous determination of these antioxidants.

Also, no significant differences in the results were found between the proposed approach and the reference method (Table 2), demonstrating the feasibility of applying the proposed method to the simultaneous determination of antioxidants in commercial

Table 1. Analytical parameters obtained from calibration curves for TBHQ, PG, and BHA using the proposed method, compared against references.

Method	Linear range	Intercept	Slope	*R*	LOD/mol L^{-1}
Proposed method					
TBHQ	$(1–10) \times 10^{-6}$ mol L^{-1}	2.64×10^{-8} A	3.38×10^{-2} L mol^{-1}	0.999	4.87×10^{-7} (0.081 mg L^{-1})
PG	$(1\text{-}10) \times 10^{-6}$ mol L^{-1}	1.57×10^{-7} A	1.58×10^{-1} L mol^{-1}	0.997	1.04×10^{-7} (0.022 mg L^{-1})
BHA	$(1\text{-}10) \times 10^{-6}$ mol L^{-1}	2.87×10^{-9} A	4.01×10^{-2} L mol^{-1}	0.998	5.18×10^{-7} (0.093 mg L^{-1})
HPLC					
TBHQ	$(0.6\text{-}30) \times 10^{-5}$ mol L^{-1}	-15137 mAU	2.69×10^{9} mAU L mol^{-1}	0.999	1.10×10^{-5} (1.8 mg L^{-1})
PG	$(0.5\text{-}24) \times 10^{-5}$ mol L^{-1}	-47689 mAU	1.16×10^{10} mAU L mol^{-1}	0.999	1.02×10^{-5} (2.2 mg L^{-1})
BHA	$(0.6\text{-}28) \times 10^{-5}$ mol L^{-1}	-4916.6 mAU	2.98×10^{9} mAU L mol^{-1}	0.999	1.16×10^{-5} (2.1 mg L^{-1})
Literature					
TBHQ	(1-15) mg L^{-1}	9.18×10^{-7} A	1.36×10^{-1} L mg^{-1}	0.999	0.073 mg L^{-1}
PG	(1-15) mg L^{-1}	1.05×10^{-6} A	1.15×10^{-1} L mg^{-1}	0.997	0.54 mg L^{-1}
BHA	(0.5-15) mg L^{-1}	8.83×10^{-7} A	2.16×10^{-1} L mg^{-1}	0.999	0.19 mg L^{-1}

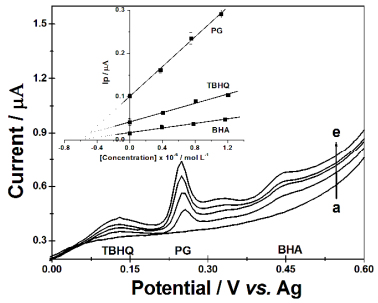

Figure 7. Linear sweep voltammograms recorded using a MWCNT-SPE at a scan rate of 70 mV s^{-1} for determination of TBHQ, PG and BHA. (*a*) Antioxidant-free soybean biodiesel; (*b*) biodiesel containing 250 mg L^{-1} concentrations of TBHQ, PG, and BHA; (*c*-*e*) successive additions of 4.02×10^{-7} mol L^{-1} TBHQ, 3.72×10^{-7} mol L^{-1} PG, and 3.87×10^{-7} mol L^{-1} BHA. Other conditions as in Figure 6.

biodiesel samples.

The novel methodology was also applied to cosmetic oil samples containing TBHQ. Two samples of the kukui and date oil were fortified with PG or BHA. In the fortified samples containing PG and TBHQ, an overlapping of antioxidant peaks was observed, possibly owing to matrix effects that compromised simultaneous detection. To separate the peaks, deconvolution was applied, enabling baseline definition enhancement and satisfactory simultaneous quantification of TBHQ and PG. As shown in Figure 8, separation of the partially overlapping peaks, achieved with deconvolution from LSV peaks, proved crucial to obtaining enhanced baseline definition and suitable quantification of TBHQ in the presence of PG in the cosmetic oil sample fortified with 440 mg L^{-1} PG.

The standard addition curve (Figure 8, inset) displayed satisfactory linearity and, together with the recovery rates (Table 3) and LOD values (Table 4), demonstrates that the proposed electroanalytical method associated with peak deconvolution can be successfully employed for simultaneous determination of antioxidants in cosmetic oil samples.

Table 2. Recovery rates of TBHQ, PG, and BHA from biodiesel samples using the standard addition method.

			Proposed approach			HPLC		
Sample	Analyte	Spiked/mg L^{-1}	Found[(a)]/mg L^{-1} ± *sd*	Recovery/%	RSD/%	Found[(a)]/mg L^{-1} ± *sd*	Recovery/%	RSD/%
A	TBHQ	500	501±5.5	100	1.1	417±1.8	83.4	0.36
	PG	500	517±25	103	5.1	474±0.5	94.7	0.10
	BHA	500	501±14	100	2.7	479±7.1	95.8	1.4
B	TBHQ	250	266±11	106	4.4	244±0.25	97.6	0.10
	PG	250	246±7.3	98.2	2.9	260±0.37	104	0.15
	BHA	250	231±8.4	92.4	3.4	252±5.3	101	2.1
C	TBHQ	300	302±11	100	3.7	278±0.21	92.6	0.07
	PG	50	49.0±2.0	98.1	4.0	50.3±4.3	100	8.6
	BHA	250	245±14	97.9	5.7	263±0.30	105	0.12
D	TBHQ	400	392±4.2	98.1	1.1	348±0.24	87.0	0.06
	PG	300	293±25	97.7	8.2	299±0.30	99.8	0.10
	BHA	600	610±7.5	102	1.2	617±0.90	103	0.15

[(a)] Average of three determinations.
sd: standard deviation for average of three determinations.
RSD: relative standard deviation for the average values.

Table 3. Recovery rates of TBHQ, PG, and BHA from cosmetic oil samples using the standard addition method.

			Proposed approach			Deconvolution procedure		
Sample	Analyte	Spiked/mg L^{-1}	Found[a]/mg L^{-1} ± *sd*	Recovery/%	RSD/%	Found[a]/mg L^{-1} ± *sd*	Recovery/%	RSD/%
A	TBHQ	-	1219±19	-	-	-	-	-
	BHA	530	538±32	101	6.0			
B	TBHQ	-	812±71	-	-	1116±74	-	-
	PG	440	344±35	75.9	6.9	414±33	94.1	9.4

[a] Average of three determinations.
sd: standard deviation for average of three determinations.
RSD: relative standard deviation for the average values.

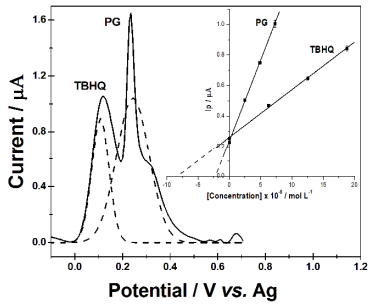

Figure 8. Linear sweep voltammograms recorded using a MWCNT-SPE at a scan rate of 70 mV s^{-1} for simultaneous electrochemical oxidation of TBHQ and PG in cosmetic oil samples spiked with 440 mg L^{-1} PG. (Inset) Calibration curve for a sample containing 440 mg L^{-1}, with successive additions of 6.28 × 10^{-6} mol L^{-1} TBHQ and 2.38 × 10^{-6} mol L^{-1} PG. Other conditions as in Figure 6.

Table 4. Limits of detection of TBHQ, PG, and BHA in biodiesel and cosmetic oil samples.

Sample	TBHQ	PG	BHA
Biodiesel	162 mg L^{-1}	50.8 mg L^{-1}	212 mg L^{-1}
Cosmetic oil	158 mg L^{-1}	67.9 mg L^{-1}	205 mg L^{-1}

Conclusions

MWCNT-SPEs were employed in conjunction with a cationic surfactant to resolve a selectivity limitation, and proved a successful alternative approach to allow simultaneous determination of antioxidants in biodiesel and cosmetic oil samples. CTAB, the cationic surfactant, contributed towards enhancing current intensity and displacing the oxidation peak potentials of the antioxidants, facilitating their detection at low concentrations. Moreover, the novel method afforded fast response, sensitivity, selectivity, and satisfactory repeatability and reproducibility in the determination of antioxidants in commercial biodiesel, requiring a single simple pretreatment step. When more complex samples, such as the cosmetic material, were analyzed, simultaneous determination entailed previous deconvolution to resolve the problem of overlapping peaks.

Finally, the satisfactory recovery tests were comparable to those achieved using HPLC methods, demonstrating that the combined approaches can be successfully employed to improve electroanalysis of target antioxidants in routine quality control of biodiesel and cosmetic oil samples.

Notes and references

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