

# Analytical Determination of Benzophenone-3 in Sunscreen Preparations Using Boron-Doped Diamond Electrodes

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## Abstract

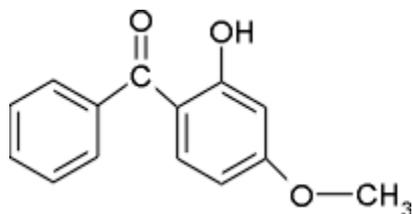
A new electroanalytical procedure was developed for the determination of Benzophenone-3 (BENZO) in commercial sunscreen as the active ingredient. The procedure is based on the use of electrochemical methods as cyclic and square-wave voltammetry, with boron-doped diamond (BDD) electrodes. The reduction of BENZO in Britton-Robinson buffer (0.1 mol·L<sup>-1</sup>) using this type of electrode gives rise to one irreversible peak in -1.30 V (versus Ag/AgCl) in presence of cationic surfactant cetyltrimethylammonium bromide (CTABr). The proposed electrochemical method was successfully applied to the analysis of commercially available pharmaceutical preparations.

**Keywords:** Boron-Doped Diamond, Benzophenone-3 BENZO and Square-Wave Voltammetry

## 1. Introduction

Benzophenone-3 (BENZO) (**Figure 1**) is the organic compound widely used in sunscreen agent that absorbs and dissipates ultraviolet radiation or in a variety of cosmetic products [1]. BENZO also has been used as ultraviolet stabilizer in plastic surface coatings for food packaging to prevent polymer or food photodegradation [2] and is approved by the U.S. Food and Drug Administration as an indirect food additive.

The focus of pharmaceuticals and ingredients in personal care products, including organic sunscreen agents, as environmental pollutants is increasing because these compounds may enter the aquatic environment not primarily as a result of manufacturing practices, but from



**Figure 1.** Chemical structure of benzophenone-3.

their steady and widespread use in human and veterinary

daily activities [3]. Furthermore, little is known about the potential hazards associated with recurring human or ecologic exposures to these synthetic substances, many of which are bioactive. BENZO, one of these substances, has been detected in surface waters [4], drinking water, and wastewater [5]. The development of methods capable of directly quantifying BENZO in commercial pharmaceutical preparations also becomes important in quality control of sunscreens.

The most often techniques observed in the literature for the determination sunscreen composition are high-performance liquid chromatography (HPLC) [6,7] and gas chromatography (GC) coupled with various detection methods such as ultraviolet (UV) [8] and mass spectrometry [9]. However, electrochemical techniques are useful alternative methods widely used in pharmaceutical applications. They are usually easy and rapid to perform and are less expensive than chromatographic methods. In addition, the sensitivity of electrochemical methods is often greater than that of spectrophotometric procedures.

A few studies have reported the use of electroanalytical methods to determine BENZO and related compounds. Vidal, *et al.* [10] applied chemically surface-modified carbon nanoparticles for the extraction and electrochemical determination of phenolic impurities such as BENZO (2-hydroxy-4-methoxybenzophenone).

The hydrophilic carbon nanoparticles were readily suspended and separated by centrifugation prior to deposition onto suitable electrode surfaces and voltammetric analysis. Voltammetric peaks provide concentration information over a 10 - 100  $\mu\text{M}$  range and an estimated limit of detection of ca. 10  $\mu\text{M}$  (or 2.3 ppm) for BENZO. Alternatively, analyte-free carbon nanoparticles immobilized at a graphite or glassy carbon electrode surface and directly immersed in analyte solution bind BENZO with an estimated Langmuir binding constants of  $K \approx 6000 \text{ mol}\cdot\text{L}^{-1}$  at pH 9.5 and it also give characteristic voltammetric cathodic response for BENZO with a linear range of ca. 1 - 120  $\mu\text{M}$ . The estimated limit of detection is improved to ca. 5  $\mu\text{M}$  (or 1.2 ppm) for BENZO.

Razak, *et al.* [10] reported the use of differential pulse polarographic method for detection and trace determination of benzophenone (the main impurity) in phenytoin powder. The method depends upon the polarographic activity of benzophenone in Britton-Robinson buffer pH 5.6. The limit of detection was found to be  $2.5 \times 10^{-6} \mu\text{g}\cdot\text{mL}^{-1}$ . Phenytoin has been analysed polarographically after oxidation with alkaline permanganate to give benzophenone; the limit of detection was found to be  $6 \times 10^{-6} \mu\text{g}\cdot\text{mL}^{-1}$ . In a study performed by Cardoso, *et al.* [12], was proposed a methodology based on electrochemical reduction for the simultaneous determination of three sunscreen agents, namely 4-methylbenzylidene camphor (MBC), BENZO and 2-ethylhexyl-4-methoxycinnamate (EHMC) by differential-pulse polarography (DPP). The highest peak currents and optimal separation of reduction peaks were obtained by using a supporting electrolyte consisted of Britton-Robinson buffer-methanol (8:2) solution at pH 4.0 and cationic surfactant  $3.0 \times 10^{-4} \text{ mol}\cdot\text{L}^{-1}$  cetyltrimethylammonium bromide (CTABr). The methodology was validated using four commercial sunscreen preparations as a sample and the results showed high recovery rates. The efficiency of the proposed methodology was demonstrated by comparing the results obtained by DPP with those obtained by the highperformance liquid chromatography (HPLC) method.

The procedures in electroanalysis strongly depend on working-electrode materials, increasing the interest in the development of new electrode materials. Carbon materials such as pyrolytic graphite, glassy carbon, and boron-doped diamond (BDD) have been widely used for electrochemical applications [13-17]. It is well established that BDD electrodes have several advantages compared with other carbon surfaces. BDD electrodes have been extensively studied in recent years, both for their fundamental electrochemical properties [18-21] and its various applications [22,23].

The outstanding electrochemical features of this mate-

rial, including a wide potential window in aqueous solutions [24,25], very low background current [26], weak adsorption for most types of organic molecules [27], high stability of response [28,29], and good electroactivity toward certain organic species all of which deactivate the surface of other conventional electrodes [30,31]—make this new material promising for electroanalytical applications [32-37], electrosynthesis [38,39], and electrochemical combustion [40-43], as well as for use as a supporting material in electrocatalysis [44-46]. Recent studies reported in the literature have shown that several inorganic, organic and biomolecules can be satisfactorily determined with the use of BDD electrodes [32,47-49].

The combination of square-wave voltammetry (SWV) and BDD electrodes has proved to be an interesting and desirable alternative for the analytical determination of some organic molecules [49,50]. So, in view of the lack of a simple and direct electroanalytical method for the determination of BENZO, the purpose of this investigation is the development of an electrochemical method capable of directly quantifying BENZO in commercial pharmaceutical preparations available in sunscreen form, using cyclic voltammetry and SWV with BDD as the working electrode.

## 2. Experimental

The stock solution of BENZO (Merck 99%) was prepared by direct weighing in order to obtain a solution  $1.0 \times 10^{-3} \text{ mol}\cdot\text{L}^{-1}$  dissolved in methanol, followed by a dilution to a concentration of  $1.0 \times 10^{-4} \text{ mol}\cdot\text{L}^{-1}$ . The cationic cetyltrimethylammonium bromide (CTABr) (Acros, New Jersey, USA) surfactant was prepared to a concentration of 1% (m/V). The supporting electrolyte was prepared by dissolution of boric acid followed by dilution with acetic acid and phosphoric acid (all from Merck, Darmstadt, Germany) to a concentration of  $0.04 \text{ mol}\cdot\text{L}^{-1}$ . The solutions had their pH adjusted by sodium hydroxide solution (Merck, Darmstadt, Germany). All reagents were of analytical grade. The deionized water was purified with a Milli-Q plus system (Millipore, Bedford, MA, USA). The samples were prepared by direct weighing in a 15 mL beaker, followed by solubilization in 10 mL of methanol with sonication for 5 min. This solution was quantitatively transferred to a 25 mL volumetric flask and methanol was added to the mark. The use of methanol in the supporting electrolyte was necessary due to the low solubility of the sunscreen agents in aqueous medium.

The BDD electrodes were prepared in the Centre Suisse d'Electronique et de Microtechnique SA (CSEM), Neuchâtel, Switzerland, using the hot filament chemical vapor deposition (HF-CVD) technique with filament

temperatures in the range of 2440°C - 2560°C and a gaseous mixture containing methane, H<sub>2</sub>, and trimethylboron, with a final boron content of the order of 800 ppm.

The electrochemical experiments were carried out in a single-body Pyrex<sup>®</sup> glass cell provided with three electrodes and degassing facilities for N<sub>2</sub> bubbling. The BDD electrode was glued onto a copper plate using a silver paste as previously reported in the literature [49,50]. The copper plate and the BDD edges were later isolated with Araldite<sup>®</sup> resin, leaving an exposed area of 0.025 cm<sup>2</sup>.

The reference electrode used was Ag/AgCl, where the all potentials are referred to this electrode. The auxiliary electrode was a 2.0 cm<sup>2</sup>-Pt foil. The electrochemical experiments were also performed using a Model 283 EG&G PARC electrochemical instrument controlled by a personal micro computer through the EG&G Princeton Applied Research model 270 Research Electrochemistry Software. All solutions were deoxygenated by bubbling N<sub>2</sub> for 10 min prior to measurements and the solutions were blanketed with the gas during measurements.

Analytical curves were obtained by means of spiking the supporting electrolyte. The measurements were performed without pre-treatment of the solutions, but pH was appropriately adjusted to the desired value.

### 3. Results and Discussion

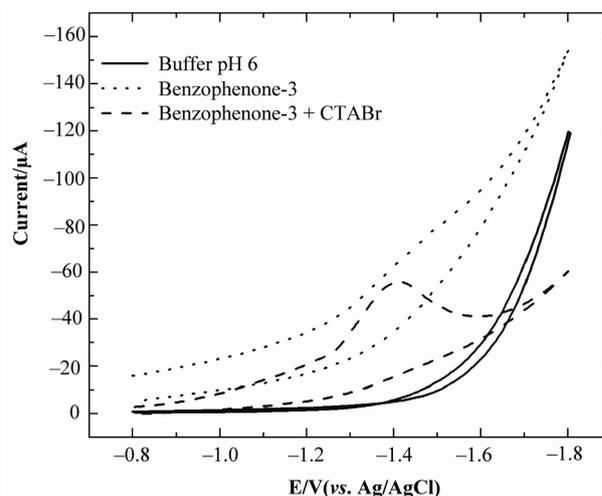
#### 3.1. Electrochemical Behavior

A cathodic polarization was necessary for conditioning the BDD surface prior to electroanalytical determinations. Such pre-treatment improves the voltammetric response of BDD surfaces, resulting in very low quantification limits and high data reproducibility [20]. Salazar-Banda, *et al.* [21] observed that after cathodic pre-treatments BDD electrodes exhibit dynamic electrochemical behavior—*i.e.*, a progressive decrease in the electron transfer rate for the Fe(CN)<sub>6</sub><sup>4-/3-</sup> redox couple as a function of time. This behavior has to be associated with a loss of superficial hydrogen due to oxidation by oxygen from the air. These results stress the need for performing cathodic pre-treatment just before the electrochemical experiments are conducted, in order to ensure reliable and reproducible results. In the literature there are several papers that used BDD electrode cathodically pretreated for electroanalytical applications [45,46,49-51]. Thus, before each analysis the BDD electrodes were pre-treated at + 3.2 V, in order to oxidize possible adsorbed species on the electrode surface, and after at -2.8 V (*vs.* Ag/AgCl), 30 s each, in HClO<sub>4</sub> solution (0.1 mol·L<sup>-1</sup>).

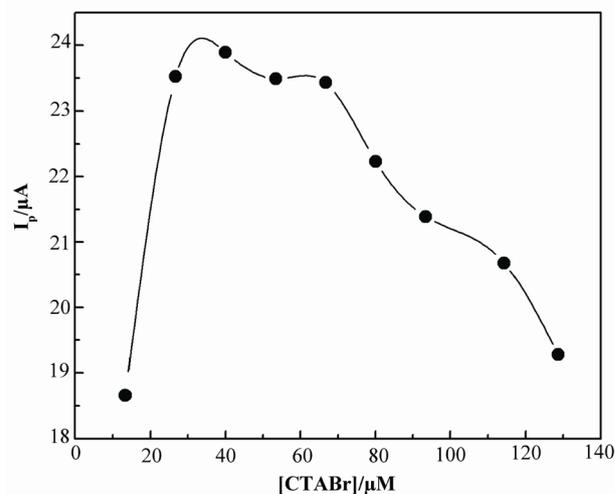
In this investigation, cyclic (CV) and square wave voltammetry (SWV) were utilized as electroanalytical

tools for BENZO determination in aqueous solutions using sunscreen such as amount (commercial pharmaceutical preparations). Initially the cyclic voltammetric experiments were conducted using a standard solution of BENZO (2.0 × 10<sup>-4</sup> mol·L<sup>-1</sup>) in Britton-Robinson buffer solution (pH 6). The voltammetric profile of currents shown in **Figure 2** reveals a peak related to reduction of BENZO on the BDD electrode in presence of cationic surfactant cetyltrimethylammonium bromide (1.0% m/v).

It can be observed (**Figure 2**) the presence of a well-defined irreversible peak in the presence of surfactant (CTABr) cationic BENZO reduction in BDD, as well a



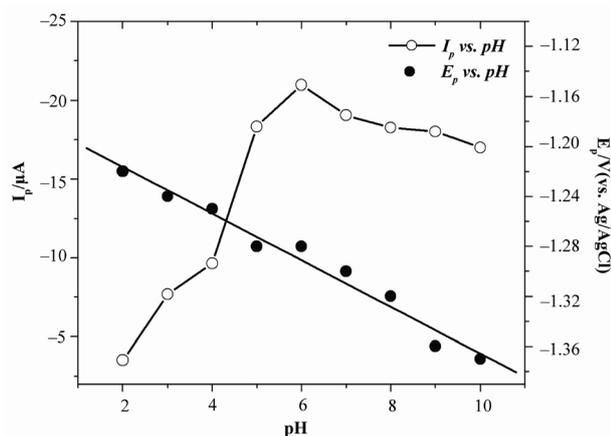
**Figure 2.** Cyclic voltammogram obtained in media of B-R buffer solution (pH 6) on a BDD electrode (solid line) and for benzophenone-3 (2.0 × 10<sup>-4</sup> mol·L<sup>-1</sup>) in presence (dashed line) and absence (dotted line) of CTABr (1.0% m/v) on a BDD electrode at 0.1 V·s<sup>-1</sup>.



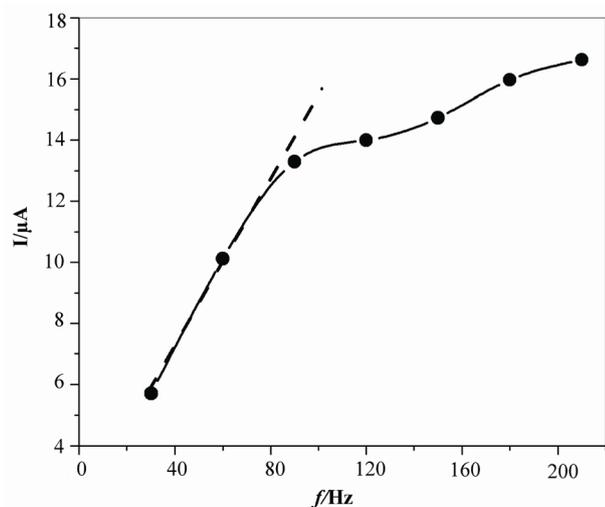
**Figure 3.** Dependence of the current peak of benzophenone-3 (1.0 × 10<sup>-4</sup> mol·L<sup>-1</sup>) on the CTABr concentration in B-R buffer solution (pH 6) on a BDD electrode at 0.1 V·s<sup>-1</sup>.

**Britton-Robinson buffer solution (pH 6), Scan rate  $0.1 \text{ V}\cdot\text{s}^{-1}$ .** shift in peak potential for considerably less negative value and thus away from discharge potential of electrolyte. The influence of concentration on CTABr BENZO reduction in BDD was investigated (Figure 3). However, the BENZO reduction response on BDD was studied in presence of CTABr in range of  $1.30 \times 10^{-5}$  until  $1.43 \times 10^{-4} \text{ mol}\cdot\text{L}^{-1}$  using as electrolyte B-R buffer solution (pH6). The best results with respect to enhancement and shape of the peak current were obtained with  $4.0 \times 10^{-5} \text{ mol}\cdot\text{L}^{-1}$  of CTABr.

Meanwhile, the influence of pH of supporting electro-



**Figure 4.** Influence of pH on peak current and peak potentials for cyclic voltammetry on a BDD electrode for benzophenone-3 ( $1.0 \times 10^{-4} \text{ mol}\cdot\text{L}^{-1}$ ) in Britton-Robinson buffer solutions ( $0.1 \text{ mol}\cdot\text{L}^{-1}$ ). [CTABr] =  $4.0 \times 10^{-5} \text{ mol}\cdot\text{L}^{-1}$  and Scan rate,  $0.1 \text{ V}\cdot\text{s}^{-1}$ .



**Figure 5.** Dependence of the current peak on frequency at 20 mV as amplitude value for experiments carried out under the following conditions: [CTABr] =  $4.0 \times 10^{-5} \text{ mol}\cdot\text{L}^{-1}$ , benzophenone-3 ( $1.0 \times 10^{-4} \text{ mol}\cdot\text{L}^{-1}$ ) in Britton-Robinson

buffer solution (pH 6) and  $E_s = 2 \text{ mV}$ .

lyte on the reduction of BENZO in the presence of CTABr was studied in the pH range of 2 - 10 by using CV. These experiments showed that the analytical signal obtained had a significant increase between pH 2 and 6 (Figure 4) and that to higher pH values the peak current decreases slightly up to pH 10. Quantitatively, data on the response of peak current showed the best values with neutral solutions. This finding led to the choice of Britton-Robinson buffer at pH 6 and CTABr ( $4.0 \times 10^{-5} \text{ mol}\cdot\text{L}^{-1}$ ) as electrolyte for the analytical determinations.

It is also observed that with increasing pH of electrolyte, there is a shift of peak potential to more negative values, indicating that a chemical reaction (proton transfer reaction) precedes the process that occurs at the electrode surface [52].

### 3.2. Optimization of SWV Parameters

Several experimental parameters related to the square-wave potential scan, such as frequency ( $f$ ) and amplitude ( $E_{sw}$ ), were studied and optimized to provide maximal current peak ( $I_p$ ) and repeatability. Thus, the amplitude and frequency of SWV for the standard solution of BENZO ( $1 \times 10^{-4} \text{ mol}\cdot\text{L}^{-1}$ ) in B-R buffer solution pH 6 with CTABr were analyzed. SWV amplitude was evaluated using 100 Hz as frequency value and 2 mV as scan increment. The maximum current peak at amplitude was obtained in approximately 20 mV. Likewise, Figure 5 reveals that the frequency exhibits linear behavior when  $I_p$  does not exceed 90 Hz, whereas for values higher than 120 Hz no contribution can be observed in the electroanalytical response. Linear behavior of frequency as a function of  $I_p$  is characteristic of an electrochemical irreversible process [53,54]. The solid lines presented in Figure 5 show the deviations of the linearity between  $I_p$  vs frequency.

### 3.3. Analytical Application

The electroanalytical determination of BENZO was performed using the maximal values of peak current as a function of amplitude and the frequency values. In this case, these conditions are interrelated and optimal peak current oxidation of BENZO was obtained on BDD electrodes using 90 Hz and 20 mV vs Ag/AgCl as SWV frequency and amplitude, respectively.

With these optimized voltammetric parameters, an electroanalytical methodology were developed for determination of BENZO in pharmaceutical preparations. The square-wave voltammograms of the standard solutions as a function of BENZO concentration in aqueous solution pH 6 (B-R buffer) in presence of CTABr are

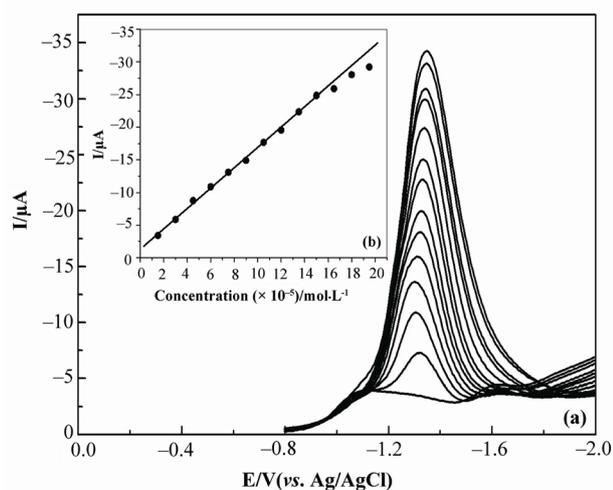
shown in **Figure 6(a)**. The calibration plot yielded a straight line ( $r = 0.998$ ,  $n = 3$ ) for BENZO (**Figure 6(b)**). Linear regression analysis of current ( $\mu\text{A}$ ) versus concentration ( $\text{mol}\cdot\text{L}^{-1}$ ) profiles showed a reasonable linearity from  $1.5 \times 10^{-5}$  to  $1.95 \times 10^{-4}$   $\text{mol}\cdot\text{L}^{-1}$  on the BDD electrode, as shown in the inset of **Figure 6**.

The determination (LD) and quantification (LQ) limits for BENZO were obtained in aqueous solutions (B-R buffer, pH 6) using the procedure recommended by IUPAC [55-57]. Thus, the standard deviation of the mean value of currents ( $S_B$ ) measured at the BENZO reduction potential for 10 voltammograms of the blank solution in different samples was used in conjunction with the slope of the straight line ( $b$ ) of the analytical curves (**Figure 6(b)**) and Equation 1 and 2:

$$LD = \frac{3S_B}{b} \quad (1)$$

$$LQ = \frac{10S_B}{b} \quad (2)$$

The detection and quantification limits were obtained for five determinations of BENZO in pure water using BDD electrodes and SWV as the analytic technique. The results of the linear regression of the analytic curve and detection and quantification limits are presented in **Table 1**. The SWV method was applied to determine the BENZO content in commercial sunscreen. Determination of BENZO content in the preparation was performed by using the standard addition method. Each sample of cosmetic was treated as described in experimental section.



**Figure 6.** (a) Square-wave voltammetry responses of a BDD electrode for different benzophenone-3 concentrations in Britton-Robinson buffer solution (pH 6); (b) Linear dependence of the peak current on benzophenone-3 concentration.  $[\text{CTABr}] = 4.0 \times 10^{-5} \text{ mol}\cdot\text{L}^{-1}$ ,  $f = 90 \text{ Hz}$ ,  $a =$

$20 \text{ mV}$ ,  $E_s = 2 \text{ mV}$ .

**Table 1.** Result of the linear regression of the analytic curve and detection and quantification limits obtained for benzophenone-3 in medium of B-R buffer pH 6.

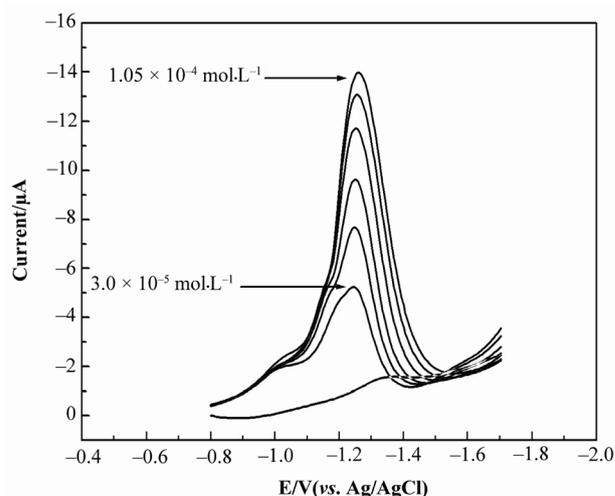
| Sample       | Intercept ( $\mu\text{A}$ ) | Slope ( $\text{mA}/\text{mol}\cdot\text{L}^{-1}$ ) | $S_B$ ( $\mu\text{A}$ ) | DL ( $\times 10^{-7}$ $\text{mol}\cdot\text{L}^{-1}$ ) | QL ( $\times 10^{-7}$ $\text{mol}\cdot\text{L}^{-1}$ ) |
|--------------|-----------------------------|--|-------------------------|--|--|
| Benzophenone | $1.20 \pm 0.45$             | $1.48 \times 10^7 \pm 18.5$                        | 0.007                   | $1.37 \pm 0.12$  | $4.54 \pm 0.4$   |

All measurements were performed in triplicate. The recovery efficiencies ( $\%R$ ) for the systems under investigation were calculated using Equation 3, where the “found” value refers to the concentration obtained by extrapolation of the analytical curve in the corresponding standard solution of BENZO.

$$\%R = 100 \frac{[\text{Benzophenone-3}]_{\text{found}}}{[\text{Benzophenone-3}]_{\text{added}}} \quad (3)$$

The pharmaceutical preparations analyzed were sunscreen containing BENZO (5% w/w). In **Figure 7** it can be observed that the voltammetric behavior of the BENZO present in the pharmaceutical preparation is similar to that obtained with a standard solution (**Figure 6(a)**).

No influence of others agents content in sunscreen such as octyl metoxycinnamate, propyleneglycol or 4-methylbenzilidene camphor on the voltammetric response was thus observed in the interest potential range. The recoveries of known amounts of BENZO contained in pharmaceutical preparations (**Table 2**) ranged from 97.2% to 98.1%.



**Figure 7.** Square-wave voltammograms profiles of benzophenone-3 contained in a commercial pharmaceutical preparation in Britton-Robinson buffer solution (pH 6).  $[\text{CTABr}] = 4.0 \times 10^{-5} \text{ mol}\cdot\text{L}^{-1}$ ,  $f = 90 \text{ Hz}$ ,  $a = 20 \text{ mV}$ ,

$$E_s = 2 \text{ mV.}$$

**Table 2. Recoveries of benzophenone-3 samples in commercial cosmetic preparations (nominal conc. 5.0% w/w) using square wave voltammetry experiments carried out using the following conditions:  $f = 90 \text{ Hz}$ ,  $a = 20 \text{ mV}$  and  $E_s = 2 \text{ mV}$  ( $n = 3$ ).**

| Sunblock Lotion | Added (mol·L <sup>-1</sup> benzophenone-3) | Found (mol·L <sup>-1</sup> benzophenone-3) | Recovery (%) | R.S.D (%) |
|-----------------|--|--|--------------|-----------|
| A               | $1.00 \times 10^{-5}$                      | $9.81 \times 10^{-6}$                      | 98.1         | 0.8       |
| B               | $1.00 \times 10^{-5}$                      | $9.72 \times 10^{-6}$                      | 97.2         | 1.1       |
| C               | $1.0 \times 10^{-5}$                       | $9.78 \times 10^{-6}$                      | 97.5         | 0.9       |

#### 4. Conclusions

In this investigation, BENZO was found to provide a reductive peak when cyclic and square-wave voltammetry experiments were conducted using BDD electrodes. Based on these experiments, an electroanalytical method for the determination of BENZO in water and commercial sunscreen was developed. The electrochemical responses of pharmaceutical preparations were identical to those of standard BENZO and no influence of others agents content in sunscreen on the voltammetric responses was observed. BENZO recoveries values ranged from 97.2% to 98.1% demonstrate the elevated efficiency of the methodology. Consequently, given it's easily of use, high sensitivity, and brevity, the method proposed can be successfully used to determine trace amounts of BENZO in several commercial products.

#### 5. Acknowledgements

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