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Square-wave voltammetric determination of bezafibrate in pharmaceutical formulations using a cathodically pretreated boron-doped diamond electrode

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ABSTRACT

The determination of bezafibrate (BZF) using square-wave voltammetry (SWV) and a cathodically pretreated boron-doped diamond electrode is proposed. Cyclic voltammetry results showed one irreversible oxidation peak for BZF at 1.20 V (*vs.* Ag/AgCl (3.0 mol L^{-1} KCl)) in a 0.04 mol L^{-1} Britton–Robinson (BR) buffer solution (pH 2.0). Under optimized SWV conditions, a linear analytical curve is obtained for the BZF concentration range 0.10–9.1 μmol L^{-1} in the BR buffer solution (pH 2.0), with a detection limit of 0.098 μmol L^{-1}. The obtained recoveries range from 93.4 to 108%. The proposed novel method was successfully applied in the determination of the BZF content in several pharmaceutical formulations (tablets) and the results are in close agreement (at a 95% confidence level) with those obtained using a comparative spectrophotometric method.

1. Introduction

Bezafibrate—BZF (2-(4-{2-[(4-chlorobenzoyl)amino]ethyl}-phenoxy)-2-methylpropanoic acid; Fig. 1) is a derivative of fibric acid that is used for the treatment of hyperlipidemia. This drug reduces the blood levels of low-density lipoprotein (LDL) cholesterol and/or triglycerides, while increasing that of high-density lipoprotein (HDL) cholesterol [1]. Hence, because BZF is a compound of great pharmacological significance, controlling its content in commercial formulations is important, even vital for patients' health during treatment. Consequently, there is an interest in the development of accurate and validated analytical methods for BZF quantification in pharmaceutical samples.

Several analytical methods to determine BZF in pharmaceutical formulations and biological fluids have been reported in the literature, including those by capillary electrophoresis [2], chromatography [3–6], and spectrophotometry [5,7]. However, to the best of our knowledge there are no published reports about a voltammetric method for BZF determination, despite the fact that such methods are increasingly being used in the determination of a wide range of compounds of pharmaceutical interest.

Boron-doped diamond (BDD) electrodes have been advantageously used as an alternative to other conventional electrodes (e.g., glassy-carbon or platinum electrodes) and are particularly attractive in electroanalytical applications for pharmaceutical compounds [8–16], due to a very wide working potential window, very low and stable background current, long term stability, low sensitivity to dissolved oxygen, and an extreme electrochemical stability in both alkaline and acidic media [17–19].

In this article, we report on the development of a novel method for the determination of BZF in pharmaceutical formulations by square-wave voltammetry (SWV) using a cathodically pretreated BDD electrode. The proposed method is fast and simple for quantitative BZF determination, with minimal sample pretreatment. The obtained results are statistically equal to those from a comparative spectrophotometric method [5].

2. Experimental

2.1. Reagents and solutions

All chemicals were of analytical grade (BZF from Sigma-Aldrich; boric acid, acetic acid, orthophosphoric acid, and sodium hydroxide from Merck) and all solutions were prepared with ultra-purified water (obtained with a Milli-Q system—Millipore®) with resistivity

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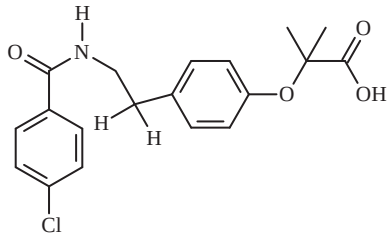

Fig. 1. Chemical structure of bezafibrate.

greater than 18 MΩ cm. Commercial pharmaceutical samples (tablets) of BZF were purchased from a local drugstore.

After appropriate investigation, as reported further below, the following Britton–Robinson buffer was chosen as supporting electrolyte: 0.04 mol L^{-1} in acetic, orthophosphoric, and boric acids, with pH adjusted to 2.0 with a 0.2 mol L^{-1} NaOH solution. Hereinafter, this supporting electrolyte will be simply referred as the BR buffer.

A 10 mmol L^{-1} BZF ethanolic stock solution was prepared before use. BZF working solutions were prepared by appropriate dilution of this stock solution with the BR buffer.

2.2. Apparatus

The voltammetric measurements were carried out using an Autolab PGSTAT-30 (Ecochemie) potentiostat/galvanostat controlled with the GPES 4.0 software. All the electrochemical experiments were conducted in a three-electrode single-compartment glass cell (with degassing facilities for bubbling N_2), including a BDD electrode (8000 ppm; 0.26 cm^2 exposed area; Adamant, Switzerland) as working electrode, a Pt wire as auxiliary electrode, and an Ag/AgCl (3.0 mol L^{-1} KCl) reference electrode, to which hereinafter all working electrode potentials are referred. Detailed information on the preparation of the diamond films was reported elsewhere [20]. Prior to the experiments, the BDD electrode was electrochemically pretreated in a 0.5 mol L^{-1} H_2SO_4 solution, either anodically by applying 0.5 A cm^{-2}, during 20 s, or cathodically by applying -0.5 A cm^{-2}, during 80 s. With the anodic or cathodic pretreatment, the BDD surface is made predominantly oxygen or hydrogen terminated, respectively [21–23].

2.3. Analytical procedures

After optimizing the experimental parameters for the proposed method, the analytical curve was obtained by addition of aliquots of the previously prepared BZF standard solution into the measurement cell containing 10 mL of the BR buffer. Square-wave (SW) and differential pulse (DP) voltammograms were obtained after each aliquot addition. Thus, the obtained analytical parameters were compared and the resulting best voltammetric method was chosen to quantify BZF in commercial pharmaceutical samples.

To prepare the solutions of the commercial pharmaceutical samples of BZF, 10 tablets of each pharmaceutical product were reduced to a homogeneous fine powder in a mortar with a pestle. These powders were weighed and transferred to 25 mL calibrated volumetric flasks containing ethanol; after sonication for 15 min, the volumes of the flasks were completed with ethanol; when necessary, non-dissolved solids were filtered using a filter paper. Then, 200 μL of these solutions were diluted to 2 mL using the BR buffer. For each sample, an aliquot of this solution was directly transferred to the electrochemical cell containing 10 mL of the BR buffer, after which the voltammogram was obtained. Finally, the BZF concentration in each sample solution was determined directly by interpolation in the previously obtained analytical curve.

For the recovery studies (done in triplicate), aliquots of the standard solution of BZF were added to the solutions of the commercial pharmaceutical samples of BZF.

2.4. Comparative method

The results obtained using the proposed SWV method were compared with those from a spectrophotometric method [5]. For such, accurate representative powdered amounts of the commercial pharmaceutical samples of BZF were dissolved in a 0.1 mol L^{-1} NaOH aqueous solution; when needed, non-dissolved solids were filtered using a filter paper. After appropriate dilution with the NaOH solution, absorbance was measured at 230 nm, in a quartz cell.

3. Results and discussion

3.1. Electrochemical behavior of BZF

The cyclic voltammogram obtained with a cathodically pretreated BDD electrode for a 30 μmol L^{-1} BZF solution in the BR buffer is shown in Fig. 2. As can be seen, an anodic current due to the oxidation of BZF is observed with a peak potential at 1.20 V and no reduction peak is observed, which indicate that this is an irreversible charge-transfer process.

The analytical performance of BDD electrodes depends on their surface termination, i.e., whether they are hydrogen or oxygen terminated [21,23]. Looking for an improved electrochemical response for BZF determination, the BDD electrode was either anodically or cathodically pretreated and its response was assessed, as presented in Fig. 3. Although, the anodically pretreated BDD presented a less positive oxidation peak potential, the cathodically pretreated BDD presented a better peak definition and a higher current intensity. Thus, the cathodic pretreatment of the electrode clearly leads to a larger electrochemical activity for BZF oxidation, similarly to what was previously observed for several other analytes [9,11–15,24–28].

Next, the influence of the duration (or total charge used) of the cathodic pretreatment of the BDD electrode on the analytical signal was investigated: 60, 80, and 160 s. As can be seen in Fig. SM-1 in the supplementary material, the highest and better-defined oxidation peak current was obtained after 80 s of pretreatment. Thus, the subsequent BZF analytical determinations were all carried out using a BDD electrode that was cathodically pretreated during 80 s. This pretreatment, which was repeated daily before starting the voltammetric measurements, was always

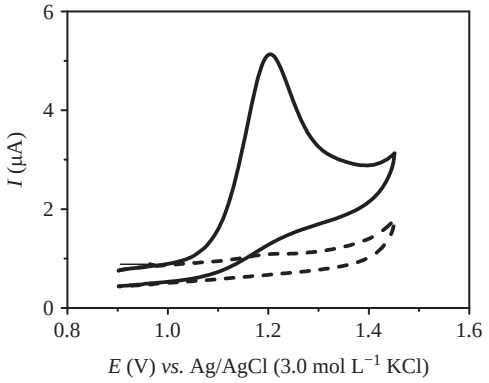

Fig. 2. Cyclic voltammograms (50 mV s^{-1}) in a 0.04 mol L^{-1} BR buffer solution (pH 2.0) obtained using a cathodically pretreated BDD electrode: dashed line without and solid line with the addition of 30 μmol L^{-1} BZF.

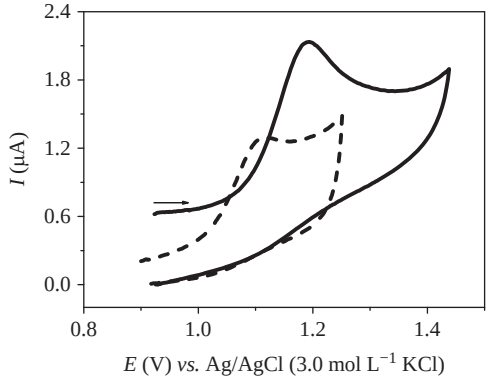

Fig. 3. Cyclic voltammograms (50 mV s^{-1}) for a 10 μmol L^{-1} BZF in 0.04 mol L^{-1} BR buffer solution (pH 2.0) obtained using an anodically (dashed line) or cathodically (solid line) pretreated BDD electrode.

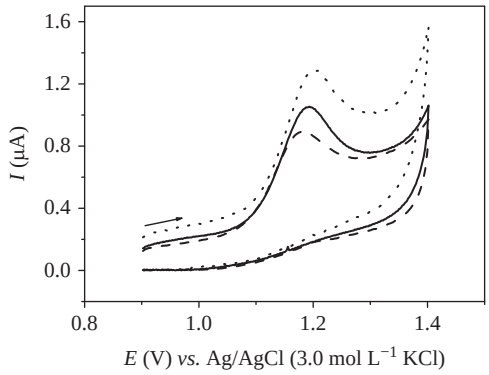

Fig. 4. Cyclic voltammograms (50 mV s^{-1}) for 5.0 μmol L^{-1} BZF in different supporting electrolytes (pH 2.0) obtained using a cathodically pretreated BDD electrode: 0.10 mol L^{-1} phosphate buffer solution (dotted line), 0.04 mol L^{-1} BR buffer solution (solid line), and 0.01 mol L^{-1} sulfuric acid (dashed line).

preceded by a 20 s anodic pretreatment, which cleansed the electrode surface by oxidizing any adsorbed contaminant.

3.2. Effect of the pH and composition of the supporting electrolyte

The effect of pH on the voltammetric response (at 50 mV s^{-1}) for a 5.0 μmol L^{-1} BZF solution with the cathodically pretreated BDD electrode was investigated in the pH range 2.0–6.0, using a 0.04 mol L^{-1} BR buffer solution. As can be observed in Fig. SM-2 in the supplementary material, a decrease of the solution pH leads to an increase of the anodic current and the peak potential is shifted toward more positive values, with the highest oxidation peak current at pH 2.0. Thus, the voltammetric response was investigated using two other supporting electrolytes at pH 2.0: 0.1 mol L^{-1} phosphate buffer solution and 0.01 mol L^{-1} H_2SO_4. As can be seen in Fig. 4, the best response (higher analytical signal) is obtained using the 0.04 mol L^{-1} BR buffer solution. Thus, this buffer solution was chosen as the supporting electrolyte for further experiments.

3.3. Effect of the scan rate

Cyclic voltammograms were obtained at different scan rates from 0.020 to 0.300 V s^{-1}, as shown in Fig. 5. The oxidation peak for BZF in the BR buffer shifted slightly toward more positive potentials as the scan rate increased, a characteristic typical of irreversible electrochemical reactions [29]. On the other hand, the logarithm of the oxidation peak current (I_{ap}) is linearly dependent

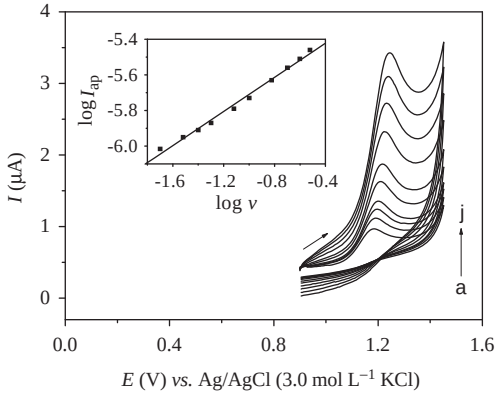

Fig. 5. Cyclic voltammograms for a 5.0 μmol L^{-1} BZF in a 0.04 mol L^{-1} BR buffer solution (pH 2.0) obtained using a cathodically pretreated BDD electrode at different scan rates (v): (a) 0.020, (b) 0.030, (c) 0.040, (d) 0.050, (e) 0.075, (f) 0.100, (g) 0.150, (h) 0.200, (i) 0.250, and (j) 0.300 V s^{-1}. Insert: linear dependence of log I_{ap} with log v—see text.

on the logarithm of the scan rate (see insert in Fig. 5), with a slope of 0.48, which is in close agreement with the theoretical value of 0.50 for diffusion-controlled processes [29].

A linear dependence of I_{ap} with the square root of the scan rate ($v^{1/2}$) was also found (data not shown), in accordance with:

$$I_{ap}(A) = 1.88 \times 10^{-8} + 6.10 \times 10^{-6}\left[v^{1/2}\left(V\,s^{-1}\right)^{1/2}\right] (r = 0.9981)$$

Additionally, using Laviron's equation for an irreversible electrode process [30], the αz value was estimated as 1.1. Assuming that the value of the transfer coefficient (α) is equal to 0.5, which is commonly done for totally irreversible systems [31], the number of electrons transferred (z) in the electrooxidation of BZF was estimated as 2.2, i.e., approximately 2. Consequently, assuming $z=2$, we propose that the oxidation of BZF is represented by the reaction shown in Fig. 6; the oxidation product of this reaction was previously detected by Razavi et al. [32] as a breakdown product when BZF was degraded using γ-radiolysis.

3.4. Controlled potential electrolysis

The number of electrons transferred may also be estimated by controlled-potential electrolysis. Hence, a 10 μmol L^{-1} BZF solution in the BR buffer was electrolyzed at 1.3 V during 900 s, with continuous stirring. The number of electrons transferred was calculated using the relationship $Q=zF\Delta n$, where Q and Δn are the electrical charge passed and the change in the amount of BZF during the controlled potential electrolysis, respectively, and F is the Faraday constant. The change in the BZF concentration was calculated using SW voltammograms obtained before and after the electrolysis. Then, as the volume of the BZF solution was 10 mL, the value of Δn was calculated as 1.48×10^{-8} mol. The value of Q, obtained from the difference between the integrated area of the chronoamperogram for the electrolysis of the 10 μmol L^{-1} BZF solution in the BR buffer and that of solely the BR buffer, was 2.73 mC. The resulting z value is 1.91, thus also indicating (in agreement with the cyclic voltammetric study) that two electrons per molecule are involved in the oxidation of BZF in the BR buffer, as shown in Fig. 6.

3.5. Optimization of the SWV and DPV parameters

Before recording any analytical curve for BZF determination using the cathodically pretreated BDD electrode, the experimental parameters that affect the SWV and DPV responses were optimized for a 5.0 μmol L^{-1} BZF solution in the BR buffer.

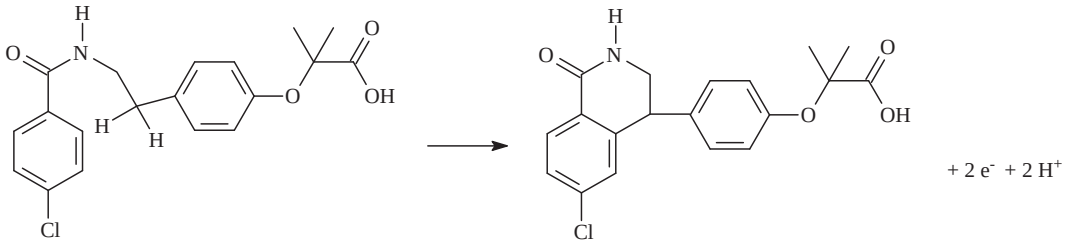

Fig. 6. Proposed electrooxidation reaction of BZF (adapted from Razavi et al. [32]).

For SWV, the corresponding investigated ranges were: 10–70 s^{-1}, for the square-wave frequency (f); 10–60 mV, for the pulse amplitude (a); 1–7 mV, for the scan increment (ΔE_S). The obtained optimized values were $f=50\ s^{-1}$, $a=40$ mV, and $\Delta E_S=4$ mV. Additionally, the slope of 0.049 V obtained from the E_{ap} *vs.* log f plot (see Fig. SM-3 in the supplementary material) was used to, once more, estimate the number of electrons transferred in the redox process by the following equation [33]:

$$E_{ap} = (2.3RT/azF)\log f \quad (1)$$

where E_{ap} is the anodic peak potential, α, z, and F have the previously assigned meanings, and other symbols have their usual meanings. The αz value was estimated to be 1.2 and thus, if α is again assumed as 0.5, z is estimated as equal to 2.4, i.e., again a value of approximately 2, in agreement with those results obtained by cyclic voltammetry and controlled potential electrolysis.

For DPV, the studied parameter ranges were: 10–150 mV, for the pulse amplitude (a); 10–35 mV s^{-1}, for the scan rate (v); and 3–15 ms, for the modulation time (t). The optimized values were $a=100$ mV, $v=30$ mV s^{-1}, and $t=3$ ms.

3.6. Analytical curves

The previously optimized SWV and DPV experimental parameters were employed to record the corresponding analytical curves for BZF in the BR buffer using a cathodically pretreated BDD electrode. The analytical parameters thus obtained for both the SWV and DPV proposed methods are summarized in Table 1, where the detection limit (*LOD*) is equal to three times the standard deviation of the blank solution divided by the slope of the analytical curve. As can be observed, the best values for the analytical parameters (broadest linear range and lowest detection limit) were obtained using SWV. Hence, this analytical method for the determination of BZF was selected for further development.

Fig. 7 shows the SW voltammograms obtained for BZF reference solutions at different concentrations (0.10 to 9.1 μmol L^{-1}) in the BR buffer. The insert in this figure depicts the respective analytical curve obtained for BZF, whose corresponding equation is I_{ap} (μA)=0.052+0.31 [c (μmol L^{-1})], where I_{ap} is the anodic peak current and c the BZF concentration. The calculated *LOD* value was 0.098 μmol L^{-1}.

Here it should be mentioned once again that there are no papers reporting on electroanalytical methods for the determination of BZF in pharmaceutical formulations or biological fluids. Thus, the analytical characteristics resulting from our proposed novel method and those obtained with other methods are summarized in Table 2. From these data, it can be seen that the analytical parameters for the voltammetric determination of BZF herein proposed are better than those for other analytical methods, except that proposed by Krebs et al. [7]. However, this method involves reacting BZF with palladium(II) ion and eosin, to obtain a ternary complex, with addition of methylcellulose as a surfactant to increase the solubility and color intensity of the complex, whereas the method herein proposed only requires minimal sample pretreatment.

Table 1
Analytical parameters for the voltammetric determination of BZF in a 0.04 mol L^{-1} Britton–Robinson buffer (pH 2.0) by square-wave voltammetry (SWV) and differential pulse voltammetry (DPV), using a cathodically pretreated BDD electrode.

	SWV	DPV
Peak potential (V)	1.19	1.15
Linear range (μmol L^{-1})	0.10 to 9.1	0.40 to 9.1
Correlation coefficient, r	0.9996	0.9999
Slope (μA μmol^{-1} L)	0.31	0.48
Intercept (μA)	0.052	0.153
Detection limit (μmol L^{-1})	0.098	0.37

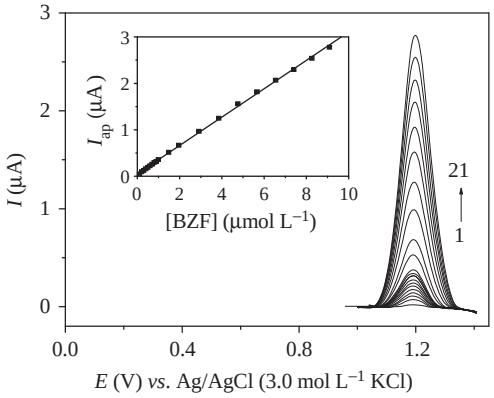

Fig. 7. Square-wave voltammetric curves in a 0.04 mol L^{-1} BR buffer solution (pH 2.0) obtained using a cathodically pretreated BDD electrode for the following concentrations of BZF: (1) 0, (2) 0.10, (3) 0.20, (4) 0.30, (5) 0.40, (6) 0.50, (7) 0.60, (8) 0.70, (9) 0.80, (10) 0.90, (11) 1.0, (12) 1.5, (13) 2.0, (14) 2.9, (15) 3.9, (16) 4.8, (17) 5.7, (18) 6.5, (19) 7.4, (20) 8.3, and (21) 9.1 μmol L^{-1}. Insert: Corresponding analytical curve.

Table 2
Comparison of the analytical parameters obtained using different methods for the determination of BZF in pharmaceutical formulations.

Method	Concentration range (mol L^{-1})	*LOD* (mol L^{-1})	Reference
HPLC	5.5×10^{-4}–2.2×10^{-3}	–	[2]
HPLC	6.9×10^{-7}–1.4×10^{-4}	2.8×10^{-7}	[3]
HPLC	2.8×10^{-7}–4.1×10^{-5}	–	[4]
HPLC	2.8×10^{-6}–1.4×10^{-3}	6.4×10^{-7}	[5]
Spectrophotometric	6.9×10^{-6}–4.1×10^{-5}	1.2×10^{-6}	[5]
Spectrophotometric	1.7×10^{-7}–8.3×10^{-7}	2.5×10^{-8}	[7]
Voltammetric	1.0×10^{-7}–9.1×10^{-6}	9.8×10^{-8}	This work

Table 3
BZF content in pharmaceutical formulations (200 mg tablets) determined by the proposed square-wave voltammetric (SWV) method, using a cathodically pretreated BDD electrode, and a comparative spectrophotometric method [5].

Samples	BZF (mg/tablet)		Average error (%)[b]
	Comparative method[a]	SWV method[a]	
A	212 ± 1	209 ± 2	−1
B	210 ± 2	207 ± 1	−1
C	209 ± 1	211 ± 1	1
D	211 ± 1	203 ± 1	−4

[a] Average of 3 measurements.
[b] Average error=[100 × (SWV method—comparative method)]/comparative method.

The intra-day repeatability of the oxidation peak current was determined based on 10 successive measurements of a 0.99 μmol L^{-1} BZF solution, when a relative standard deviation (RSD) of 0.42% was obtained. The inter-day repeatability of the oxidation peak current, evaluated by measuring it for similar freshly prepared solutions over a period of 5 days, presented a RSD value of 3.1%. Hence, we can conclude that the developed method yields results with adequate repeatability.

3.7. Determination of BZF in pharmaceutical formulations

First, the effect of some possible interferents (commonly present in the analyzed pharmaceutical formulations) was investigated by the addition of these compounds to a standard 0.99 μmol L^{-1} BZF solution in the BR buffer. Thus, starch, polyvinyl alcohol, methylcellulose, and magnesium stearate were tested as possible interferents at the concentration ratios (standard solution:interferent compound) of 1:1, 1:10, and 10:1. The corresponding oxidation peak currents were compared with those obtained in the absence of each interferent. Analyzing the obtained responses, clearly these compounds do not significantly interfere ($< 5\%$) in the determination of BZF under the used working conditions. Consequently, we concluded that BZF might be accurately determined by the proposed method even in the presence of those concomitants; this was further confirmed by addition and recovery studies.

Next, four commercial pharmaceutical samples (tablets) containing BZF were analyzed to evaluate the validity of the herein-proposed method. Addition and recovery studies were carried out by addition of known volumes of a BZF standard solution to that of a given sample, followed by analysis using SWV. Good recoveries (not shown) were obtained for the investigated commercial tablets, ranging from 93.4 to 108%; clearly the proposed method does not suffer from any significant effects of matrix interference.

Finally, the BZF content in the commercial tablets was comparatively determined (in triplicate) by the proposed method and a spectrophotometric one [5]. The obtained average values, standard deviations, and average errors are presented in Table 3. As can be seen in this table, no significant differences were observed between the values found for the content of BZF in the tablets using the SWV proposed method and the comparative one. Besides, considering that the paired *t*-test [34] was applied to these results and the calculated *t* value (1.470) is smaller than the critical value (3.182, $\alpha = 0.05$), one may conclude that the results obtained with either method are not statistically different, at a 95% confidence level.

4. Conclusions

From the results of the present study, one may conclude that the BZF content in pharmaceutical formulations can be determined by square-wave voltammetry using a cathodically pretreated BDD electrode. After optimization of the experimental parameters, a BZF detection limit of 0.098 μmol L^{-1} and a relative standard deviation smaller than 0.5% for 0.99 μmol L^{-1} BZF solutions (intra-day, $n=10$) were attained. Addition-recovery tests yielded satisfactory results, with values similar to those obtained using a comparative spectrophotometric method. The results here reported allow to unequivocally conclude that the combination of SWV and a cathodically pretreated BDD electrode is a feasible alternative for the analytical determination of BZF in commercial tablets without time-consuming sample preparations or the need of expensive apparatus.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at http://dx.doi.org/10.1016/j.talanta.2012.10.033.

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