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Improving the Analytical Performances of the Ibuprofen Voltammetric Determination at Bare Graphite Electrode Using Semi-Derivative Linear Sweep Voltammetry

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In this work, a bare graphite electrode was applied for the simple and cost-effective ibuprofen determination. Analytical performances improvement was achieved taking advantage of the semi-derivative processing of the signal obtained by linear sweep voltammetry. The semi-differentiation led to transformation of the asymmetric and broad ibuprofen current peaks into much more symmetrical, bell-shaped and detectable semi-derivative signals, as well as to sensitivity enhancement. Under the optimized conditions (3 min accumulation time and pH 4.5) the peak current varied with ibuprofen concentrations in two linear ranges: from 2 μmol L^{-1} to 100 μmol L^{-1} and from 100 μmol L^{-1} to 500 μmol L^{-1} with a limit of detection of 0.6 μmol L^{-1} (S/N=3). The method was successfully applied for the determination of ibuprofen in pharmaceutical formulations with satisfactory recovery values (99.2%–101.6%). The proposed sensor also demonstrated good selectivity and reproducibility.

Keywords: ibuprofen; graphite electrode; semi-derivative voltammetry

1. INTRODUCTION

Ibuprofen ($C_{13}H_{18}O_2$: 2-[4-(2-methylpropyl)phenyl]propanoic acid) is a medication, which belongs to the class of the nonsteroidal anti-inflammatory drugs [1]. It is among the most widely used analgesic, anti-inflammatory, and antipyretic agents, commonly available over-the-counter in various dosage forms such as tablets, capsules, and suspensions.

Several analytical methods for ibuprofen determination in pharmaceutical samples have been reported in the literature, including chromatographic [2-6], spectrophotometric [7], spectrofluorimetric

[7-10], electrophoretic [11, 12], and electrochemical [13-21]. The high performance liquid chromatographic (HPLC) assay, established by the U.S. Pharmacopeia Convention [22], and the alkaline titration, recommended by the British Pharmacopeia [23] are the official methods for ibuprofen determination in pharmaceutical preparations. However, the HPLC involves the use of a sophisticated and expensive equipment, time-consuming sample preparation procedures, a large volume of organic solvents, and skilled personal, while the titration method is not enough sensitive and suffers from the interference of the sample matrix. Among the alternative methods for ibuprofen determination, the electroanalytical attract the attention, as they are simple, fast, sensitive, and cost effective. They have been shown to be very effective in drug analysis [24-39].

The commonly applied electrochemical techniques for ibuprofen determination are mainly voltammetric, such as differential pulse voltammetry (DPV) and square wave voltammetry (SWV), and the carbon based working electrodes, including boron-doped diamond electrodes (BDD) are the currently used [13-21]. The analytical signal is the current of ibuprofen oxidation. The BDD electrodes reveal the advantage to allow ibuprofen determination without the interference of the oxygen evolution reaction due to their wide potential window in aqueous solutions [15, 18, 20]. However, as BDD is a semi-conductor doped material and usually is not considered as a typical electrode material for electrochemical applications, a recognized format for BDD electrodes is not currently commercially available [40]. Attention has to be also paid to the carbon paste electrodes (CPE), due to their simple preparation technique and simple surface renewal procedure, as well as to the disposable screen printed carbon electrodes, as they allow avoiding the tedious cleaning processes. However, their application to ibuprofen determination involves complex and time-consuming procedures for electrode modification, to improve the sensitivity of the analysis [13, 14, 17, 19, 21]. Therefore, in this work, ibuprofen determination was performed at bare graphite electrode. Analytical performances improvement was achieved by semi-derivative processing of the signal obtained using the very simple and well known technique linear sweep voltammetry.

2. EXPERIMENTAL

2.1. Reagents and Solutions

Ibuprofen (Ib), C_2H_5OH, CH_3COOH, CH_3COONa, NaOH, and KCl were purchased from Sigma and Spectrum Chemical. All the chemicals were of analytical reagent grade (purity ≥99%) and were used as such without additional purification. Ibuprofen stock solution was prepared by dissolving the substance in ethanol. The stock solution was stored at 4^{o}C protected from light. Acetate buffer (Ac 0.1 mol L^{-1}) with pH values varying in the range from 3.0 to 6.0 was obtained by mixing appropriate amounts of CH_3COOH and CH_3COONa aqueous solutions. The final pH was adjusted by potentiometric titration with NaOH or CH_3COOH.

The pharmaceutical formulations Nurofen (200 mg Ib/tablet) and Advil (200 mg Ib/tablet) were acquired from the local drug stores. For each analysis, ten tablets were powdered in a mortar and a weight corresponding to one tablet was dissolved in ethanol to prepare the respective stock solution. The

insoluble excipients were removed by filtration. The working solutions were prepared through dilution of the stock solutions in the supporting electrolyte to obtain final concentrations within the linear range of the calibration curve.

2.2. Instrumentation and Procedures

The electrochemical measurements were performed employing a model 440A Electrochemical Analyzer (CH Instruments Inc., USA) applying various voltammetric techniques: cyclic voltammetry (CV), linear sweep voltammetry (LSV), and differential pulse voltammetry (DPV). The DPV voltammograms were registered applying a potential increment of 0.005 V, amplitude of 0.05 V, pulse width of 0.05 s, sampling width of 0.0167 s, and pulse period of 0.5 s. The recorded LSV curves were treated with a semi-derivative technique by using the CH Instruments 440A Electrochemical Analyzer built-in software package. The program performs numerical differentiation employing the algorithm of Savitzky and Golay [41].

All the experiments were performed in an electrolysis cell of a conventional type at ambient temperature. A bare disk electrode made from spectrographic graphite (Ringsdorff Werke, Germany, 6 mm in diameter, 13% porosity) served as a working electrode. The auxiliary electrode was a Pt wire (BASi MW-1033), while a Ag, AgCl/KClsat electrode (BASi MF-2052) was used as a reference.

3. RESULTS AND DISCUSSION

3.1. Ibuprofen Electrochemical Behavior

Ibuprofen electrochemical behavior at bare graphite electrode was investigated by cyclic voltammetry. The measurements were carried out in acetate buffer solution (0.1 mol L^{-1}, pH 5.0) at different scan rates (20 mV s^{-1} - 150 mV s^{-1}), starting with the accumulation of the corresponding analyte (200 μmol L^{-1}) for 30 s at open circuit potential. As shown in Figure 1, the ibuprofen cyclic voltammograms reveal the appearance of a single irreversible oxidation peak with no corresponding reduction peak in the reverse potential scan. The irreversible character of the oxidation process was confirmed by the observed positive shift of the peak potentials with the increase in scan rate. The relationships between the ibuprofen anodic peak potential (E_{Ib}, V) and the logarithm of the scan rate (ν, mV s^{-1}) was found to be linear:

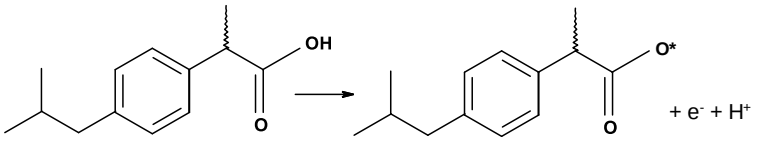
$$E_{\mathrm{Ib}} = 0.046 \ln \nu + 0.9788 \quad (R^2 = 0.9929)$$

in accordance with Laviron's equation for irreversible processes [42]:

$$E_{\mathrm{pa}} = E^{\mathrm{o}} - \frac{RT}{(1-\alpha)nF} \ln \frac{RTk_{\mathrm{s}}}{(1-\alpha)n\mathrm{F}} + \frac{RT}{(1-\alpha)nF} \ln \nu,$$

where E^o (V) is the formal potential, α is the electron transfer coefficient, k_s is the standard heterogeneous rate constant of the reaction, n is the charge transfer number, T is the temperature (K), F is the Faraday constant (C mol^{-1}), and R is the gas constant (J mol^{-1} K^{-1}).

From the slope of the plot E_{lb} versus ln v (Figure 1), the charge transfer number of the ibuprofen electrochemical reaction was found to be 1.11 ($n \approx 1$) by assuming of $\alpha = 0.5$. Therefore, the rate limiting step of the ibuprofen oxidation should be the radical formation, which involves one electron and one proton, in agreement with the reported in the literature [13, 17]:



The formation of the radical-cation is followed by a decarboxylation process [13, 17].

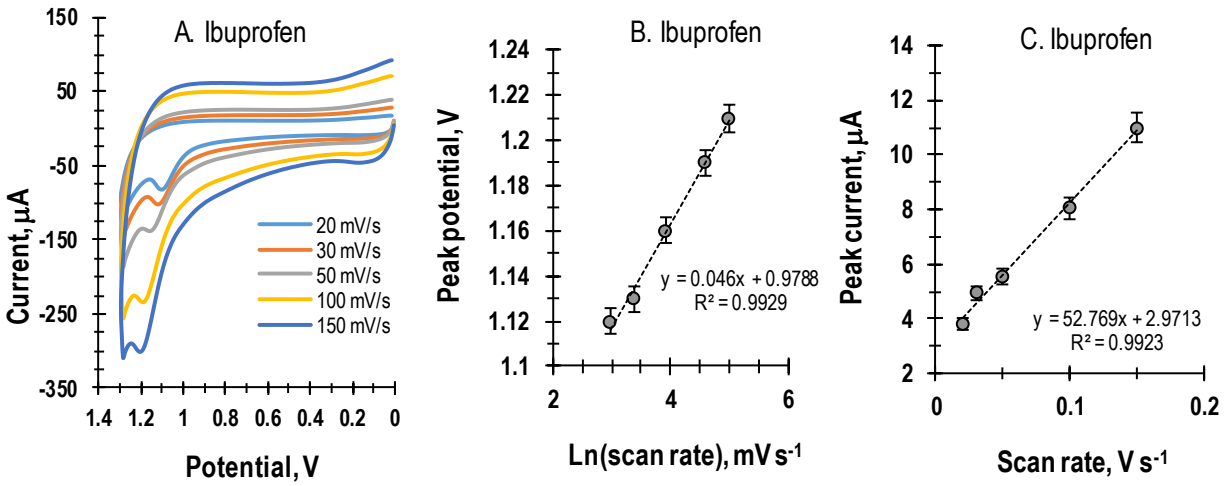


Figure 1. (A) CV response of ibuprofen (200 µmol L^{-1}) at different scan rates; (B) Linear relationship between the anodic peak current and the scan rate; (C) Relationship between the anodic peak potential and the logarithm of the scan rate. Ac 0.1 mol L^{-1}, pH 5.0. Accumulation time 30 s at open circuit potential.

3.2. Optimization of the Experimental Conditions

3.2.1. Accumulation Time Optimization

Ibuprofen preconcentration at the electrode surface was performed to improve the performances of its analytical determination, taking advantage of the graphite adsorption properties. The effect of the adsorption or accumulation time on the electrochemical response of ibuprofen (200 µmol L^{-1}, Ac 0.1 mol L^{-1} at pH 5.0) was investigated by cyclic voltammetry (data not shown). The adsorption was achieved at open-circuit potential under stirring (700 rpm) for different time periods within a range of 0 to 5 min. As expected, the peak current increased as the accumulation time increased to reach a maximum

at the 3th minute (Figure 2). Then it declined to some extent, which was ascribed to the electrode surface saturation. Henceforward, the optimum time for ibuprofen accumulation was fixed at 3 min, thus achieving almost 30-fold enhancement in peak current. Hence, the bare graphite electrode is suitable for ibuprofen determination by adsorptive stripping voltammetry.

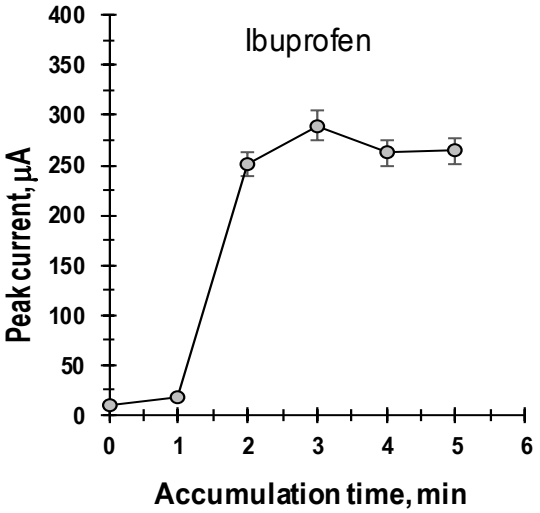


Figure 2. Effect of the accumulation time on the ibuprofen (200 μmol L^{-1}) peak current. Ac 0.1 mol L^{-1} at pH 5.0.

3.2.2. pH Optimization

The effect of pH on the electrochemical response of ibuprofen (200 μmol L^{-1}) on the bare graphite electrode in Ac 0.1 mol L^{-1} with pH values varying within the range of 3.0 to 6.0 was investigated by cyclic voltammetry (data not shown). The anodic peak current of ibuprofen increased from pH 3.0 to 4.5, and decreased for pH values beyond 4.5 (Figure 3). It should be noted that at pH ≈ pK_a ibuprofen coexists as neutral and anionic species, while at pH > pK_a it exists as anion species, which results in peak current decrease (pK_a is in the range of 4.5 - 5.3) and demonstrates that the neutral molecules are more easily oxidized than the deprotonated species. The peak current decrease at lower pH values (pH < pK_a) can be associated with ibuprofen solubility decrease.

Thus, further experiments were performed at pH 4.5 which is the optimum for the sensitive ibuprofen determination. Also, the oxidation peak potential of ibuprofen shifted negatively over the entire pH range of 3.0 to 6.0 (Figure 3). The relationship between the pH and the anodic peak potential E_{Ib} (V) was found to be linear:

$$E_{Ib} = 1.5089 - 0.0579\text{pH} \quad (R^2 = 0.9977)$$

with a slope of the regression line very close to the Nernstian value of 0.059 V/pH for a process involving the exchange of an equal number of protons and electrons, as demonstrates the above presented reaction scheme.

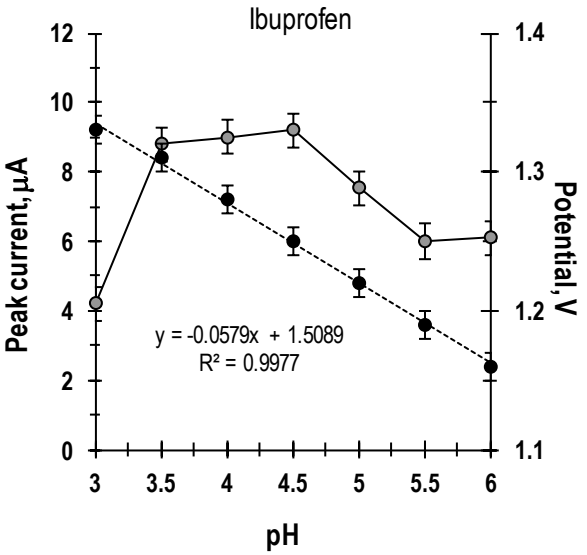


Figure 3. Effect of pH on the anodic peak current and anodic peak potential of ibuprofen. Scan rate 0.1 V s^{-1}. Accumulation time 30 s at open circuit potential. Ac 0.1 mol L^{-1}; Ibuprofen 200 µmol L^{-1}.

3.3. Analytical Performances Evaluation

The method usually applied for the sensitive voltammetric species determination is differential pulse voltammetry. However, the voltammograms resulting from ibuprofen determination by DPV at bare graphite electrode exhibit the appearance of broad asymmetric peaks, because of the irreversibility of the oxidation process and the interference of the oxygen evolution reaction (Figure 4).

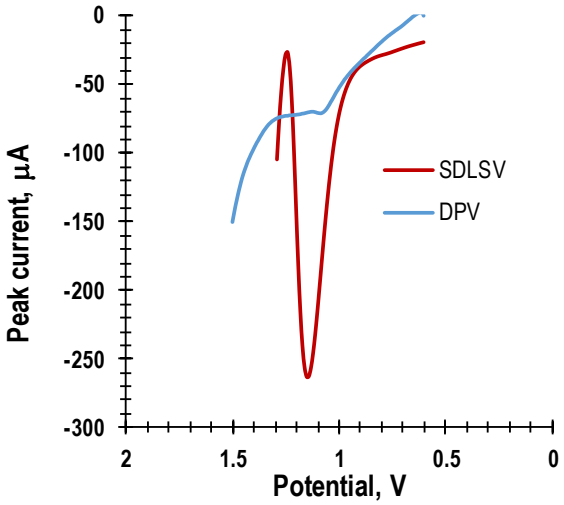


Figure 4. Voltammetric response of ibuprofen (200 µmol L^{-1}) recorded by DPV and SDLSV at bare graphite electrode. Ac 0.1 mol L^{-1}, pH 4.5; 3 min accumulation time.

Hence, further analysis for the evaluation of the analytical performances of the ibuprofen determination were carried out by semi-derivative linear sweep voltammetry (SDLSV). The semi-differentiation allowed the transformation of the asymmetric and broad ibuprofen current peaks into

much more symmetrical, bell-shaped and detectable semi-derivative signals (Figure 4). In addition, the signal processing led to sensitivity enhancement, as the peaks current of the semi-derivative voltammograms was significantly higher compared to the DPV peaks current. These facts proved the benefits of the semi-derivative signal processing to improve the analytical performances of the ibuprofen determination at bare graphite electrode.

The current response of ibuprofen with concentrations increasing in the range of 2 μmol L^{-1} to 500 μmol L^{-1} at bare graphite electrode under optimum conditions recorded by linear sweep voltammetry followed by semi-derivative signal processing is shown in Figure 5. The reliability of the semi-derivative linear sweep voltammetry for ibuprofen determination was tested by calibration curve construction. The calibration plot (Figure 5) demonstrated that the peak current (I_{Ib}, μA) increased proportionally to the ibuprofen concentration (C_{Ib}, μmol L^{-1}) in two dynamic linear ranges: 2 μmol L^{-1} to 100 μmol L^{-1} and 100 μmol L^{-1} to 500 μmol L^{-1}, described by the following regression equations:

$$I_{Ib} = 1.6909C_{\underline{Ib}} \ (R^2 = 0.9915) \text{ and } I_{Ib} = 0.3517C_{\underline{Ib}} + 125.17 \ (R^2 = 0.9915).$$

The appearance of two linear concentration ranges was attributed to the adsorption process. It did not alter the kinetics of the electrode reaction at low ibuprofen concentrations, while the saturation of the electrode surface at higher ibuprofen concentrations provoked a peak current intensity decrease.

The sensitivity of the determination, evaluated from the slopes of the linear calibration plots, was found to be 1.6906 μA L $μmol^{-1}$ and 0.3517 μA L $μmol^{-1}$, correspondingly. The limit of detection (S/N = 3) was found to be 0.6 μmol L^{-1}. Table 1 compares the analytical characteristics of the method suggested in this work with the reported in the literature.

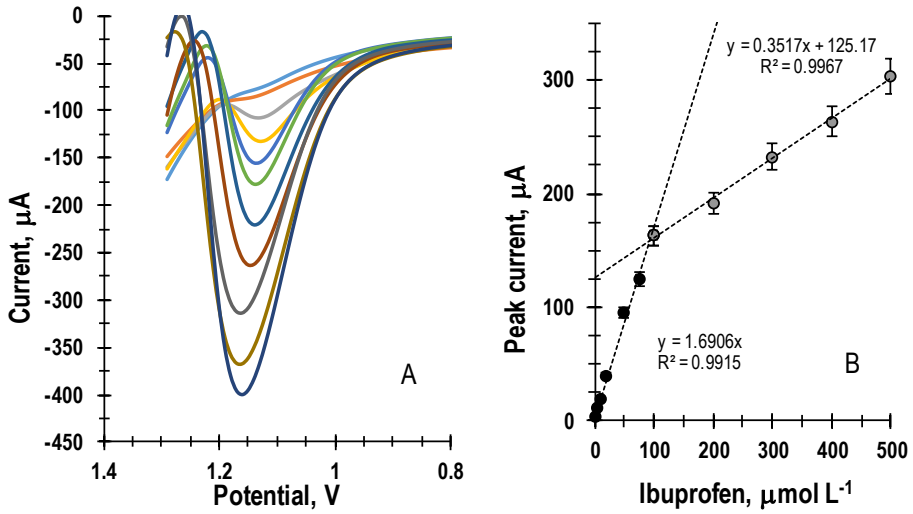


Figure 5. (A) SDLSV response of ibuprofen with different concentrations (2 μmol L^{-1} - 500 μmol L^{-1}) at bare graphite electrode under optimum conditions; (B) Calibration plot for ibuprofen determination.

As shown in Table 1, the analytical characteristics of the determination such as sensitivity, limit of detection, and linear concentration range are comparable or better than those achieved by using most

of the chemically modified electrodes and BDD. These promising performances were ascribed to the applied semi-derivative signal processing. Therefore, coupling of the bare graphite electrode with the suggested in this work approach for ibuprofen sensing results in improvement of the analytical performances of its determination.

Table 1. Comparison of the analytical performances of some voltammetric methods for ibuprofen determination at different electrodes. A-τ – amperometric method; aSPCE - activated screen printed carbon electrode; BDD – boron doped diamond electrode; CPE – carbon paste electrode; CNF – carbon nanofiber; GCE – glassy carbon electrode; MWCNT – multiwalled carbon nanotubes; Poly(L-Asp) – poly(L-aspartic acid); SPCE – screen printed carbon electrode; SPGE – screen printed graphite electrode.

Electrode	Method	Linear range, μmol L^{-1}	Sensitivity, μA L $μmol^{-1}$	LOD, μmol L^{-1}	Ref.
Poly(L-Asp)/GCE	SWV	1-150	0.031	0.22	17
CNF/SPCE	DPV	0.8-30	1.17	0.35	13
BDD	DPV	0.949-6.69	0.054	0.41	20
BDD	SWV	0.949-6.69	0.014	0.93	23
GCE	SWV	1.45-3.87	4.42	0.96	16
BDD	DPV	20-400	0.00694	3.80	15
MWCN/CPE	DPV	2.36-242	0.228	9.10	14
MWCNT/GCE	A-τ	10-1000	2.94	1.90	43
aSPCE	DPV	0.5-20	0.26	0.059	44
Graphite electrode	SDLSV	20-500 2-100 100-500	1.6906 0.3517	0.60	This work

The reproducibility of the analysis was found to be very satisfactory (RSD = 2.89%, n = 5), in contrast to the repeatability (RSD = 4.94%, n = 3). The poor repeatability was attributed to the ibuprofen desorption.

The selectivity of the determination was assessed by measuring the SDLSV response of ibuprofen in the presence of the common drug excipients (cellulose, lactose, sucrose, starch, and magnesium stearate), as well as in the presence of caffeine (Caf) and paracetamol (Par), which are combined with ibuprofen in some pharmaceutical formulations. It was found that excipients did not affect the current response of ibuprofen. The 2.5-fold excess of paracetamol, corresponding to that in the ibuprofen and caffeine combined tablets (Ib 200 mg/tablet + Par 500 mg/tablet) did not provoke Ib signal change, as the oxidation peaks potential difference of Ib and Par at bare graphite electrode under the selected experimental conditions was found to be 730 mV, this avoiding the interference. However, the presence of caffeine, even in a concentration ratio of Ib:Caf =4:1, i.e. in excess of ibuprofen like in some pharmaceutical combinations (Ib 400mg/tablet + Caf 100 mg/tablet), the selectivity of the analysis was not satisfactory, because of the Caf and Ib peaks overlapping.

3.4. Analytical Application

The proposed analytical protocol was applied for ibuprofen determination in the commercially available pharmaceutical preparations Nurofen and Advil. As shown in Table 2, the amount of ibuprofen found is in good agreement with the declared by the producer, this confirming the viability of coupling of the bare graphite electrode with the semi-derivative linear sweep voltammetric technique for real samples analysis.

Table 2. Real samples analysis (average of three determinations).

Sample	**Ibuprofen**		
	Label value mg	Found mg	% detected
Nurofen	200	196 ± 2	98.0
Advil	200	194 ± 3	97.0

In addition, recovery tests were performed to check the accuracy of the proposed analytical protocol by spiking the pharmaceutical tablet preparation sample with appropriate quantity of the standard ibuprofen solution. The satisfactory recovery values (98% - 102%) shown in Table 3 confirmed the accuracy of the determination and suggested that the developed in this work analytical protocol for ibuprofen determination at bare graphite electrode has a practical significance.

Table 3. Recovery test results (average of three determinations).

Sample	**Spiked level μmol L^{-1}**	**Found level μmol L^{-1}**	**Recovery %**
Nurofen	25.0	25.3 ± 1	101.2
	50.0	49.8 ± 2	99.6
	75.0	76.2 ± 4	101.6
Advil	25.0	24.8 ± 2	99.2
	50.0	51.1 ± 3	100.4
	75.0	74.7 ± 5	99.6

4. CONCLUSION

Semi-derivative voltammetry was applied for improving the analytical performances of the ibuprofen determination at bare graphite electrode. As a result, sensitivity, limit of detection, and linear concentration range comparable or better than those attained by using most of the chemically modified electrodes were achieved. It was demonstrated that the bare graphite electrode as sensing element in

conjunction with the semi-derivative technique offers a simple, efficient, and cost-effective determination of ibuprofen in pharmaceutical preparations.

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