

Research Article

Anodic Determination of Acetylsalicylic Acid at a Mildly Oxidized Boron-Doped Diamond Electrode in Sodium Sulphate Medium

Codruța Cofan¹ and Ciprian Radovan²

¹Department of Chemistry, School of Pharmacy, University of Medicine and Pharmacy "Victor Babes" Timisoara, Piata E. Murgu, no. 2, 300041 Timisoara, Romania

²Laboratory of Electrochemistry, West University of Timisoara, Pestalozzi Street, no. 16, 300115 Timisoara, Romania

Correspondence should be addressed to Codruța Cofan, cofancodruta@umft.ro

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Differential pulse voltammetry (DPV) and chronoamperometry (CA) were used to detect and determine acetylsalicylic acid (ASA) at a mildly oxidized boron-doped diamond (BDD) electrode in a neutral sodium sulphate solution as supporting electrolyte. ASA determination in unbuffered medium was achieved using neutralized standard and real samples. Over the concentration range of 0.01 mM–0.1 mM, linear calibration plots of anodic current peaks in DPV and anodic currents in CA experiments versus concentration were obtained with very high correlation coefficients and good sensitivity values. The limits of detection were situated around 1 μ M. The association of DPV and CA techniques with standard addition method represented a suitable option for the determination of ASA in real samples such as pharmaceutical formulations.

1. Introduction

Acetylsalicylic acid (ASA) or aspirin, the world's oldest and best known nonsteroidal anti-inflammatory drug, continues to receive special attention due to its clinical effects on inflammation, fever, renal function, and platelet aggregation [1, 2]. Recent studies have shown that administered in specific dosages, aspirin has the ability to prevent cardiovascular events and different types of cancer and to reduce even the incidence of Alzheimer's disease occurrence [3–5]. ASA has also an antioxidant effect. In contrast, evidence proves that it induces formation of free-radicals which are involved in gastrointestinal damage and development of gastroduodenal ulcer [6–9]. After entering the bloodstream, acetylsalicylic acid is rapidly metabolized in salicylic acid (SA), the compound known to be primarily responsible for the pharmacological activity of ASA [1, 4, 10, 11]. The therapeutic action and the toxic effects of this widely consumed active substance promote ASA as a drug continuously subjected to extensive research.

A survey in the literature indicates a variety of analytical techniques used for the detection and determination of ace-

tylsalicylic acid. Generally, ASA is indirectly determined after the conversion to salicylic acid, its main hydrolysis product [4, 10]. The conventional "back-titration" method specified by British Pharmacopoeia and the Trinder reaction are methods of reference for the determination of ASA and salicylates, respectively [12–14]. In time, "back-titration" and Trinder reaction have been replaced by methods such as spectroscopy, mass spectrometry, UV-VIS spectrophotometry, spectrofluorimetry, gas chromatography, different types of liquid chromatography, and capillary electrophoresis. The latter methods, used independently or coupled with various detection modes, were applied for ASA investigation in biological fluids, pharmaceutical preparations, and even waste waters [4, 5, 10, 13, 15, 16]. The detection and determination of aspirin using the above-mentioned techniques have been achieved in both single [13, 15, 17, 18] and multicomponent systems [10, 19–29].

Acting as electroactive substance through salicylic acid, aspirin's main hydrolysis product, ASA has also been electrochemically studied from a mechanistic or analytical perspective, using a range of methods, electrode types, and, supporting electrolytes [12, 30–48].

Boron-doped diamond (BDD) is a very important material for electroanalysis, since it exhibits several electrochemically valuable properties such as its very wide electrochemical window in aqueous solutions resulting from the high overpotentials of the oxygen and hydrogen evolution reactions, low and stable voltammetric and amperometric background current, its excellent chemical and electrochemical stability in aggressive conditions, and its good responsiveness to a range of analytes without any conventional pretreatment [49–59].

Several important studies reported the determination of ASA in pharmaceutical formulations based on its hydrolysis to salicylate at controlled temperature conditions, using unmodified or modified graphite [30, 46], carbon paste [30] and glassy carbon [32, 33, 36, 37, 39, 47] electrodes, and different supporting electrolytes, some of them having the inconvenience of methanol [30, 33, 36], diethylether, or ethanol-diethylether [37] content.

Published data reports the use of a boron-doped diamond (BDD) electrode for the electrochemical evaluation of salicylic acid in acidic media [34]. At the same time, the voltammetric study of SA electrochemical oxidation at BDD electrode is merely presented. Mineralization of salicylic acid in acidic aqueous solution by electrochemical advanced oxidation processes using a BDD electrode as anode has also been explored [45]. Only one published paper [48] describes the determination of acetylsalicylic acid from pharmaceutical products by square-wave voltammetric data, using a specially treated boron-doped diamond electrode with very high overpotential for ASA oxidation in an H_2SO_4 medium and without a preliminary hydrolysis step.

This paper presents the cyclic voltammetry (CV) investigation and the determination of acetylsalicylic acid by anodic differential pulse voltammetry (DPV) and chronoamperometry (CA), using a stationary mildly oxidized unmodified BDDE and a very simple and easy accessible supporting electrolyte, a neutral sodium sulphate solution. The actual report continues by outlining specific applications of DPV and CA techniques explored at a BDD electrode coupled with standard addition method to the analysis of two commercialized pharmaceutical formulations.

2. Experimental

The electrochemical data were obtained from CV, DPV, and CA measurements. A Metrohm three-electrode cell equipped with a stabilized BDDE working electrode as a 3 mm diameter stationary disc embedded in a PEEK (PolyEtherEtherKetone) rod, a platinum foil counter-electrode, and a saturated calomel reference electrode (SCE), was used to perform the electrochemical measurements. The unmodified commercial boron-doped diamond electrode supplied by Windsor Scientific Ltd. for electroanalytical use was a mirror-polished doped polycrystalline industrial diamond (microcrystalline, doping degree cca. 0.1% boron) prestabilized in our laboratory by mild electrochemical oxidation at +2 V versus SCE in neutral and alkaline media and several hundreds repeated alternate polarization cycles between -1 and $+2$ V

versus SCE in acidic and neutral media. All voltammograms were collected using an Autolab PGstat 20 EcoChemie system controlled by a PC running GPES Software version 4.9. The CV measurements obtained corresponded to restricted potential limits ranged between 0 V and $+1.25$ V versus SCE and a scan rate between 0.005 and 0.03 Vs^{-1} , usually of 0.03 Vs^{-1} . Working parameters for the exemplified differential pulse voltammograms involved a modulation time of 0.05 s, an interval time of 0.25 s, an initial potential of 0 V, an end potential of 1.25 V, a step potential of 0.00405 V, a modulation amplitude of 0.02502 V, and a scan rate of 0.0162 Vs^{-1} . CVs, DPVs, and CAs were recorded at stationary electrode in quiescent solutions, in a controlled argon atmosphere, and at room temperature ($23 \pm 1^\circ\text{C}$).

Before starting each series of electrochemical measurements, the working electrode was carefully cleaned, degreased, and treated to remove fouling by polishing with alumina aqueous suspension, and finally thoroughly washed with double-distilled water. Each determination was repeated three times with good reproducibility of the practically stabilized state of electrode surface recovered by simple means of cleaning of the electrode, short resting period, and brief stirring of the solution between the successive measurements.

The supporting electrolyte was a 0.1 M Na_2SO_4 unbuffered solution, pH practically 7. The substances used were analytical grade Merck reagents. Acetylsalicylic acid standard solutions were freshly prepared at room temperature ($23 \pm 1^\circ\text{C}$), by addition of an NaOH diluted solution in order to transform the target substance into freely water-soluble salt. The explored concentrations of ASA for determination of a coherent electroanalytical method ranged between 0.01 and 0.1 mM in DPV exploration and between 0.01 and 0.09 mM in CA experiments. The higher investigated concentration ranges had no relevance for electroanalytical purpose, and a distinct access to a low limit of detection is being desirable.

The electroanalytical application of DPV and CA methods associated with standard addition method for detection and determination of acetylsalicylic acid was verified using *Aspirin* tablets (BAYER) and *Acid Acetilsalicylic* tablets (SICOMED). The real samples from pharmaceutical formulations were aqueous solutions freshly prepared by dissolution of *Aspirin* tablets and *Acid Acetilsalicylic* tablets, respectively. 250 mL as stock solutions were made up from a single *Aspirin* or *Acid Acetilsalicylic* tablet, under similar conditions as standard solutions. Very small volumes of the standard solutions were added to obtain the desired additional concentrations while maintaining a practically constant solution volume in the cell. The final working solution volume in the cell was 50 mL. All the dilutions of the investigated standard and real sample solutions were made using the simple, easy accessible, unbuffered sodium sulphate supporting electrolyte.

3. Results and Discussion

A series of cyclic voltammetry data recorded in a neutral unbuffered sodium sulphate solution used as supporting

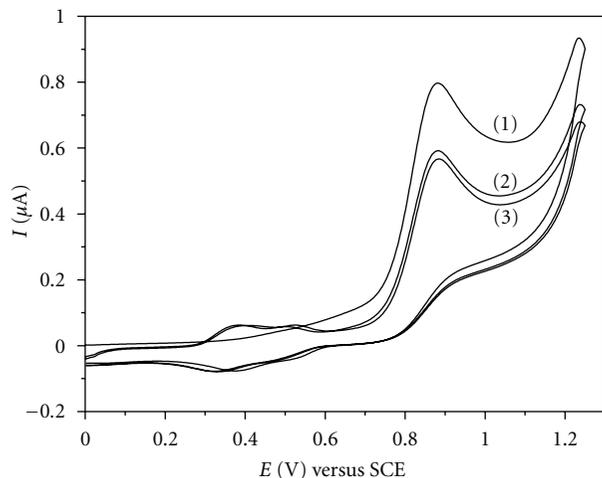


FIGURE 1: Cyclic voltammograms of 0.03 mM ASA. Supporting electrolyte: 0.1 M Na_2SO_4 pH 7; starting potential: 0 V versus SCE; potential range: 0 V \rightarrow +1.25 V \rightarrow 0 V versus SCE; scan rate: 0.03 Vs^{-1} ; (1)–(3): scan 1–scan 3.

electrolyte represented the starting point in evaluating the electrochemical behavior of ASA at an unmodified BDDE. Figure 1 depicts typical examples of anodic cyclic voltammetric responses corresponding to electrochemical oxidation of 0.03 mM ASA at an unmodified BDDE in a neutral 0.1 M Na_2SO_4 solution. The CV successive scans were collected in the potential range between 0 V versus SCE and +1.25 V versus SCE, starting in the positive direction from 0 V versus SCE, at a scan rate of 0.03 Vs^{-1} . On the forward branch of the first scan, a well-defined anodic current peak attributable to anodic oxidation of ASA disposed around +0.9 V versus SCE.

The practical overlapping of second and third scans disposed below the first one corresponded to a stationary state of diffusively controlled anodic process. Voltammograms for ASA solutions, with anodic and cathodic branches (obtained but not presented here in the figures), corresponded to an irreversible electrochemical behavior of the studied compound at an unmodified BDDE. Our work relates only to the analytically oriented investigations without any consideration of the mechanistic aspects.

The influence of the scan rate on ASA anodic oxidation at BDDE in unbuffered 0.1 M Na_2SO_4 solution (pH 7) has been investigated for 0.03 mM ASA final concentration in the electrochemical cell, under cyclic voltammetric conditions. CV scans (see Figure 2) initiated by potential sweep in the positive direction starting from 0 V versus SCE were recorded for scan rates between 0.005 and 0.03 Vs^{-1} . A progressive increase of current peaks manifested around +0.9 V versus SCE and corresponding to ASA anodic oxidation was remarked while increasing scan rate.

The diffusively controlled anodic oxidation process of ASA at BDDE and the absence of adsorbed reaction products on electrode surface were confirmed by the linear dependency and zero intercept of anodic current peak, I , versus

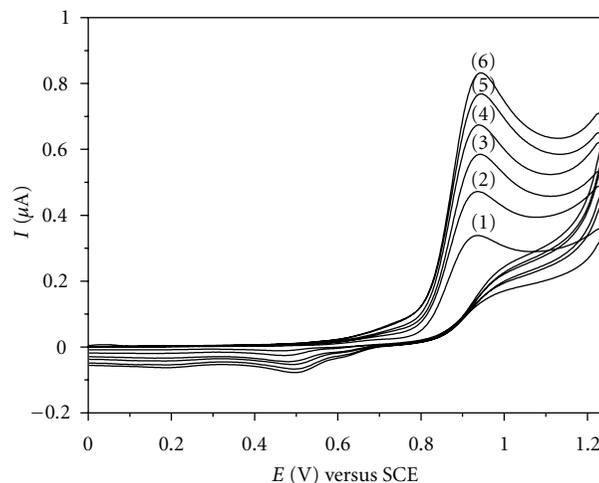


FIGURE 2: Cyclic voltammograms of 0.03 mM ASA. Effect of scan rate: (1) 0.005 Vs^{-1} , (2) 0.01 Vs^{-1} , (3) 0.015 Vs^{-1} , (4) 0.02 Vs^{-1} , (5) 0.025 Vs^{-1} , (6) 0.03 Vs^{-1} ; supporting electrolyte: 0.1 M Na_2SO_4 pH 7; starting potential: 0 V versus SCE; potential range: 0 V \rightarrow +1.25 V \rightarrow 0 V versus SCE.

square root of scan rate, $\nu^{1/2}$ ($I = 4.82\nu^{1/2}$, where I (μA), ν (Vs^{-1})) obtained with very good values of determination parameter ($R^2 = 0.999$).

In addition, besides the good reproducibility and the detailed aspect regarding the control of anodic process by diffusion, the less positive potential of current peaks comparatively with literature data obtained at a strong oxidized BDD electrode [48] can be mentioned.

ASA concentration effect (not presented here) on the optimum anodic response in CV exploration at an unmodified BDDE using a neutral sodium sulphate solution as supporting electrolyte was also evaluated. The series of CVs obtained for ASA standard solution were recorded over the concentration range of 0.01 mM–0.08 mM. Calibration plot data of anodic current peaks versus concentration of ASA exhibited good linearity and sensitivity (see Table 1). LOD value of 1.02 μM has been calculated according to $3\sigma/\text{slope}$ criterion, where σ was estimated as the standard deviation applied to the net amperometric signal measured for the lowest analyte concentration corresponding to calibration plot and RSD ranged between 2 and 3%.

After this preliminary discussion of cyclic voltammetry data, and confirmation of a diffusely controlled anodic process, more detailed investigations with electroanalytical application purposes were conducted using two other different techniques, differential pulse voltammetry, and chronoamperometry.

3.1. Differential Pulse Voltammetry Data. A series of anodic DPVs presented in Figure 3 involving ASA concentration effect at an unmodified BDDE in a 0.1 M Na_2SO_4 (pH 7) supporting electrolyte were recorded over the concentration range of 0.01 mM–0.1 mM and using ASA standard solution.

Under conditions of the applied parameters of differential pulse voltammetry technique, sharp and well-defined

TABLE 1: Parameters of calibration plots ($I = aC + b$; I (μA); a ($\mu\text{A mM}^{-1}$); C (mM); b (μA)), determination coefficient, and LOD values for acetylsalicylic acid (ASA) determination using CV, DPV, and CA methods.

Figure	Method	Concentration range (mM)	Regression equation of linear calibration plot	Sensitivity ($\mu\text{A mM}^{-1}$)	R^2	LOD (μM)
—	CV	0.01–0.08	$I = 24.175C + 0.039$	24.175	0.998	1.02
Figure 3	DPV	0.01–0.1	$I = 12.86C + 0.041$	12.86	0.998	1.03
Figure 5	CA	0.01–0.09	$I = 5.684C - 0.009$	5.684	0.997	1.03
Figure 6	CA ^a	0.01–0.08	$I = 21.397C + 0.034$	21.397	0.998	1.08

^a Continuous addition, stirred solution.

current peaks corresponding to ASA oxidation manifested around +0.9 V versus SCE.

Calibration plot (for calibration data, see Table 1) of anodic current peak, I , versus ASA concentration showed a satisfactory high sensitivity of $12.86 \mu\text{A mM}^{-1}$ and a very good linearity with a determination coefficient, $R^2 = 0.998$. LOD value of $1.03 \mu\text{M}$, very close to that one obtained when using CV technique, was calculated according to the same $3\sigma/\text{slope}$ criterion previously mentioned.

The potential usefulness of DPV method at the determination of ASA content in real sample solutions was verified using aqueous solutions from tablets of *Aspirin* (BAYER) and *Acid Acetilsalicylic* (SICOMED), respectively.

Figure 4(a) depicts a series of DPVs as an example involving ASA determination in an *Aspirin* real sample solution. The exemplified tested real sample was prepared under the conditions mentioned in the experimental part and using a 0.5953 g *Aspirin* tablet. 0.2 mL *Aspirin* initial solution was diluted to 50 mL final volume in 0.1 M Na_2SO_4 (pH 7) supporting electrolyte (0.2/50 dilution), and very small volumes of ASA standard solution were then added. ASA final supplementary concentrations in the tested real sample were 0.01 mM and 0.02 mM, respectively. Value of 473.9 mg ASA/tablet represented the average content determined using anodic DPV technique at BDDE associated with standard addition method. The investigation of 5 *Aspirin* tablets with an average weight of 0.5946 g led to a value of 471.2 mg ASA/tablet. According to the general BAYER product specification, each single tablet should contain 500 mg ASA.

A similar evaluation, Figure 4(b), corresponding to ASA determination was conducted using an aqueous real sample prepared from a 0.5925 g *Acid Acetilsalicylic* tablet. Practical results following application of DPV associated with standard addition method gave a content of 477.1 mg ASA/tablet. An average content of 472.2 mg ASA/tablet was obtained when investigating 5 *Acid Acetilsalicylic* tablets with 0.5917 g average weight. ASA content value in *Acid Acetilsalicylic* tablets indicated by the SICOMED supplier was 500 mg/tablet.

The matrix effects, which can be attributed to particular ingredients present in the tablets, were insignificant in their impact on quantitative evaluation of ASA in real samples.

3.2. Chronoamperometry Data. The preliminary evaluation of cyclic voltammetric data for the detection and determination of acetylsalicylic acid at an unmodified BDDE using as supporting electrolyte a neutral unbuffered sodium sulphate

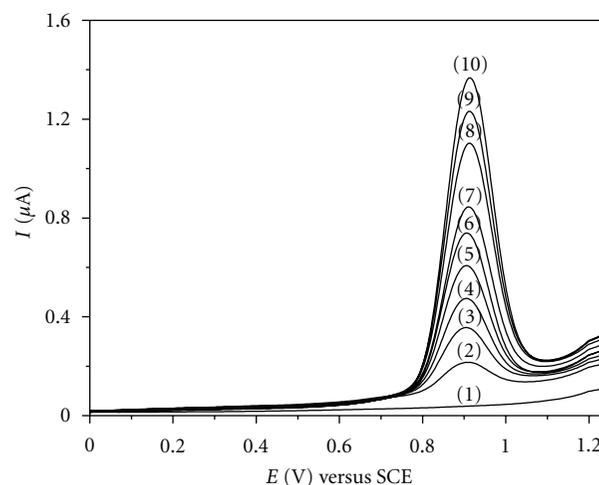


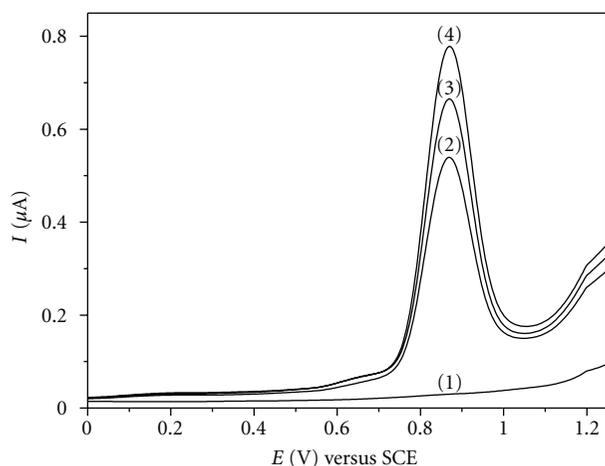
FIGURE 3: Differential Pulse Voltammograms. Effect of ASA concentration: (1) supporting electrolyte, (2) 0.01 mM, (3) 0.02 mM, (4) 0.03 mM, (5) 0.04 mM, (6) 0.05 mM, (7) 0.06 mM, (8) 0.08 mM, (9) 0.09 mM, (10) 0.1 mM; supporting electrolyte: 0.1 M Na_2SO_4 pH 7.

solution, constituted, as already mentioned, a basis for the chronoamperometric study of ASA electrochemical behavior at the same working electrode.

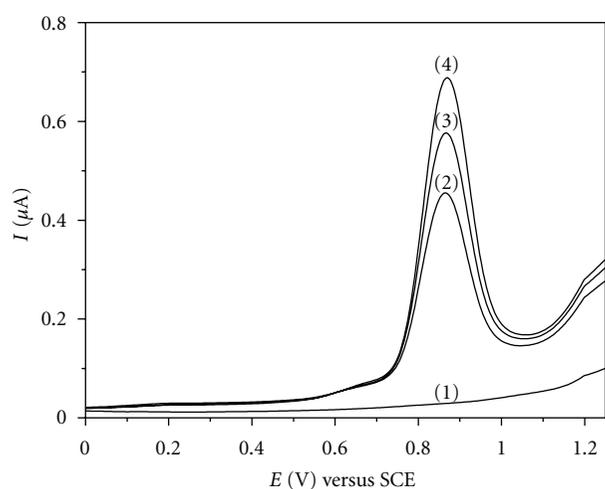
The detailed investigation using the chronoamperometry (CA) method, similar to our former study [57] at a fixed potential and sufficient time for a conventionally quasistationary state, was conducted to establish several working conditions and calibration plots data available as support for applications in practical analytical purposes, that is, the determination of ASA content in real samples obtained from pharmaceutical formulations.

Figure 5 shows a series of chronoamperograms regarding the effect of ASA concentration on the useful anodic response at unmodified BDDE, using standard solutions in 0.1 M Na_2SO_4 (pH 7) supporting electrolyte.

The tested analyte was added in increasing concentration, from 0.01 mM to 0.09 mM, and chronoamperograms were recorded at one potential level, +0.9 V versus SCE, which corresponded to optimum ASA anodic amperometric signal. Calibration plot of anodic currents read at 120 s (a sufficient time period for obtaining a conventional steady state) versus ASA concentration (see Table 1) was linear, presenting a very good determination parameter ($R^2 = 0.997$) and a satisfactory sensitivity value ($5.68 \mu\text{A mM}^{-1}$). Under these conditions



(a)



(b)

FIGURE 4: (a) Differential pulse voltammograms. (1) supporting electrolyte; (2) 0.2/50 dilution of *Aspirin* initial solution in supporting electrolyte; (3) 0.2/50 dilution of *Aspirin* initial solution in supporting electrolyte and ASA addition, 0.01 mM ASA final supplementary concentration; (4) 0.2/50 dilution of *Aspirin* initial solution in supporting electrolyte and ASA addition, 0.02 mM ASA final supplementary concentration; supporting electrolyte: 0.1 M Na_2SO_4 pH 7. (b) Differential pulse voltammograms. (1) supporting electrolyte; (2) 0.2/50 dilution of *Acid Acetilsalicylic* initial solution in supporting electrolyte; (3) 0.2/50 dilution of *Acid Acetilsalicylic* initial solution in supporting electrolyte and ASA addition, 0.01 mM ASA final supplementary concentration; (4) 0.2/50 dilution of *Acid Acetilsalicylic* initial solution in supporting electrolyte and ASA addition, 0.02 mM ASA final supplementary concentration; supporting electrolyte: 0.1 M Na_2SO_4 pH 7.

and according to $3\sigma/\text{slope}$ criterion, the calculated LOD was $1.03 \mu\text{M}$.

A continuous chronoamperogram (see Figure 6) recorded at one potential level, $+0.9 \text{ V}$ versus SCE, and over the concentration range of 0.01 mM – 0.08 mM , was obtained under the conditions of progressive addition, in a stepwise fashion, of an ASA standard solution to the stirred solution of

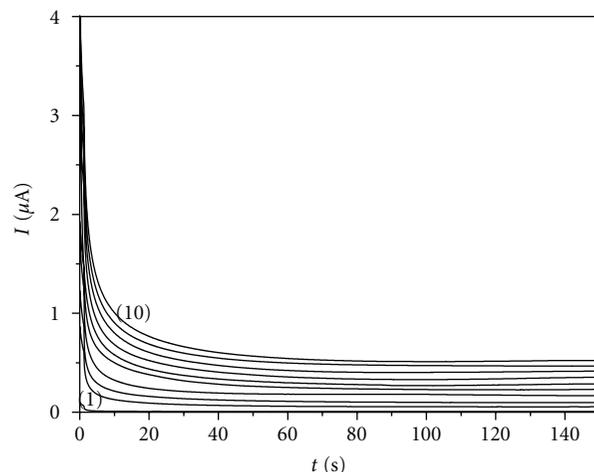


FIGURE 5: Chronoamperograms. Effect of ASA concentration at one potential level, $+0.9 \text{ V}$ versus SCE, around the corresponding current peak potential from CVs. (1) supporting electrolyte, (2) 0.01 mM, (3) 0.02 mM, (4) 0.03 mM, (5) 0.04 mM, (6) 0.05 mM, (7) 0.06 mM, (8) 0.07 mM, (9) 0.08 mM, (10) 0.09 mM; supporting electrolyte: 0.1 M Na_2SO_4 pH 7.

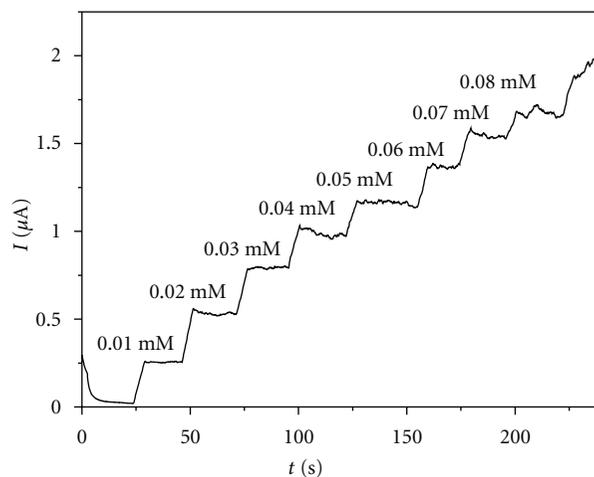


FIGURE 6: Continuous chronoamperogram at one potential level, $+0.9 \text{ V}$ versus SCE, around the corresponding current peak potential from CVs; progressive addition of ASA in the concentration range of 0.01 mM – 0.08 mM ; supporting electrolyte: 0.1 M Na_2SO_4 pH 7; stirred solution.

0.1 M Na_2SO_4 supporting electrolyte. No fouling of electrode surface occurred over the above-mentioned concentration range, characteristic aspect which suggested the further application of a BDD electrode as sensor for continuous ASA determination.

Linear plot (for calibration data, see also Table 1) of anodic currents read at 25 s, 50 s, 75 s, ..., and 225 s, respectively, versus ASA concentration presented a high sensitivity of $21.397 \mu\text{A mM}^{-1}$ and a very good determination coefficient ($R^2 = 0.998$), and a $1.08 \mu\text{M}$ LOD value was determined.

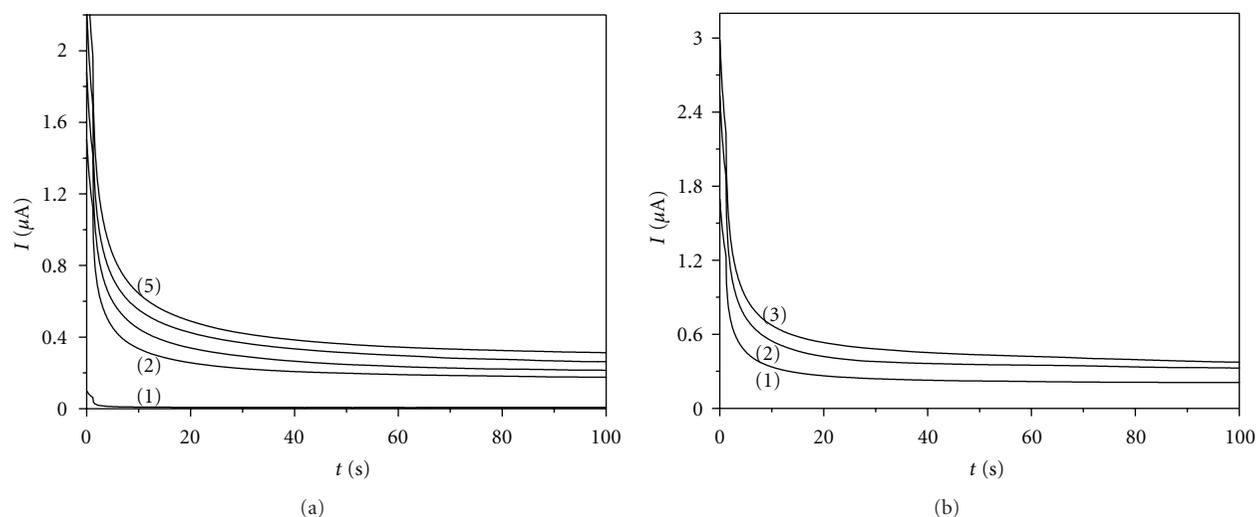


FIGURE 7: (a) Chronoamperograms, at one potential level, +0.9 V versus SCE. (1) supporting electrolyte; (2) 0.2/50 dilution of *Aspirin* initial solution in supporting electrolyte; (3) 0.2/50 dilution of *Aspirin* initial solution in supporting electrolyte and ASA addition, 0.01 mM ASA final supplementary concentration; (4) 0.2/50 dilution of *Aspirin* initial solution in supporting electrolyte and ASA addition, 0.02 mM ASA final supplementary concentration; (5) 0.2/50 dilution of *Aspirin* initial solution in supporting electrolyte and ASA addition, 0.03 mM ASA final supplementary concentration; supporting electrolyte: 0.1 M Na_2SO_4 pH 7; currents read at 100 s. (b) Chronoamperograms, at one potential level, +0.9 V versus SCE. (1) 0.2/50 dilution of *Acid Acetilsalicylic* initial solution in supporting electrolyte; (2) 0.2/50 dilution of *Acid Acetilsalicylic* initial solution in supporting electrolyte and ASA addition, 0.02 mM ASA final supplementary concentration; (3) 0.2/50 dilution of *Acid Acetilsalicylic* initial solution in supporting electrolyte and ASA addition, 0.03 mM ASA final supplementary concentration; supporting electrolyte: 0.1 M Na_2SO_4 pH 7; currents read at 100 s.

The utility of chronoamperometric method for the assessment of ASA in single component systems was suggested by the relatively high sensitivities, RSD values between 2 and 3%, and also by low values of limit of detection. Thus, the potential usefulness of the elaborated method was then verified by practical data of chronoamperometry associated with standard addition method obtained from ASA determination in real samples of *Aspirin* (BAYER) and *Acid Acetilsalicylic* (SICOMED).

Figure 7(a) illustrates an example of chronoamperograms recorded at one potential level, +0.9 V versus SCE, for a real sample of *Aspirin*, and for the mixture of real sample with ASA standard solution added to ensure 0.01 mM, 0.02 mM, and 0.03 mM ASA final supplementary concentrations in the system. In order to prepare the aqueous solution of real sample, a 0.5954 g *Aspirin* tablet was used according to the protocol described in the experimental section. A 0.2 mL *Aspirin* initial solution diluted to 50 mL volume with supporting electrolyte constituted the final volume of the real sample. Using CA technique coupled with standard addition method, the ASA average content in *Aspirin* real sample was 494.4 mg/tablet. It should be noted that the 491.7 mg ASA per tablet represented the average content determined when 5 *Aspirin* tablets with an average weight of 0.5951 g were investigated. According to the BAYER product specification, one *Aspirin* tablet contains 500 mg acetylsalicylic acid.

The other example of ASA determination in pharmaceutical formulations refers to using of an *Acid Acetilsalicylic* (SICOMED) aqueous solution. The initial solution of

real sample was prepared by solubilization of a 0.5847 g *Acid Acetilsalicylic* tablet using the volume control regime described in the experimental part. The real sample solution resulted from 0.2 mL *Acid Acetilsalicylic* initial solution diluted to 50 mL final volume with sodium sulphate supporting electrolyte (0.2/50 dilution). Very small volumes corresponding to final concentrations of 0.02 mM and 0.03 mM ASA standard solutions were added in the real sample and chronoamperograms at the same one potential level, +0.9 V versus SCE, were recorded (see Figure 7(b)). Thus, for the chosen example, the determined average content was 467.9 mg ASA/tablet. ASA content value in *Acid Acetilsalicylic* tablets indicated by the SICOMED supplier was 500 mg ASA per tablet. The investigation of 5 *Acid Acetilsalicylic* tablets with an average weight of 0.5842 g gave an average content of 466.3 mg ASA/tablet.

The association of differential pulse voltammetry, and chronoamperometry techniques with standard addition method proved to be very useful in analytical evaluation of both ASA-containing pharmaceutical products, *Aspirin* (BAYER) and *Acid Acetilsalicylic* (SICOMED). The matrix effects which can be attributed to the presence of adjacent inactive ingredients in pharmaceutical formulations were relatively minor and did not significantly perturb ASA determination. The average analytical data obtained for both pharmaceutical preparations corresponded to very good degrees of component recovery.

Linear calibration data and LOD values obtained are summarized in Table 1.

4. Conclusions

The detection and determination of acetylsalicylic acid by differential pulse voltammetry and chronoamperometry using a mildly oxidized boron-doped diamond electrode and an easily accessible, simple unbuffered sodium sulphate solution as supporting electrolyte has been achieved.

Very good linearities of the calibration plots of anodic current peaks and anodic currents, respectively, versus ASA concentration resulted from DPV and CA data. Adjacent analytical data regarding RSD, LOD, and sensitivities were obtained.

The association of differential pulse voltammetric and chronoamperometric methods with standard addition method has been successfully used for a fast analytical evaluation of pharmaceutical formulations which contain acetylsalicylic acid without significant matrix effects. The average content of ASA in BAYER and SICOMED tablets, explored as real samples, was measured in good accordance with those indicated by the suppliers.

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