Voltammetric behavior of rutin at a boron-doped diamond electrode. Its electroanalytical determination in a pharmaceutical formulation

Research Article

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Abstract: This paper examined for the first time, the possibilities of the usage of a boron-doped diamond electrode for the redox behavior of rutin using cyclic and adsorptive stripping voltammetry. The cyclic voltammograms showed a pair of redox peaks at lower potentials followed by an irreversible oxidation peak at higher positive potential. Using square-wave adsorptive stripping voltammetry, the compound yielded a well-defined voltammetric response in Britton-Robinson buffer, pH 4.0 at +0.48 V (*vs*. Ag/AgCl) (after 60 s accumulations at a fixed potential of 0.2 V). The calibration curve was linear in the concentration range from 0.01 μg mL^{-1} to 0.1 μg mL^{-1} (1.64×10^{-8} M - 1.64×10^{-7} M). A detection limit of 0.0017 μg mL^{-1} (2.78×10^{-9} M) was observed without any chemical modifications and electrochemical surface pretreatments. As an example, the practical applicability of boron-doped diamond electrode was tested with the measurement of rutin in dietary supplement products.

Keywords: *Rutin • Boron-doped diamond electrode • Square-wave adsorptive stripping voltammetry • Dietary supplement.*
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1. Introduction

Flavonoids are a large group of polyphenolic compounds that are widely present in fruits and vegetables with a wide range of pharmacological, biochemical, and physiological activities. Flavonoids and related polyphenols are generally characterized by the presence of two benzene rings (A and B), which can be linked by an oxygen-containing heterocycle (C). These compounds are naturally occurring antioxidants; they can protect biomolecules against attacks caused by the free radicals, and they decrease the possibility of free radical creation or even divert these radicals into less reactive or non-reactive products. Flavonoids can be classified into anthocyanins, flavones, isoflavones, flavanones, flavonols, and flavanols [1-6]. Rutin, (3′,4′,5,7-tetrahydroxyflavone-3β-D-rutinoside), is the glycoside of the aglycone, quercetin, in fact, two of the most representative flavonols in nature. Rutin has the same structure as quercetin except that it has a specific sugar molecule in place of one of quercetin's hydroxyl groups on the C ring which dramatically changes the activity of the molecule. Rutin is also known as vitamin P and thought to be an activating factor for vitamin C. It has clinically relevant functions, such as antibacterial, antioxidant, antihypertensive, anti-inflammatory, antitumor and anti-ageing. Furthermore, it can be used in the treatment of diseases such as capillary bleeding by diluting the blood, reducing capillary permeability and lower blood pressure [7-12]. Based on these properties, rutin is widely applied in medicine, and various preparations containing rutin are registered as drugs worldwide [13]. Hence, it is very important to develop a simple, economical, fast, sensitive, and efficient method for the determination of rutin. Various analytical methods have been reported in the literature for the determination of this compound in different matrices (*e.g.* herbs, pharmaceutical preparations,

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fruits and cereals). These particularly include high-performance liquid chromatography [14-18], capillary electrophoresis [19-23], chemiluminescence [24-29] and spectrophotometry [18,30,31]. Generally, some of these methods are considered to behighly sensitive (limits of detection up to 1.5×10^{-13} M) and selective, but on the other hand they are long lasting, expensive and often very laborious when some procedures such as derivatization, extraction and purification are included. Besides, the demands for highly skilled personnel often restrict their use in routine analytical practice.

On the other hand, voltammetric methods satisfy many of the requirements for such tasks, particularly owing to their simplicity, good stability, high sensitivity, speedy procedure and low cost. Therefore, it has been widely used to detect organic molecules, including drugs and polyphenols [32,33]. Due to the electroactive nature of rutin, considerable efforts have been devoted to develop voltammetric methods for its detection in the recent years. Although lower detection limits were achieved with the hanging mercury drop electrode (HMDE) [34,35], the electrochemical determination of rutin was mostly based on its adsorptive property at carbon-based electrodes. Unfortunately, the oxidation of phenolic compounds at bare solid electrodes produces phenoxy radicals which couple to form a passivating polymeric film on the electrode surface. This is why the literature on the electrochemical determination of rutin on unmodified carbon electrodes, such as glassy carbon electrode (GCE) [36,37], carbon paste electrode (CPE) [38] and screen printed electrode (SPE) [39], is limited. A large number of papers in the literature involve the use of modified electrodes [40-57]. The evaluation of the analytical performances of some reported electrodes for determination of rutin is presented in Table 1.

Recently, boron-doped diamond (BDD) electrode has been extensively used in electrosynthesis, electroanalysis, electrochemical combustion, and as electrocatalyst supports. BDD electrode exhibits a number of advantages over conventional electrodes such as: extremely high anodic potentials, low and stable background current, favorable electron-transfer kinetics, long-term stability of response, low sensitivity to dissolved oxygen, an extreme electrochemical stability in both strongly alkaline and acidic media, and a good resistance to surface fouling due to weak adsorption. Boron doping allows diamond to be turned into a good electrical conductor [58-60]. The electrode is now available commercially in polycrystalline boron-doped form. In our research group, various voltammetric techniques based on the oxidation of organic compounds at BDD electrode have been successfully developed [61-63].

To our knowledge, no study related to the determination of rutin using a BDD electrode has appeared in the literature. The present work thus deals, for the first time, with the highly sensitive analysis of rutin by square-wave adsorptive stripping voltammetric technique (SW-AdSV) using a BDD electrode without any chemical modifications and/or electrochemical pretreatment of electrode surface. This simple, low-cost and practical analytical approach is illustrated on quantification of rutin in dietary supplement products (single-ingredient).

2. Experimental procedure

2.1. Chemicals

Rutin standard was purchased from Sigma. Samples of rutin-containing tablets were procured from commercial local pharmacies. Other reagents used were of analytical grade, and their solutions were prepared with deionised water further purified *via* a Milli-Q unit (Millipore).

Stock standard solutions (1 mg mL^{-1} rutin) were prepared in methanol and stored in dark bottles at 4^0C when not in use. The working solutions were prepared daily by diluting aliquots of the stock solution with 0.1 M Britton-Robinson (BR) buffer solution as supporting electrolyte. The pH of the solutions ranged from 1.0 to 8.0.

2.2. Sample preparation

Solgar® tablets labeled as containing 500 mg rutin (without any other additive drugs) was used for the present analytical applications. Other ingredients listed in drug information leaflet are dicalcium phosphate, microcrystalline cellulose, vegetable cellulose, vegetable stearic acid, vegetable magnesium stearate, silica, and vegetable glycerin. Ten tablets were weighed and the average mass per tablet was determined. The tablets were carefully ground to a fine powder with a mortar and pestle. An adequate amount of the resulting powder was weighed and transferred into a 10-mL calibrated, dark volumetric flask, which was filled to the mark with methanol. The contents of the flask was sonicated for about 20 min to complete dissolution. The desired concentrations of rutin were obtained by taking suitable aliquots of the clear supernatant liquor and diluting with BR buffer, pH 4.0. An aliquot volume of these solutions was transferred to the voltammetric cell containing the same buffer solution and analyzed in the day of preparation according to the procedure developed for the pure electrolyte. The nominal content of the tablet amounts was calculated from the corresponding regression equations of previously plotted calibration curves.

Table 1. Comparison of the analytical performance of some electrodes previously reported for rutin determination.

Electrode	Linear working range (M)	LOD (M)	pH	Reference
HMDE	4.0×10^{-9}-8.5×10^{-8}	5.0×10^{-10}	6.0	[34]
HMDE	2.0×10^{-7}-1.4×10^{-6}	7.0×10^{-9}	6.0	[35]
GCE	3.28×10^{-7} -3.28×10^{-5}	2.51×10^{-8}	4.46	[36]
SPE	2.0×10^{-6}-1.5×10^{-5}	1.0×10^{-7}	5.0	[39]
GR-MnO$_2$/CILE	1.0×10^{-8}-5.0×10^{-4}	2.73×10^{-9}	-	[40]
Fc-S/AuNPs/GCE	5.0×10^{-8}-3.0×10^{-5}	1.0×10^{-8}	7.0	[41]
CILE	8.0×10^{-8}-1.0×10^{-4}	1.6×10^{-8}	3.0	[42]
MCCE-Cu$_3$(PO$_4$)$_2$	9.90×10^{-8}-2.5×10^{-6}	1.2×10^{-8}	6.9	[43]
MWNTs/DDMIMPF$_6$	3.0×10^{-8}-1.5×10^{-6}	1.0×10^{-8}	2.09	[44]
PAMAM/G-C/GCE	1.0×10^{-9}-2.0×10^{-6}	6×10^{-10}	6.0	[45]
AuNPs/en/ MWNTs/GCE	4.8×10^{-8}-9.6×10^{-7}	3.2×10^{-8}	3.5	[46]
LF/GCE	5×10^{-10}-1.0×10^{-8}	2.5×10^{-10}	4.6	[47]
CCEM	9.90×10^{-7}-8.07×10^{-6}	2.65×10^{-8}	6.0	[48]
IL-(AMIMBr)/CPE	4.0×10^{-8}-1.0×10^{-5}	1.0×10^{-8}	3.29	[49]
IL-(BPPF6)/CPE	5×10^{-7}-1.0×10^{-4}	3.58×10^{-7}	2.5	[50]
ss-HGCE	4.0×10^{-9}-1.0×10^{-6}	1.0×10^{-9}	5.0	[51]
CeO$_2$-AuE	5.0×10^{-7}-5.0×10^{-4}	2.0×10^{-7}	6.5	[52]
SWNTs/AuE	2.0×10^{-8}-5.0×10^{-6}	1.0×10^{-8}	5.0	[53]
RCPE	1.1×10^{-6}-3.1×10^{-6}	7.1×10^{-9}	5.0	[54]
PABSA/GCE	2.5×10^{-7}-1×10^{-5}	1×10^{-7}	4.0	[55]
MWNTs-IL-Gel/GCE	7.2×10^{-8}-6.0×10^{-6}	2×10^{-8}	3.0	[56]
MWCNTs-CHIT/ABPE	2.0×10^{-8}-1.0×10^{-5}	1.0×10^{-9}	-	[57]

GR-MnO$_2$/CILE: carbon ionic liquid electrode modified by a graphene-MnO$_2$ nanocomposite, Fc-S/AuNPs/GCE: ferrocene benzyne derivative gold nanoparticles modified glassy carbon electrode, CILE: carbon ionic liquid electrode modified by nafion, graphene oxide and ionic liquid composite, MCCE-Cu$_3$(PO$_4$)$_2$: carbon composite electrode modified with copper(II) phosphate immobilized in a polyester resin, MWNTs/DDMIMPF$_6$: multi-walled carbon nanotubes-ionic liquid (1-dodecyl-3-methylimidazolium hexafluorophosphate) composite electrode, PAMAM/G-C/GCE: glassy carbon electrode coated with graphene nanosheets, chitosan and a poly (amidoamine) dendrimer, AuNPs/en/MWNTs/GCE: gold nanoparticles/ethylenediamine/multi-walled carbon nanotubes modified glassy carbon electrode, LF/GCE: lead film modified glassy carbon electrode, CCEM: carbon-composite electrode modified with copper(II) immobilized in a cationic resin, IL-(AMIMBr)/CPE: ionic liquid (1-amyl-3-methylimidazolium bromide) modified carbon paste electrode, IL-(BPPF6)/CPE: ionic liquid (N-butylpyridinium hexafluorophosphate) modified carbon paste electrode, ss-HGCE: single-sided heated graphite cylindrical electrode, CeO$_2$-AuE: gold electrode modified with CeO$_2$ nanoparticles, SWNTs/AuE: single-walled carbon nanotubes modified gold electrode, RCPE: rigid carbon-polyurethane composite electrode, PABSA/GCE: poly(p-aminobenzene sulfonic acid) modified glassy carbon electrode, MWNTs-IL-Gel/GCE: multi-walled carbon nanotubes and ionic liquid composite film modified glassy carbon electrode, MWCNTs-CHIT/ABPE: acetylene black paste electrode modified with multi-walled carbon nanotubes-chitosan composite film.

2.3. Apparatus

All experiments of cyclic (CV) and square-wave adsorptive stripping (SW-AdSV) voltammetry were performed using an Autolab PGSTAT 128N electrochemical system (EcoChemie, The Netherlands) driven by the GPES 4.9 software. The potentiostat was connected to a personal computer. All SW voltammograms were smoothed using a Savicky and Golay algorithm and baseline-corrected by the moving average method (peak width of 0.01 V), using the software supplied with the equipment. A classical three-electrode cell of volume 10 mL was used with a platinum wire as an auxiliary electrode and an Ag/AgCl (3 M NaCl) electrode (Model RE-1, BAS, USA) as a reference electrode. The working electrode was a boron-doped diamond (BDD) working electrode

(Windsor Scientific Ltd.; Ø: 3mm, diameter). Before each experiment, the BDD electrode was polished manually with slurries prepared from 0.01 μm aluminum oxide on a smooth polishing pad (BAS velvet polishing pat), and then ultrasonically cleaned in deionised water thoroughly in order to remove any residual alumina. Solution pH was measured using a WTW inoLab pH 720 meter with a combined electrode (glass-reference electrodes).

2.4. Adsorptive stripping voltammetric procedure

The general procedure for stripping voltammetric analysis of rutin was as follows: the three-electrode system was immersed in a voltammetric cell containing

the required aliquot of the rutin working solutions and supporting electrolyte at a desired pH. A selected accumulation potential was then applied to a BDD surface for a selected pre-concentration period, while the solution was stirred at 600 rpm. At the end of the accumulation period, the stirring was stopped and a 10 s rest period was allowed for the solution to become quiescent. Then, the voltammogram was recorded by scanning the potential toward to positive direction between 0.0 to +1.2 V using SW waveform.

The best instrumental parameters for SWV, which was used for investigating the determination of rutin, were as follows: frequency, 125 Hz; pulse amplitude, 40 mV; scan increment, 8 mV. Successive measurements were carried out by repeating the above assay protocol on the working electrode. All measurements were performed in triplicate at laboratory temperature.

3. Results and discussion

The electrochemical behavior of rutin at BDD electrode was first investigated by means of CV. The cyclic voltammograms were recorded for 400 µg mL^{-1} rutin at pH 4.0 within the range 0.0 to +1.2 V at a scan rate of 100 mV s^{-1}. Rutin exhibited one distinct and well-defined oxidation peak (I$_a$) with a maximum at about +0.494 V and one broad peak (II$_a$) at more positive potential (*ca.* + 0.75 V) as shown in Fig. 1. On scanning in the negative direction, a reduction peak (I$_c$) at about +0.401 V appeared corresponding to reduction of the oxidation products formed in anodic peak I$_a$. The difference of peak potentials of the redox pair I$_a$/I$_c$ is 93 mV. The anodic voltammetric behavior of rutin on GCE [36,37] and SPE [39] has been recently discussed. Similar observations have been reported in literature, i.e., two oxidation and one reduction peak, however peak separations of I$_a$/I$_c$ (ΔE_p) are 28 and 200 mV for GCE and SPE, respectively. It reveals the fact that the reversibility of this process is seriously increased on GCE. Moreover, the peak potentials of secondary process II$_a$ on GCE and SPE were considerably higher than that obtained on BDD electrode, having potentials of +1.08 and 1.1 V, respectively.

From the figure, it is seen that subsequent scans with the same electrode surface resulted in a decrease of primary Ia and secondary IIa processes. However, it is important to note that rutin adsorbed film could be removed easily from BDD electrode surface by polishing pretreatment only.

The influence of scan rate on the oxidation of rutin for relatively lower rutin concentration of 400 µg mL^{-1} in the range of 100–600 mV s^{-1} was checked by CV at pH
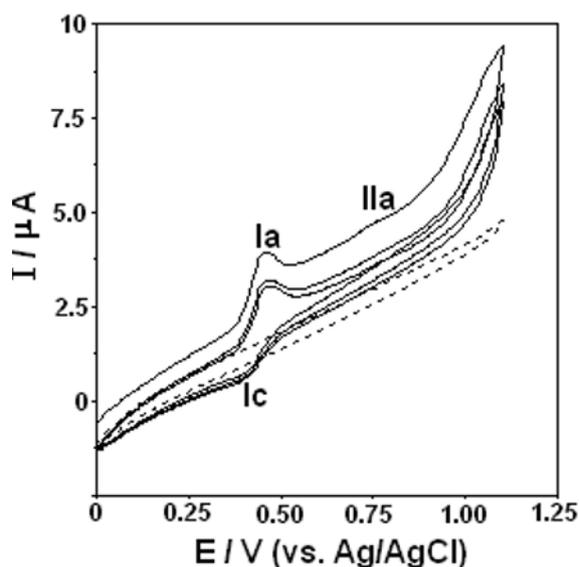
Figure 1. The cyclic voltammograms of 400 μg mL^{-1} rutin solutions in BR buffer pH 4.0. Scan rate, 100 mV s^{-1}. Dashed lines represent background current.

4 (not shown). Since the initial oxidation step (I$_a$) was more intense, it was selected for analysis purposes. The current response (*i*p) was linearly proportional to the scan rate (*v*) according to the relationship:

i_p (µA) = (0.51 ± 0.05) + (0.0094 ± 0.0001) *v* (mV s^{-1}), with a correlation coefficient of *r* = 0.9978

This suggests that the electrode reaction at the BDD electrode is controlled by the adsorption process.

The AdSV response of rutin at BDD electrode was examined using SW excitation waveform, which combines good sensitivity with high speed, and reduces problems with poisoning of the electrode surface. As a consequence, further work was dedicated towards studying the influence of acidity of the supporting electrolyte using SW-AdSV approach. As can be seen in Fig. 2, the effect of the pH on peak potential was investigated in the pH range 1.0-8.0 of BR buffer by carrying out adsorptive measurements on 1 µg mL^{-1} rutin solutions with an open-circuit mode at 60 s. It was observed that rutin presented a well-defined peak at pH values of <7.0. In addition, pH values of >8.0 were avoided because there were no oxidation peak observed. The results show that the peak potential is shifted towards less positive values as the pH of supporting electrolyte was gradually increased. The relationship between the peak potential and pH of BR buffer (over a pH range between 1.0 and 8.0) could be fit to the linear regression equation of *E*p (V) = (0.730 ± 0.001) – (0.0597 ± 0.0003) pH, *r* = 0.9989. The slope of the equation is

very close to the anticipated value of 59 mV. This result revealed that an equal number of participated protons and transferred electrons is involved in the oxidation of rutin on the BDD electrode, which confirms the results obtained in the literature [37,38,40]. The current of the initial peak I_a increased with increasing pH in acidic solution, the maximum current being obtained at pH 4.0, and afterwards, the current decreased drastically with
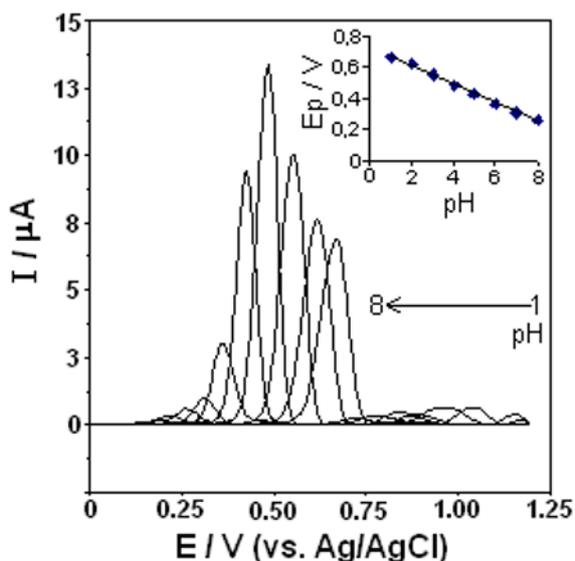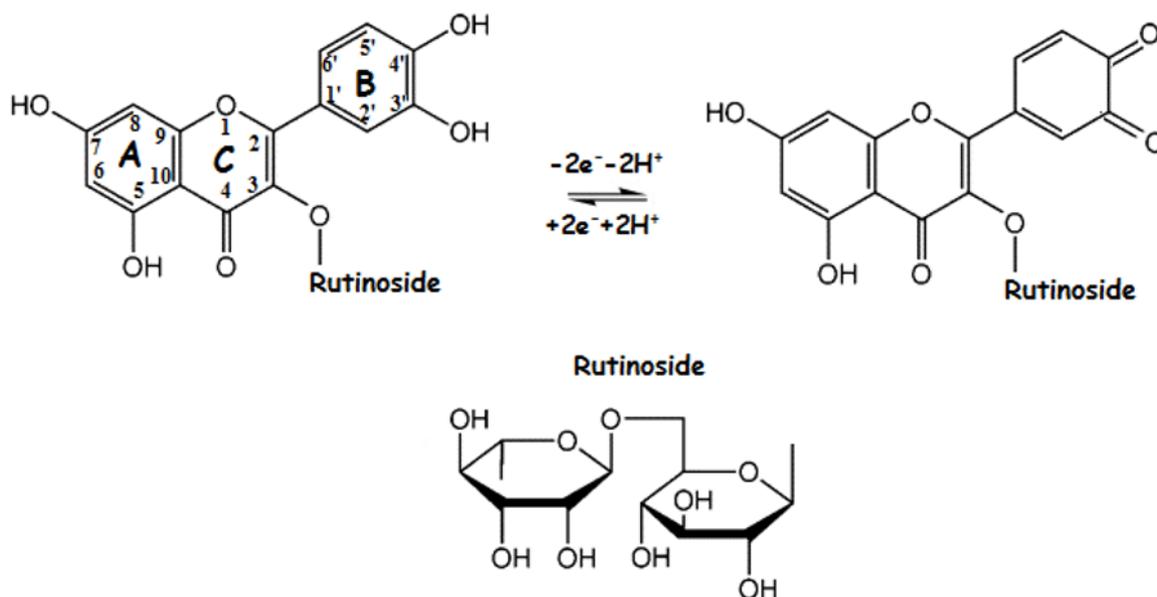

Figure 2. SW stripping voltammograms of 1 μg mL^{-1} rutin in BR buffer with different pH values (1.0, 2.0, 3.0, 4.0, 5.0, 6.0, 7.0 and 8.0). Inset: plot of E_p vs. pH. Accumulation time 60 s at open-circuit condition; SW parameters: frequency, 50 Hz; scan increment, 8 mV; pulse amplitude, 20 mV.

increasing pH up to 8.0, and then it almost disappeared. Since, the sharper response and best sensitivity was obtained at pH 4.0 using 0.1 M BR buffer solution, this condition was selected for further experiments.

Based on the detailed mechanism of rutin oxidation previously discussed using carbon-based electrodes, such as GCE [36,37] and SPE [39], we may assume that a single pair of oxidation-reduction peaks I_a/I_c corresponds to the oxidation of the catechol moiety, (3',4'-dihydroxy groups) on the B-ring of rutin and the reduction of the σ-quinone (3',4'-diquinone) products, respectively (Fig. 3). The peak II_a is assigned to the irreversible electrochemical oxidation of resorcinol moiety (5,7-dihydroxy groups) of ring A.

The attention was then turned to the effect of pre-concentration/stripping conditions, such as accumulation time and potential (data not presented) for 0.1 μg mL^{-1} rutin under the optimum experimental conditions. The influence of the accumulation time upon the analytical signal was examined in the range 0-300 s at open-circuit condition. The current increased linearly with accumulation time till 60 s beyond which the peak current was almost constant, which indicated that the accumulation of rutin at the electrode surface nearly reached a saturation state. The accumulation time of 60 s is very short and doubtlessly advantageous for practical use of this electrode. Hence, this accumulation time was chosen in all of the subsequent work. The influence of the accumulation potential either at open-circuit condition or at a potential range from +0.1 V to +0.5 V was studied with accumulation time of 60 s. The

Figure 3. The proposed mechanism for the electrochemical oxidation / reduction of rutin at BDD electrode.
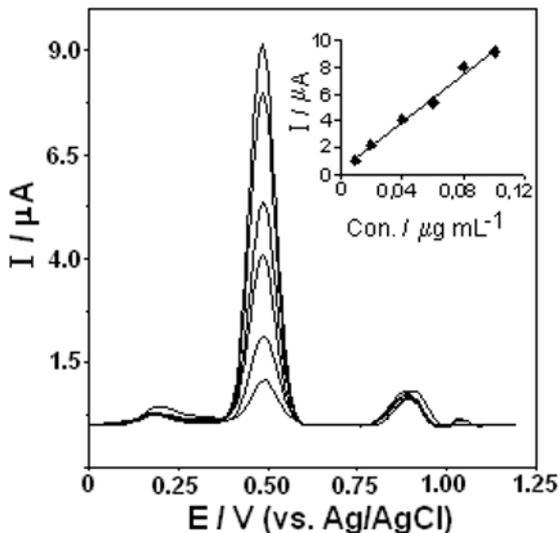
Figure 4. SW stripping voltammograms in BR buffer, pH 4.0 containing different concentrations of rutin (from inner to outer: 0.01, 0.02, 0.04, 0.06, 0.08 and 0.1 μg mL^{-1}). Inset depicts a corresponding calibration plot for the quantitation of rutin. Pre-concentration period, 60 s at a fixed potential of 0.2 V; SW parameters: frequency, 125 Hz; scan increment, 8 mV; pulse amplitude, 40 mV.

value for the stripping current at at open circuit voltage was nearly equal to the value obtained at +0.1 V. The results show that the peak current of rutin reached a maximal value as the potential of 0.2 V was used, so for further study this value of potential was chosen.

The SW response markedly depends on the parameters of the excitement signal. In order to obtain the maximum development of the SW-AdSV peak current, the various instrumental conditions (square-wave frequency, 25 Hz $\leq f \leq$ 150 Hz; square-wave amplitude, 10mV $\leq \Delta E_{sw} \leq$ 60 mV; and scan increment, 4mV $\leq \Delta E_s \leq$ 12mV) were studied for 0.1 μg mL^{-1} rutin in selected electrolytes following pre-concentration for 60 s at a fixed potential of 0.2 V. The variation in the f values show that its increase promoted an increase in the peak current due to the increase in the effective scan rate. However, the background current and noise were also increased at f values higher than 125 Hz. This was attributed to the greater contribution of the capacitive current at higher frequencies. The voltammetric responses for rutin determination as a function of variation in ΔE_{sw} demonstrated that peak current values increased upon increase of this parameter. However, the best peak morphology and sharper peak was obtained at 40 mV. In addition, at higher values of 8 mV, an increase in ΔE_s resulted in a decrease in peak current. To account for the results, in subsequent experiments, values of f = 125 Hz, ΔE_{sw} = 40 mV, and ΔE_s = 8 mV were adopted.

The previously optimized SWV parameters were employed to record the calibration curve for rutin in 0.1 M BR buffer (pH 4.0) using the BDD electrode. The proposed method offered well-defined concentration dependence. Fig. 4 displays stripping voltammograms obtained by successive additions of rutin in the concentration range from 0.01 μg mL^{-1} to 0.1 μg mL^{-1} (1.64×10^{-8} M - 1.64×10^{-7} M). The peak current at a potential of +0.48 V increased proportionally with the rutin concentration (Fig. 4, inset) to yield a highly linear calibration plot according to the relationship, i_p (μA) = – (0.013 ± 0.001) + (100 ± 5) C (μg mL^{-1}) (r = 0.9936, n: 6) where i_p is the adsorptive stripping peak current, C the rutin concentration, r the correlation coefficient and n the number of experiments.

The sensitivity of the proposed method was checked in terms of limits of detection (LOD) and quantitation (LOQ) values. LOD and LOQ were calculated according to formulas:

LOD = 3 SD/m and LOQ = 10 SD/m

where SD is the standard deviation of the peak current (three runs) of the lowest concentration of the linearity range (0.01 μg mL^{-1}) and m is the slope of the related calibration equation. LOD and LOQ were found to be 0.0017 μg mL^{-1} (2.78×10^{-9} M) and 0.0057 μg mL^{-1} (9.26×10^{-9} M), respectively.

It is interesting to compare the determination of rutin on BDD electrode with other voltammetric methods. Although the electroactive phenolic groups of rutin and other flavonoids are oxidized at low applied potential, adsorption of the electrochemically generated product changes the bare electrode surface of the commercial options, *i.e.*, glassy carbon, platinum, carbon paste, on successive scans, which leads to lack of repeatability and reproducibility of the method, and limits electroanalytical applications [38,64,65] (as it was mentioned earlier, BDD electrode is less prone to this drawback). Accordingly, it is apparent that the modified electrodes are mostly dominating in the electrochemical determination of rutin. For unmodified BDD electrodes in present paper, comparable or even lower LOD values were found in comparison with those using various solid modified electrodes reported in last decades (Table 1). The methods using LF/GCE and PAMAM/G-C/GCE as modified electrodes are considered to be the most sensitive electrochemical methods for determination of rutin with the lowest LOD values. However, it is important to note that electrode modification is frequently considered a tedious and laborious process, and the prices of modifying substances are usually so high that they can limit the

use of these types of electrodes in routine analysis [66]. On the other hand, despite the great sensitivity of HMDE [34], the toxicity of the mercury was the greatest drawback in the practical application of this electrode. Based on the above, the present methodology on the bare BDD electrode is simple and low cost in addition to sufficient analytical sensitivity for application to real samples.

In order to determine the precision of the determinations, standard solutions of rutin (0.06 µg mL^{-1}) were analyzed seven times within the same day (intra-day variation) and on four different days (inter-day variation). The relative standard deviations (R.S.D.) were calculated to be 7.4 and 7.8% for intra-day and inter-day repeatability, respectively, which are acceptable for voltammetric applications.

The applicability of the BDD electrode for SW-AdSV determination of rutin was verified by analysis of rutin-containing dietary supplement samples (Solgar® tablets, declared content of rutin 500 mg per tablet). The analyzed solutions were prepared as described above (in Section 2.4) after simply dissolving samples in selected medium and diluting the resulting solution to a target concentration within the linear range. The dilute real samples were almost similar to aqueous samples in behavior. The mean value of 0.0591 µg mL^{-1} of rutin was found in the measurement cell. Taking into account the successive dilutions of the sample, rutin content was calculated to be 492.5 mg per tablet which approximates the label value of 500 mg per tablet declared by producer. The validity was assessed by applying calibration curves and the recovery experiments. In order to detect the interaction between the excipients and rutin recovery, studies were carried out adding standard rutin solution to the sample solution in a voltammetric cell, and voltammetric responses were evaluated. Recovery of rutin was calculated by comparing the concentration obtained from the spiked mixtures with those of the pure rutin. The recovery of five-independent experiments was 102.7% with R.S.D. of 3.5%, demonstrating the accuracy of the proposed method.

4. Conclusions

The present study related the practical and suitable application of a BDD electrode in combination with SW-AdSV was, for the first time, used for the determination of rutin in dietary supplements. The sensitivity in terms of LOD (in the ppb order) reached without any electrode surface modification clearly demonstrates the superiority of this electroanalytical approach.

By comparison with already reported various chromatographic methods, this electrochemical procedure can be applied without previous separation, which is the main advantage if analytical costs and analysis time is considered. There is an additional advantage of avoiding consumption of large amounts of toxic organic solvents. In conclusion, it may represent the simple, fast, cheap and extremely sensitive alternative to the existing analytical methods dealing with real samples.

Free-radical scavenging and cytoprotective activities of flavonoids as antioxidants are mainly driven by electron donor properties. Bearing this important knowledge in mind, in addition to the practical application of the voltammetric technique described in this study, the data obtained above may be useful, at least in part, from a pharmacological point of view and to design the preventive strategies against to attacks caused by the free radicals.

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