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Electrochemical determination of resveratrol in dietary supplements at a boron-doped diamond electrode in the presence of hexadecyltrimethylammonium bromide using square-wave adsorptive stripping voltammetry

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Abstract: A sensitive electroanalytical methodology for the determination of resveratrol is presented for the first time using adsorptive stripping voltammetry at a bare boron-doped diamond (BDD) electrode. In cyclic voltammetry, resveratrol shows one irreversible and an adsorption-controlled oxidation peak at a BDD electrode. The voltammetric results indicated that in the presence of hexadecyl trimethyl ammonium bromide, the BDD electrode remarkably enhanced the oxidation of resveratrol, which leads to an improvement in the peak current with a shift of the peak potential to more positive values. Using the square-wave stripping mode, the compound yielded a well-defined voltammetric response in 0.1 M nitric acid solution containing 100 $\mu\text{mol L}^{-1}$ hexadecyl trimethyl ammonium bromide at 0.74 V (*vs.* Ag/AgCl), after 60 s accumulation at the open-circuit condition. A linear calibration graph was obtained in the concentration range 0.025 to 60.0 $\mu\text{g mL}^{-1}$, with a detection limit of 0.0063 $\mu\text{g mL}^{-1}$. The applicability of the proposed method was verified by analysis of resveratrol in commercial dietary supplements.

Keywords: resveratrol; boron-doped diamond electrode; square-wave adsorptive stripping voltammetry; hexadecyl trimethyl ammonium bromide.

INTRODUCTION

Resveratrol (3,4',5-trihydroxystilbene, RES) is a naturally occurring polyphenolic phytoalexin produced by a wide variety of plants as a defence substance against biotic or abiotic stress.¹ The main sources of resveratrol include grapes, knotweed, blueberries, pistachio nuts and peanuts.² RES exists in two isomeric forms as *trans*- and *cis*-RES, whereby the *trans*-form appears predominantly and has been proved to be more biologically active.³ RES has been positively linked

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to health benefits, including anti-oxidative effect,⁴ analgesic effect,⁵ cardioprotective effect,⁶ anticarcinogenic properties⁷ and anti-aging properties.⁸ Thus, it has been used as industrial material in the form of food additives and pharmaceuticals. Due to the above-mentioned interest in RES, several analytical methods have been reported in the literature for the determination of this compound in different matrices. These particularly include high-performance liquid chromatography (HPLC),^{9–10} ultrahigh pressure liquid chromatography (UHPLC),¹¹ liquid chromatography coupled to electrospray ionization-mass spectrometry (LC-ESI-MS),¹² gas chromatography-mass spectrometry (GC-MS)¹³ and capillary electrophoresis (CE).¹⁴ Electrochemical techniques, such as the voltammetric ones, are the area promising alternatives to classical approaches due to their simplicity, good stability, high sensitivity, speedy procedure and low cost. Hitherto, only a few reports have been published concerning electrochemical oxidation mechanism and voltammetric determination of RES at unmodified silver¹⁵ and carbon electrodes, such as glassy carbon electrode (GCE),^{16,17} carbon paste electrode (CPE)¹⁸ and graphite.¹⁹ Furthermore, a few articles were reported using modified electrodes.^{20–22}

A boron-doped diamond (BDD) electrode is a type of sp^3 carbon material that was discovered at the end of 20th century.²³ This electrode became a popular electrode material for electro-analysis because of its commercial availability and interesting advantageous properties, such as wide potential range, low and stable background current, reduced adsorption effects and high current density.²⁴ It also exhibits excellent chemical and electrochemistry stability in aggressive media, and enables high precision measurements.^{25,26} Due to these advantages, BDD electrodes have been used as the working electrode to sense different target compounds of pharmaceutical,²⁷ environmental,²⁸ food²⁹ and biological^{30–32} interest.

Surfactants play a very important role in electro-analytical studies, *i.e.*, as solubilising organic compounds, and for providing a specific orientation of the molecules at the electrode interface, which greatly influences the electrochemical process of electro-active species.³³ Furthermore, adsorption of surfactants on electrodes might significantly change the redox potential, charge transfer coefficients and diffusion coefficients of electrode processes, thus changing the stability of electrogenerated intermediates and electrochemical products. Surfactants are often used as selective masking agents to improve selectivity and sensitivity in electrochemical analysis. Additionally, besides the electrode material, a medium containing a surfactant could prevent fouling of the electrode due to its unique molecular structure, a hydrophilic head and a hydrophobic end, properties.^{34,35} Hexadecyl trimethyl ammonium bromide (HTAB, or cetyltrimethylammonium bromide (CTAB)) is a cationic surfactant that is widely used in daily life, *e.g.*, in shampoos, hair conditioning products and cosmetics. The recent reports of ongoing research revealed that a few organic compounds, such as cap-

saicin,³⁵ benzo[*a*]pyrene³⁶ and pterostilbene,³⁷ were determined sensitively and selectively using a BDD electrode in the presence of surfactants.

In this work, a BDD electrode was evaluated in the development of a square-wave adsorptive stripping voltammetric method for RES determination in commercial dietary supplements in the presence of HTAB. The proposed procedure is characterized by simplicity, with no time-consuming sample preparation step, fast analytical response, and good precision and accuracy.

EXPERIMENTAL

Apparatus

All cyclic voltammetric (CV) and square-wave adsorptive stripping voltammetric (SW-AdSV) measurements were realized using a μ Autolab type III electrochemical system (EcoChemie, The Netherlands) and a computer-controlled potentiostat driven by the GPES 4.9 software package. All SW-AdS 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. All measurements were conducted using a three-electrode configuration in a classical 10 mL electrochemical cell. The working electrode was a boron-doped diamond (BDD) electrode (Windsor Scientific Ltd., 3.0 mm, diameter), the reference electrode an Ag/AgCl (3 M NaCl) electrode (Model RE-1, BAS), and the auxiliary electrode was a platinum wire. Prior to the experimental design stage, electrochemical background response of BDD electrode was investigated after electrochemical and mechanical pre-treatment. Electrochemical pre-treatment procedure of the BDD electrode in 0.5 M H₂SO₄ consisted of polarization at -1.5 V (cathodic) and 1.5 V (anodic) for 180 s in a separate cell. In the mechanical pre-treatment, the BDD electrode was polished manually with slurries prepared from 0.01 μ m aluminium oxide on a smooth polishing pad (BAS velvet polishing pat), then rinsed thoroughly with deionised water. The cathodic pre-treatment was found to be the most suitable, yielding with the best background signal and hence it was selected. Before each experiment, the BDD electrode was first polarized in a 0.5 M H₂SO₄ by applying -1.5 V during 180 s. Afterwards, the electrode was pre-treated for 60 s under the same experimental conditions. In this study, the first cathodic surface pre-treatment was performed daily before starting the experimental work. The other step in the procedure was applied before each voltammetric experiment. The pre-treatment procedure was performed in an independent electrochemical cell.

Chemicals

Standard *trans*-resveratrol was purchased from Sigma. Samples of RES-containing capsules were procured from Terraternal Com. Hexadecyl trimethyl ammonium bromide (HTAB), sodium dodecylsulphate (SDS) and Tween 20 were purchased from Sigma, Merck and Merck, respectively. Other used chemicals were of analytical grade, and their solutions were prepared with deionised water further purified *via* a Milli-Q unit (Millipore). Stock standard solutions of RES (1 mg mL⁻¹) were prepared in ethanol and stored in dark bottles at 4 °C, and these solutions were diluted to the desired concentration with the selected supporting electrolyte. Four different supporting electrolytes, namely, acetate buffer (0.1 M, pH 4.7), Britton–Robinson buffer (BR, 0.1 M, pH 2–9), phosphate buffer (0.1 M, pH 2.5 and 7.4) and nitric acid (HNO₃, 0.1 M) solutions were used.

Adsorptive stripping voltammetric procedure

The general procedure for stripping voltammetric analysis of RES was as follows: the required aliquot of an RES working solution was placed in a cell containing the selected supporting electrolyte in the absence or presence of HTAB. The previously treated BDD electrode was placed in the cell, and the solution was stirred at 500 rpm at a chosen accumulation potential throughout the selected accumulation period. Following the pre-concentration period, the stirring was stopped, and after 10 s had elapsed, anodic scans were performed over the range 0.0 to 1.0 V using the SWV technique. The best instrumental parameters for the SWV was used for investigating the determination of RES were as follows: frequency, 50 Hz; scan increment, 12 mV; pulse amplitude, 40 mV.

Sample preparation

Terraternal[®] capsules labelled as containing 300 mg RES was used for the present analytical applications. Other ingredients and groups listed in the drug information were water, hydroxy, propyl, methyl and cellulose. Ten capsules were opened and their contents weighed and mixed well. An adequate amount of the resulting powder was weighed and transferred into a dark 50-mL calibrated flask, which was filled to the volume with ethanol. The content of the flask was sonicated for about 15 min to complete dissolution. The desired concentrations of RES were obtained by taking suitable aliquots of the clear supernatant liquor and diluting with HNO₃ solution. An aliquot volume of these solutions was transferred to the voltammetric cell containing the same solution, and analyzed on the day of preparation according to the procedure developed for the pure electrolyte using the calibration curve method from the related regression equation.

RESULTS AND DISCUSSION

Initially, cyclic voltammograms were recorded to obtain information concerning the electrochemical behaviour of RES. The cyclic voltammograms recorded for 50 µg mL⁻¹ RES in 0.1 M HNO₃ using BDD electrode within the range 0.0 to 1.0 V at a scan rate of 100 mV s⁻¹ are presented in Fig. 1. RES was found to give one anodic peak at about 0.71 V vs. Ag/AgCl. No cathodic voltammetric peak was observed after inversion of the potential scanning, indicating that the RES oxidation is an irreversible redox process. As illustrated in Fig. 1, further potential cycles at the same BDD surface resulted in a decrease of the voltammetric response, which may be due to desorption of RES molecule from the electrode surface. This behaviour indicated the interfacial adsorptive character of the RES onto the BDD electrode surface.

To ascertain the effect of scan rate on the oxidation peak current of RES, scan rate studies were performed in the range 100–1000 mV s⁻¹ using CV in 0.1 M nitric acid solution. The oxidation peak shifted slightly towards more positive potentials as the scan rate increased. The oxidation peak current (I_p) of RES increased linearly with the scan rate in the range of 100–1000 mV s⁻¹, and can be expressed as: $I_p / \mu\text{A} = 0.001v / \text{mV s}^{-1} + 0.769$, $r = 0.994$. This suggests that the electrode reaction at the BDD electrode is controlled by the adsorption process.

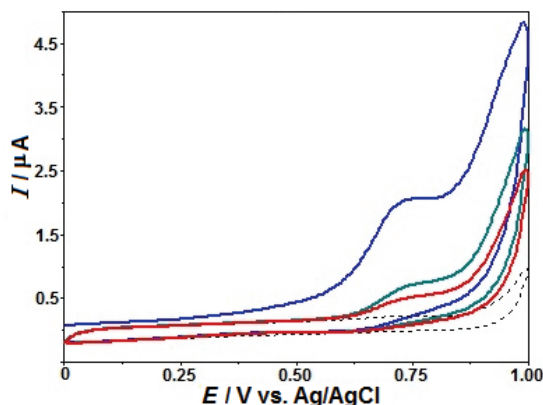


Fig. 1. Repetitive cyclic voltammetric responses of $50 \mu\text{g mL}^{-1}$ RES solutions in 0.1 M nitric acid solution for a BDD electrode. Scan rate: 100 mV s^{-1} . The dashed lines represent the background current.

Prior to the experimental design stage of a sensitive technique (SW-AdSV), the cleaning procedures of the BDD electrode are discussed. As is known, BDD electrodes without pre-treatment are not free from passivation problems, and no suitable electro-analytical responses could be obtained when RES solutions were analyzed, and thus a way to restore the initial activity of the BDD electrode surface was necessary. Three different cleaning procedures were considered. First, the electrode was treated by mechanical cleaning (polishing manually with $0.01\text{-}\mu\text{m}$ alumina slurries). The second procedure consisted of cathodic cleaning (-1.5 V for 180 s in $0.5 \text{ mol L}^{-1} \text{ H}_2\text{SO}_4$). Finally, the third procedure consisted of an anodic one (1.5 V for 180 s in $0.5 \text{ mol L}^{-1} \text{ H}_2\text{SO}_4$). The cathodic pre-treatment procedure was chosen since it yielded a much better electrode response: more intense current signal and higher reproducibility of the measurements. Furthermore, this pre-treatment was always preceded by an electrochemical cleaning procedure applying a shorter period (-1.5 V for 60 s) in between measurements in order to avoid fouling of the electrode surface because of the RES electro-oxidation reaction.

The adsorption phenomenon of RES could be used as an effective pre-concentration step prior to actual voltammetric quantification of the analyte. The AdSV response of RES at BDD electrode was examined using a SW excitation waveform, which combines high sensitivity with good peak resolution, and reduces problems with poisoning of the electrode surface. Consequently, further work was dedicated to studying the influence of pH and the nature of the supporting electrolyte using the SW-AdSV approach. The effects of various supporting electrolytes and pH values on the peak current of oxidation peak of RES were studied by SW-AdS voltammetry at a BDD electrode, with an open-circuit mode at 60 s . Thus, the buffers Britton–Robinson (pH 2.0–9.0), acetate (pH 4.7) and phosphate (pH 2.5 and 7.4), and a nitric acid solution were evaluated. All of these solutions had a concentration of 0.1 M . The influence of pH on the oxidat-

ion peak of RES in Britton–Robinson solutions of pH 2.0–9.0 is shown in Fig. 2A. It was found that the peak potential shifted negatively with increasing solution pH, indicating that the oxidation of RES at a BDD electrode is a pH-dependent reaction. The relationship between the anodic peak potential and the solution pH value (over a pH range between 2.0 and 9.0) could be fitted to the linear regression equation: E_p (V) = $-0.058\text{pH} + 0.844$, with a correlation coefficient of $r = 0.995$. The slope was found to be -58.0 mV/pH units over the pH range 2.0 to 9.0, which is very close to the theoretical value of -59 mV, demonstrating that the number of electron and proton participating in the electrode reaction is equal. The square-wave voltammograms obtained for $10 \mu\text{g mL}^{-1}$ RES in nitric acid, acetate and phosphate buffer solutions are depicted in Fig. 2B. In all voltammograms, just one well-defined oxidation peak was observed when the potential was swept from 0.1 to 1.0 V. As can be seen, RES oxidized at high potentials of 0.68 V in nitric acid and 0.65 V in phosphate (pH 2.5) buffer solutions, and a well-defined oxidation peaks and analytical signals, *i.e.*, the anodic currents density, were observed in nitric acid. In acetate (pH 4.7) and phosphate (pH 7.4) buffer solutions, the RES oxidation was observed at 0.56 V and 0.40 V, respectively, with smaller current peaks being produced than in the

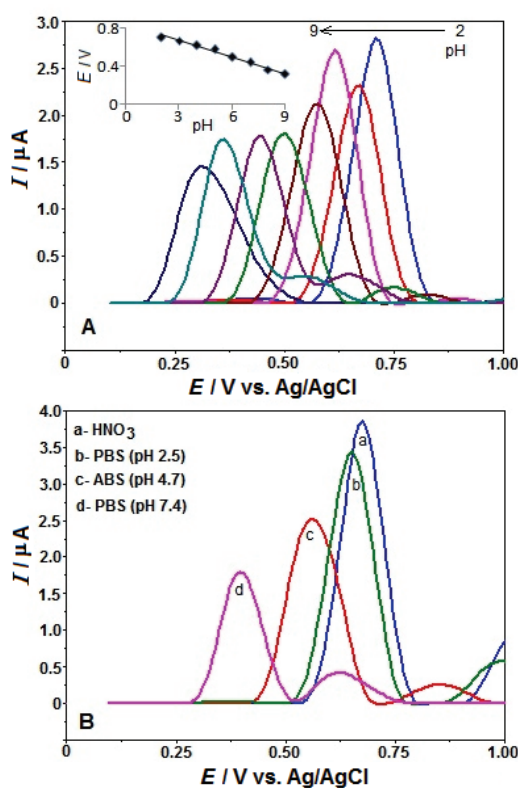
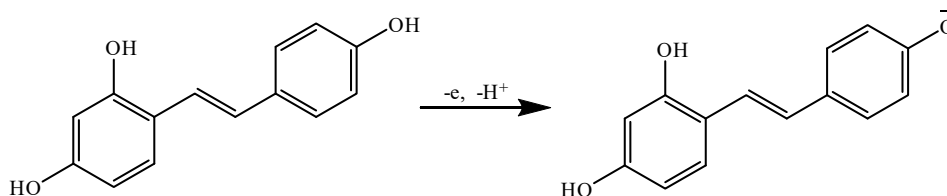


Fig. 2. SW voltammetric responses of $10 \mu\text{g mL}^{-1}$ RES solutions in Britton–Robinson buffer pH 2–9 at different pH values (A), and in various supporting electrolyte (B). Inset of (A) depicts plots of E_p vs. pH. $t_{\text{acc}} = 60$ s under open circuit conditions; SWV parameters: frequency, 50 Hz; scan increment, 8 mV and pulse amplitude, 30 mV.

nitric acid and phosphate (pH 2.5) buffer solutions. According to the obtained results, 0.1 M nitric acid solution was the most suitable medium for analytical purposes, yielding a high peak current and better peak shape, and hence, it was chosen for further experiments and development of the methodology.

RES contains an aromatic ring with a reactive hydroxyl group and has a similar chemical structure to those of flavonoids. The phenolic groups of flavonoids can be electrochemically oxidized. This phenomenon is related mainly with the hydroxyl group in phenolic part of the structure, whereas the resorcinol moiety presents lower electroactivity.¹⁶ The oxidative peak of RES detected in this experiment, corresponds to the oxidation of the 4-hydroxyl in the B ring of RES.¹⁹ The proposed mechanism for the electrochemical oxidation of RES on a BDD electrode is presented in Scheme 1.



Scheme 1. The proposed mechanism for the oxidation of RES.

In order to test the effect of the type of surfactant, including cationic (HTAB), anionic (sodium dodecylsulphate, SDS) and non-ionic (Tween 20), the electrochemical response of RES in the selected solution was also explored. A comparison of the SW-AdS voltammograms in the presence of different types of surfactants, of concentration $100 \mu\text{mol L}^{-1}$, is shown in Fig. 3A. The results showed that SDS did not affect the oxidation of RES. However, in the presence of Tween 20 or HTAB, the peak currents increased to different degrees as compared with the value obtained in their absence. Regarding the peak potentials, the surfactants induced slight shifts towards more positive values. As seen in Fig. 3A, the increases in the peak current were larger in the presence of HTAB than in the presence of Tween 20 and hence, HTAB was chosen as the most suitable surfactant for further studies. The influence of the HTAB concentration on the SW-AdSV behaviour of RES was studied within the range of 1.0 to $200 \mu\text{mol L}^{-1}$ for $10 \mu\text{g mL}^{-1}$ RES in 0.1 M nitric acid solution. It is also important to emphasize that, in the potential range considered, no HTAB oxidation process was observed. As shown in Fig 3B, the peak potential was found to be nearly constant with increasing in HTAB concentration. The inset to Fig. 3B also shows that the RES oxidation peak increased with HTAB concentration up to $100 \mu\text{mol L}^{-1}$, after which no change in the peak potential and peak current was noticed. The HTAB concentration used for further optimization studies was $100 \mu\text{mol L}^{-1}$, with this concentration providing the highest current peak and a well-defined oxid-

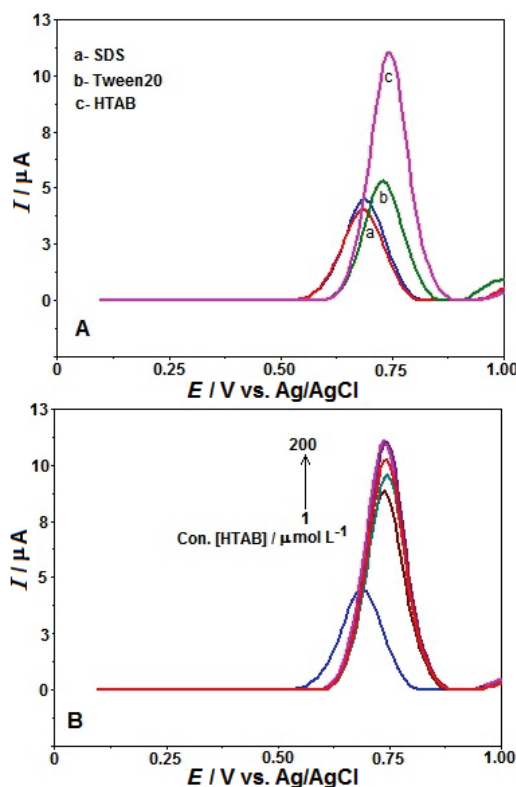


Fig. 3. SW voltammetric responses of $10 \mu\text{g mL}^{-1}$ RES in 0.1 M nitric acid solution at BDD electrode in the presence of the surfactants (A), and in the presence of different concentration of HTAB (B). Blue lines represent the voltammogram without the surfactants. Other operating conditions as indicated in Fig. 2.

ation peak at 0.75 V. On the other hand, BDD electrode in presence of $100 \mu\text{mol L}^{-1}$ HTAB as modifying solution showed a sharp and the best-defined oxidation peak, with current intensities that were almost 2.46 times higher than those obtained in the free solution. Considering the pK_a values of RES ($pK_{a1} = 9.3$, $pK_{a2} = 10.0$, $pK_{a3} = 10.6$), the compound exists in the neutral form (with a relatively high hydrophobic character) under strong acidic conditions (in 0.1 M HNO_3). Bearing all the above knowledge and experimental findings in mind, the enhancing effect of HTAB on the voltammetric response of RES could be explained by their co-adsorption on the BDD surface. Consequently, HTAB would make the electron exchange easily between the RES and the CPT-BDD electrode, and thus enhance the oxidation peak current.

As the electrode reaction is controlled by the adsorption of RES, it is important to investigate the effects of a pre-concentration period, such as accumulation time (t_{acc}) and accumulation potential (E_{acc}). Keeping the accumulation potential at open-circuit condition at a concentration of $2.5 \mu\text{g mL}^{-1}$ in 0.1 M nitric acid containing $100 \mu\text{mol L}^{-1}$ HTAB solution, the oxidation peak current of RES gradually increased with increasing accumulation time from 0 to 60 s, and reached the maximum peak current response at 60 s. With further increasing

of the accumulation time (60–360 s), there was only a slight increase in the current response. Therefore, an accumulation time of 60 s was used for each voltammetric measurement of RES. Keeping the accumulation time as 60 s at a concentration of $2.5 \mu\text{g mL}^{-1}$, the accumulation potential was investigated in either open-circuit condition or over the potential range from 0.1 to 0.7 V. The results proved that varying the accumulation potential provoked changes in the RES oxidation current. The peak current reached its maximum at an accumulation potential of 0.1 to 0.3 V and under open-circuit condition. Herein, open-circuit potential was chosen as the optimum accumulation potential since the best baseline was obtained.

Further work was dedicated towards studying the effect of the SW parameters. Thus, the frequency (f), pulse amplitude (a) and scan increment (ΔE_s) for $2.5 \mu\text{g mL}^{-1}$ RES were evaluated under the optimum experimental conditions. When f was changed from 25 to 125 Hz ($\Delta E_s = 8 \text{ mV}$, $a = 30 \text{ mV}$), the peak current increased linearly. However, the background current and noise also increased at f values higher than 50 Hz. Thus, $f = 50 \text{ Hz}$ was selected for all subsequent experiments. The influence of a was studied in the range from 20 to 60 mV (for $\Delta E_s = 8 \text{ mV}$, $f = 50 \text{ Hz}$). The peak current of RES rapidly increased until $a = 60 \text{ mV}$. However, the best peak morphology and a sharper peak were obtained at 40 mV, since the peak became wider and deformed at higher values of a . Hence, $a = 40 \text{ mV}$ was chosen for all the subsequent experiments. When ΔE_s was changed from 6 to 14 mV, and the remaining parameters were constant ($f = 50 \text{ Hz}$, $a = 40 \text{ mV}$), the recorded signal increased until the value of 12 mV, followed by a slower increase from 12 to 14 mV. In addition, at values higher than 12 mV resulted in a broadening in the voltammograms. A ΔE_s value of 12 mV was chosen for the further experiments.

Calibration was performed on the BDD electrode for the determination of RES using the following suitable conditions: accumulation at open-circuit condition; $t_{\text{acc}}=60 \text{ s}$, $f = 50 \text{ Hz}$, $a = 40 \text{ mV}$ and $\Delta E_s= 12 \text{ mV}$ in 0.1 M nitric acid containing $100 \mu\text{mol L}^{-1}$ HTAB solution. BDD electrode exhibited a good linear response to RES over two linear ranges, one from 0.025 to $2.0 \mu\text{g mL}^{-1}$ (1×10^{-7} – $8.8 \times 10^{-6} \text{ mol L}^{-1}$), and a second linear range from 2.5 to $60 \mu\text{g mL}^{-1}$ (1×10^{-5} – $2.6 \times 10^{-4} \text{ mol L}^{-1}$), Fig. 4. The linear regression equations were, respectively:

$$I_p / \mu\text{A} = 1.118(c / \mu\text{g mL}^{-1}) + 0.182 \quad (r = 0.993, n = 8)$$

and

$$I_p / \mu\text{A} = 0.289(c / \mu\text{g mL}^{-1}) + 2.729 \quad (r = 0.994, n = 10)$$

The concentration of RES could be established in the range of 0.025 – $60 \mu\text{g mL}^{-1}$ (1×10^{-7} – $2.6 \times 10^{-4} \text{ mol L}^{-1}$), the linear regression equation was:

$$I_p / \mu\text{A} = 0.327(c / \mu\text{g mL}^{-1}) + 1.261 \quad (r = 0.988, n = 18)$$

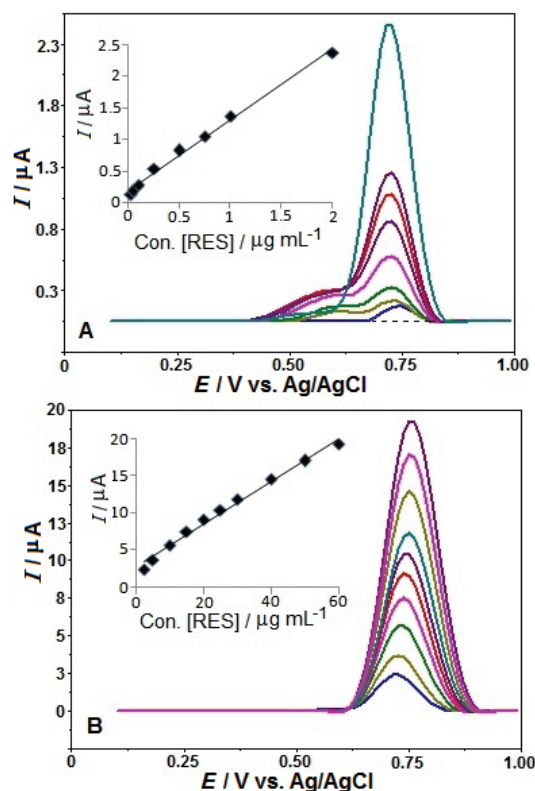


Fig. 4. SW voltammetric responses at a BDD electrode in 0.1 M nitric acid solution with $100 \mu\text{mol L}^{-1}$ HTAB containing different concentration of RES from 0.025 to $2.0 \mu\text{g mL}^{-1}$ (A) and from 2.5 to $60 \mu\text{g mL}^{-1}$ (B). The insets depict the corresponding calibration plot for the quantification of RES. $t_{\text{acc}} = 60$ s under open-circuit condition; SWV parameters: frequency, 50 Hz; scan increment, 12 mV; pulse amplitude, 40 mV.

From the data obtained from the analytical curves (0.025 – $60 \mu\text{g mL}^{-1}$), the detection (LOD) and quantification (LOQ) limits were calculated using the formulas $3s/m$ and $10s/m$, respectively, where s is the standard deviation of the response (blank) (five runs), and m is the slope of the calibration plot. The LOD and LOQ were estimated to be $0.0063 \mu\text{g mL}^{-1}$ ($2.7610^{-8} \text{ mol L}^{-1}$), and $0.021 \mu\text{g mL}^{-1}$ ($9.19 \times 10^{-8} \text{ mol L}^{-1}$), respectively. A comparison of the analytical performance of methods for the determination of RES between the results presented in this work and similar data obtained using other electrode surfaces previously reported in literature is presented in Table I. The BDD electrode exhibited a more sensitive electrochemical response for the oxidation of RES than the others, except for the silver,¹⁵ glassy carbon,¹⁷ carbon paste¹⁸ and graphite¹⁹ electrodes, the sensitivities of which were a few times higher than that of the BDD electrode. Based on the above, some advantage of the present methodology could be seen, such as a wide linear range, good analytical sensitivity and simplicity, which enables its use without a time-consuming procedure for cleaning of the electrode surface.

To estimate the repeatability of the proposed method, the BDD electrode has been evaluated by repetitive determinations of at a concentration level of $2.5 \mu\text{g}$

mL^{-1} for RES. The results of eight replicate measurements showed a relative standard deviation (*RSD*) of 2.39 %, indicating that the results are repeatable. Furthermore, inter-day repeatability was examined by measuring the current response of the BDD electrode on five consecutive days for the same concentration of RES and the *RSD* was found to be 6.35 %. The experimental results indicated that the BDD electrode possessed good sensitivity and repeatability for determination of RES.

TABLE I. Comparison of the efficiency of different electrodes used in the determination of RES

Electrode	Linear range, mol L ⁻¹	LOD / mol L ⁻¹	Reference
Silver	2×10^{-9} – 1×10^{-8}	4×10^{-10}	15
Glassy carbon	3.93×10^{-9} – 9.03×10^{-3}	1.78×10^{-7}	16
Glassy carbon	2.19×10^{-8} – 1.53×10^{-7}	1.84×10^{-8}	17
Carbon paste	5×10^{-9} – 1.65×10^{-7}	2×10^{-9}	18
Graphite	8×10^{-9} – 2×10^{-6}	4×10^{-9}	19
Modified-indium tin oxide	2×10^{-6} – 2×10^{-5}	8×10^{-7}	20
Modified-multi-walled carbon nanotube	5×10^{-7} – 8×10^{-5}	5.1×10^{-8}	21
Modified-carbon paste	1.31×10^{-7} – 4.38×10^{-6}	5.26×10^{-8}	22
BDD	1×10^{-7} – 2.6×10^{-4}	2.76×10^{-8}	This work

Voltammetric responses of BDD electrode to RES were investigated in the presence of some possible interfering inorganic ions and organic compounds. The tolerance limit was defined as the maximum concentration of potential interfering substance that causes a relative error of less than ± 5 % for determination of $2.5 \mu\text{g mL}^{-1}$ RES. The interference of some metal ions was examined. At about 50-fold excess, K^+ , Na^+ , Mg^{2+} , Ca^{2+} , Cu^{2+} , Zn^{2+} and Fe^{3+} did not significantly influence the height of the peak currents at the BDD electrode under the selected experiment conditions. The effects of different organic compounds were also examined and no substantial change was observed for $2.5 \mu\text{g mL}^{-1}$ RES in the presence of about a 10-fold excess of salicylic acid, glucose, fructose, and sucrose. However, the voltammetric peak potentials of pterostilbene overlapped with that of RES at the BDD electrode even when an analyte–interferent ratio of 1:1 was used. Therefore, when pterostilbene is present, a separation procedure is required before the determination of RES.

The applicability of the BDD electrode for the SW-AdSV determination of RES was verified by analysis of RES-containing dietary supplement samples (Terraternal[®] capsules, declared content of RES 300 mg per capsule). The analyzed solutions were prepared as described in the sample preparation section, after simple dissolution of the samples in selected medium and dilution of the resulting solution to a target concentration within the second linear range, since the *r* value was better for this range than that for the first range. Quantification for the sample was performed by means of the calibration curve method from the

related regression equation. A mean value of $29.68 \mu\text{g mL}^{-1}$ of RES was found in the measurement cell. Taking into account the successive dilutions of the sample, the RES content was calculated to be 296.8 ± 3.23 mg per capsule, which approximates the label value of 300 mg per capsule declared by the producer. In order to determine whether common excipients and filling materials present in the analyzed capsules interfered with the analysis, recovery experiments were performed by adding standard RES solutions ($5, 20$ and $40 \mu\text{g mL}^{-1}$) prepared in supporting electrolyte to 10 mL of sample solution and the SW-AdS voltammetric responses were evaluated. Recovery of RES was calculated by comparing the concentration obtained from the spiked mixtures with those of the pure RES. The recovery value was in the range from 93.1 to 97.4 %, indicating the absence of a matrix interference effect. It was found that RES amount could be quantitatively recovered by the proposed method, being thus a guarantee of the accuracy and feasibility of the voltammetric determination of RES in commercial dietary supplements.

CONCLUSIONS

A cathodically pre-treated BDD electrode was used in combination with the SW-AdSV technique to develop a novel and alternative electro-analytical method for RES determination. The results indicated that the electrochemical response of RES could be facilitated by the cationic surfactant HTAB. Taking advantage of the significant surfactant effect on the electrochemical response of RES, a BDD electrode combined with highly sensitive and accurate SW-AdSV could enable an attractive trace analysis of RES. The proposed approach is simple, fast, sensitive, precise, and accurate, being applicable directly to the analysis of samples of the commercial dietary supplements after a simple preparation of samples and without suffering from interference of other ingredients.

ИЗВОД

ЕЛЕКТРОХЕМИЈСКО ОДРЕЂИВАЊЕ РЕЗВЕРАТРОЛА У ДИЈЕТИЧКИМ СУПЛЕМЕНТИМА НА БОРОМ ДОПИРАНОЈ ДИЈАМАНТСКОЈ ЕЛЕКТРОДИ У ПРИСУСТВУ ХЕКСАДЕЦИЛТРИМЕТИЛАМОНИЈУМ-БРОМИДА ПРИМЕНОМ АДСОРПЦИОНЕ СТРИПИНГ ВОЛТАМЕТРИЈЕ СА ЧЕТВРТАСТИМ ПУЛСЕВИМА

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У овом раду је приказана осетљива електроаналитичка метода за одређивање резвератрола, први пут применом адсорпционе стрипинг волтаметрије на бором допираној дијамантској електроди (BDD). У цикличној волтаметрији, резвератрол показује један иререверзибилан, адсорпционо контролисан оксидациони пик на BDD електроди. Резултати волтаметрије индицирају да присуство хексадецил-триметиламонијум-бромида значајно поспешује оксидацију резвератрола на BDD електроди, и доводи до повећања струје пика и померања потенцијала пика ка позитивнијим вредностима. Применом адсорпционе стрипинг волтаметрије са четвртастим пулсевима таласима у режиму обогаћивања и растварања добија се добро дефинисан волтаметријски одговор у раствору

0,1 M азотне киселине који садржи $100 \mu\text{mol L}^{-1}$ хексадецилтриметиламонијум-бромида на потенцијалу од 0,74 V (у односу на Ag/AgCl), после 60 s акумулације у условима отвореног струјног кола). Добијена је линеарна калибрациона крива у концентрационом опсегу $0,025\text{--}60,0 \mu\text{g mL}^{-1}$, са границом детекције од $0,0063 \mu\text{g mL}^{-1}$. Применљивост предложене методе је потврђена анализом резвератрола у комерцијалним дијететским суплементима.

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