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Electrochemical oxidation of phenanthrenequinone dioxime and its quantification using sensing at boron doped diamond electrode

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ABSTRACT

Nowadays, there is small number of analytical procedures for the quantification of the phenanthrene and its derivatives, quinones and quinonedioximes. In recent years, different studies shows that potential application of these compounds and their complexes possess important role in many search areas, medicine, catalysis, sensors and bioorganic systems. In this paper, for the first time, we offer fast, sensitive, selective and reliable electroanalytical procedure for quantification of phenanthrenequinone dioxime (PQD) based on its oxidation. Also, its electrochemical behavior in water acidic media is given. Possible electrode mechanism based on these measurements was proposed. It was found that by employing differential pulse voltammetry (DPV) in Britton–Robinson buffer solution (BRBS) at pH 3.0 using boron-doped diamond (BDD) electrode calibration curve for PQD quantification was linear in the range of 0.3 to 7.0 μM with detection limit of 0.22 μM. Proposed method was successfully applied for the determination of PQD in blood samples with satisfactory recovery (96–102%). Proposed method can be beneficial in the chemistry of dioximes due to advantages of BDD electrode and sensitivity and selectivity of the electroanalytical procedures.

1. Introduction

Today, worldwide, breast cancer causes death around 400,000 women every year [1]. Up to date, it presents the most common female cancer. In the literature are lots of synthetic or natural compounds which possess cytotoxic properties which are approved for the clinical treatment of the cancer cells. Quinones and its derivatives could be considered as second largest group of molecules which shows this behavior [2–4]. Breaking of DNA strands and their inhibition together with alterations of cell membrane function could be possible mechanism of their anticancer activities and cytotoxic properties [5,6]. Different group of the researchers have reported that naturally isolated phenanthrene, phenanthrenequinone and its synthesized metal complexes, due to its planar structure, shows antimicrobial, anti HIV, anti-inflammatory and potential anticancer effects [7–12]. Different studies reported that possible mechanism of the action, which could explain activities of this group of molecules and its complexes, could be attributed to the production of reactive oxygen species (ROS) [13–15].

The chemistry of cobaloximes and its chemical and electrochemical behavior, dominantly due to easy transaction between different states, together with (Co(III) – Co(II) – Co(I)) conversation could play important role in the chemistry of the vitamin B_{12} and may represent potential use of this complex for the clarification of the mechanism that controls activity of this vitamin and has been extensively investigated in the recent years [16–19].

These compounds play important role in the treatment of soman poisoning and they are known to be acetylcholinesterase reactivators. However, although these compound demonstrate the wide range of applications there is small number of methods, reported in the literature, dealing with its determination, primarily based on their action on the reaction of Au(III) with potassium iodide [20–22].

Our research group extensively using the advantages of a boron-doped diamond electrode, up to date one of the best electrode materials, which lies in its low and stable background current, extreme electrochemical stability in alkaline and acidic media, excellent long-term response stability and high response sensitivity, for the application in development of electroanalytical procedure for the quantification of the various biologically active compounds important in the area of environment, food and drug analysis [23–28].

The aim of this study was to show electrochemical behavior of phenanthrenequinone dioxime in acidic water media. For that purpose cyclic voltammetry was used at BDD electrode. The proposed electrochemical oxidation mechanism is given. Differential pulse voltammetry, after optimization of the experimental parameters, was employed for the quantification of PQD. Effect of possible interferences was evaluated. The proposed analytical procedure was successfully applied for the determination of PQD in human blood samples.

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2. Experimental

2.1. Apparatus and reagents

All reagents used in this study were of analytical grade. Phenanthrenequinone dioxime, glucose, boric acid, sodium hydroxide, ascorbic acid, uric acid, dopamine, acetic acid and phosphoric acid were purchased from Sigma Aldrich. Standard solution of PQD was prepared in ethanol at the concentration value of 1.0×10^{-4} M. Britton–Robinson buffer solution was used as supporting electrolyte and it was prepared by mixing 0.04 M of the boric acid, phosphoric acid and acetic acid. The pH values of BRBS were adjusted with sodium hydroxide (0.2 M). Calibration solutions were prepared by appropriate dilution of the stock solution with supporting electrolyte.

The voltammetric measurements were performed using a potentiostat/galvanostat (AUTOLAB PGSTAT 302 N, Metrohm Autolab B.V., The Netherlands) controlled by the corresponding electrochemical software (NOVA 1.9). The electrochemical cell (total volume 10 mL) was equipped with a boron-doped diamond electrode (Windsor Scientific Ltd., Slough, Berkshire, United Kingdom) as a working electrode, an Ag/AgCl (saturated KCl) as a reference electrode and a Pt wire as a counter electrode. At the beginning of working day prior to starting the first measurement, the BDD electrode was rinsed with deionized water and gently rubbed with a piece of damp silk cloth until a mirror-like appearance of surface was obtained (with minimal probability of mechanical damage of surface). Subsequently, it was anodically pretreated by setting +2 V during 180 s in 1 M H_2SO_4 in order to clean the electrode surface (get rid of any impurities) followed by cathodic pretreatment at −2 V during 180 s to renew the hydrogen terminated surface of the working electrode [24–26]. After every measurements electrode was slightly polished with piece of cotton. In order to confirm stability and advantages of the BDD electrode before starting measurements and at the end of working day, potential/current changes in the $K_4[Fe(CN)_6]/K_3[Fe(CN)_6]$ couple was monitored. It was observed that during the day these changes are lower than 5%. All potentials reported in this paper are referred versus the above mentioned reference electrode. All measurements were done at an ambient temperature. All pH values were measured with a pH meter model Orion 1230 equipped with combined glass electrode model Orion 9165BNWP (USA). The used BDD electrode were embedded in a polyether ether ketone (PEEK) body with an inner diameter of 3 mm, a resistivity of 0.075 Ω cm and a boron doping level of 1000 ppm. These characteristics are declared by the supplier.

2.2. Analytical procedure

Electrochemical behavior of PQD on BDD electrode was evaluated by cyclic voltammetry at the scan rate of 50 mV s^{-1} (if not stated otherwise). pH of supporting electrolyte was selected from these measurements. In order to provide highest analytical signal we optimized DPV parameters, such as pulse amplitude and pulse time. For these measurements potential was swept from 0 to 1.3 V. After optimization of parameters, with the best experimental conditions (pulse time 10 ms and pulse amplitude 40 mV) the calibration curve was obtained from the addition of known amounts of stock solution of PQD in the electrochemical cell containing supporting electrolyte. Corresponding equation, limit of detection (LOD) and linear range were determined from these measurements. The LOD was calculated using the expression:

$$\mathrm{LOD} = \left(3 \times \sigma_{(\mathrm{blank})} - \mathrm{intercept}\right)/\mathrm{slope}.$$

The selectivity of the proposed method was evaluated from measurements of main containing compounds presented in investigated matrices in the presence and absence of PQD.

The applicability of the proposed procedure was tested for the quantification of PQD in human blood samples. The samples were prepared as it is mentioned below. Adequate aliquots of each sample solution were added in electrochemical cell (10.0 ml) and diluted with supporting electrolyte. In order to provide recovery of analyte and matrix effects standard addition method was used. All concentrations were determined in triplicate using calibration curve previously obtained under the optimum experimental conditions.

2.3. Preparation of blood samples

Blood samples were obtained from two apparently healthy, non-smoking male volunteers, and stored frozen until the analysis process. Samples were prepared by slightly modifying previously described procedure [29]. First, blood was centrifuged for 30 min at 15,000 rpm to get serum sample. 0.8 mL of acetonitrile was added to a 1.0 mL blood sample to remove serum protein. After vortexing for 45 s, the mixture was centrifuged for 10 min at 15,000 rpm to remove the serum protein residues. Supernatant was taken carefully and 1.0 mL of this supernatant was transferred into a 10.0 mL flask and diluted up to the volume with the BRBS (pH 3.0).

3. Results and discussions

3.1. Electrochemical behavior of PQD

Evaluation of electrochemical behavior of the PQD and optimization of pH of the Britton–Robinson buffer solution was performed by employing cyclic voltammetry. Concentration of the PQD of 2.0×10^{-5} M was used. The cyclic voltammogram obtained for the BDD electrode in the presence of mentioned concentration of the PQD in BRBS at pH 3.0, is presented in Fig. 1. Also, the corresponding CV for the measurement of the supporting electrolyte is presented in Fig. 1 (dash line). As can be seen from these measurements, the oxidation process of the PQD under these conditions occurs as two processes. First process was obtained at around +0.70 V and second at around +0.95 V. The oxidation of PQD was more pronounced at pH 3.0, and analytical signal decreased gradually with further increasing of the pH. Thus the BRBS solution at pH 3.0 was selected for the development electroanalytical procedure, once the best peak shape and highest oxidation peak current were obtained. In the reverse scan after the inversion of the potential scanning, no corresponding reduction processes were observed. It could be

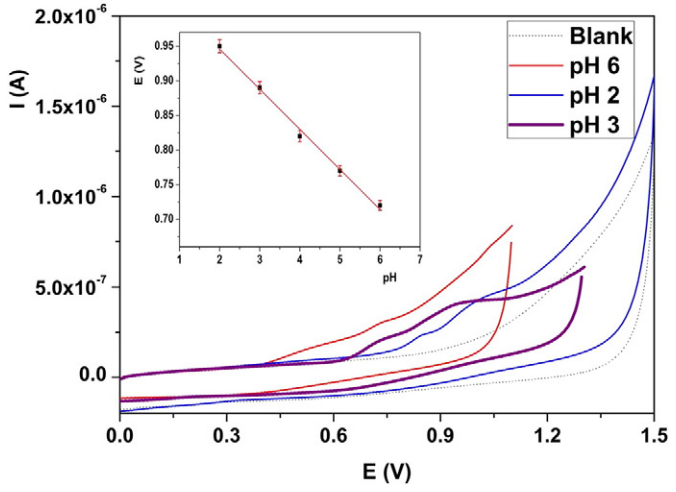

Fig. 1. Cyclic voltammograms obtained in absence (dotted line) and presence of the 2.0×10^{-5} M PQD in BRBS at pH 2.0 (blue line), pH 3.0 (purple line) and pH 6.0 (red line) using BDD electrode. Inset curve present of peak potential of the second oxidation wave of the PWD vs. pH of supporting electrolyte.