

ELECTROCHEMICAL BEHAVIOR OF QUERCETIN ON BORON-DOPED DIAMOND ELECTRODE IN DIFFERENT SUPPORTING ELECTROLYTES**Ana Đurović^{*1}, Zorica Stojanović¹, Snežana Kravić¹, Zvonimir Suturović¹, Lukas Richtera^{2,3}, Tanja Brezo-Borjan¹**

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Abstract

Quercetin is one of the most abundant flavonoid compounds with a broad spectrum of health beneficial properties. In this study electrochemical behavior of quercetin on boron-doped diamond electrode as a working electrode was investigated in different supporting electrolytes. Experiments embraced 0.1 mol/L acetate buffer, citrate buffer, phosphate buffer, 0.04 mol/L Britton-Robinson buffer and 0.05 mol/L solution of HCl, while studied quercetin concentration were in the range from 2 mg/L to 30 mg/L. Voltammograms recorded in different supporting electrolytes revealed one sharp and well-defined oxidation peak of quercetin at the potential of about +0.70 V, and it was chosen for quantification of quercetin, although in some buffers one additional protracted peak was observed. In comparison to differential pulse voltammetry, square-wave voltammetry showed higher sensitivity, so this technique could be more suitable for further development. Even though high values of correlation coefficients (> 0.9900) were obtained for all studied supporting electrolytes, the best results in terms of sensitivity were observed for citrate and Britton-Robinson buffers. These preliminary results demonstrated that boron-doped diamond electrode can be used as a sensitive sensor for precise determination of quercetin in real samples.

Introduction

Polyphenols are naturally occurring compounds produced as plant secondary metabolites that serve as protecting agents from pathogens and UV radiation. Several classes of polyphenols can be found in nature, and flavonoids represent one of the major groups of these substances widely present in many fruit and vegetables species. Quercetin (3,3',4',5,7-pentahydroxyflavone) is one of the most abundant flavonoid compound. A broad spectrum of health beneficial properties are associated with quercetin consumption including: antioxidant, anti-inflammatory, and antimicrobial activity, while it can be used as a protecting agent against cancer, pulmonary, cardiovascular diseases and neurodegenerative disorders as well [1].

Owing to its favorable health effects on human health, quercetin is not used only from its naturally sources, but also as a nutritional food ingredient and dietary supplement. Therefore, development of simple and sensitive analytical methods that can be used for its accurate determination in different matrixes is attracting great attention. A variety of methods for determination of quercetin have been reported including high pressure liquid chromatography (HPLC) [2, 3], gas chromatography (GC) [4, 5], spectrophotometry [6, 7] and capillary electrophoresis [8]. However, most of these methods are lengthy, complicated and require expensive instrumentation and skilled analysts. Due to numerous advantages that are providing electroanalytical methods, such as easy instrumental manipulation, low operating

costs, short analysis time, they can be used as an alternative techniques for quercetin determination. Voltammetric determination of quercetin was performed using different electrode materials: glassy carbon electrode (GCE) [9, 10], platinum electrode [11], but also the use of different modified electrode materials in order to increase sensitivity and selectivity was evident lately [12-14].

Boron-doped diamond is an electrode material with excellent properties including: wide potential window, low background current, exceptional inertness and stability that distinguish it from other electrode materials, and it has been proven as a versatile electrode material for the detection of the numerous analytes with low detection limit, excellent precision and stability [15, 16]. Only few reports describe the electroanalytical analysis of quercetin using boron-doped diamond electrode (BDDE). Permpool et al. [17] characterized the oxidation of quercetin using BDDE by cyclic voltammetry, and compared it to GCE. In the study published by Abdullah et al. [18] square-wave stripping voltammetric method with the presence of cationic surfactant cetyltrimethylammonium bromide in the electrolyte was developed for determination of quercetin in apple juice.

In this study we compared electrochemical behavior of quercetin in different electrolytes on bare BDDE. Cyclic voltammetry (CV), square-wave voltammetry (SWV) and differential pulse voltammetry (DPV) were used as voltammetric techniques. The best performance in terms of linearity, sensitivity, sharpness of oxidation peak was achieved in citrate and Britton-Robinson buffer. These preliminary results are promising and can be used for developing a sensitive voltammetric method for determination of quercetin in real samples.

Experimental

Chemicals

Standard stock solution of quercetin (1 g/L) was prepared by dissolution of the proper mass of standard (Sigma-Aldrich) in the ethanol, and stored in the dark at 4°C. The solutions of lower concentrations were prepared by dilution with the supporting electrolyte. 0.1 mol/L citrate buffer, 0.1 mol/L acetate buffer, 0.1 mol/L phosphate buffer, 0.04 mol/L Britton-Robinson (BR) buffer and 0.05 mol/L HCl were used as the supporting electrolytes. Doubly distilled water was used throughout the experiments.

Instrumentation

For voltammetric measurements PalmSens 4 potentiostat (GA Houten, Netherlands) connected to a personal computer using the PStTrace 5.4 software and standard three-electrode system were used. A three-electrode system consisted of BDDE diameter 3 mm (Windsor Scientific, Slough, UK), as a working electrode, platinum wire as a counter electrode, and an Ag/AgCl (3.5 mol/L KCl) as a reference electrode.

Voltammetric procedures

A 15.0 mL of the supporting electrolyte was added to the process glass. Before the analysis the working electrode was firstly wiped off with filter paper soaked with acetone, doubly distilled water, and then electrodes were rinsed with doubly distilled water and dried. Voltammograms were recorded in the presence of dissolved oxygen in quiescent solution in the anodic potential range from 0 V to +1.4 V. Cyclic voltammograms were recorded using potential step of 0.05 V and scan rate 0.3 V/s. Square-wave voltammograms were recorded after 10 s of equilibrium time using step potential of 0.01 V, amplitude 0.075 V and frequency of 25 Hz. Equilibrium time of 5 s, step potential 0.05 V, pulse potential 0.1 V, pulse time 0.05 s and scan rate of 0.06 V/s were used for performing DPV.

Results and discussion

In order to develop a sensitive and precise method for voltammetric determination of quercetin, the primary step is the choice of the optimal supporting electrolyte. Apart from having a great influence on the height of the analytical signal, the composition of the supporting electrolyte also affects the electrochemical processes conducting at the working electrode. Therefore, this study was based on the choice of the optimal supporting electrolyte for voltammetric determination of quercetin. According to the studies performed by other authors for voltammetric determination of quercetin by using BDDE as a working electrode, acetate buffer and phosphate buffer were used as the optimal supporting electrolytes [17, 18]. In this study 0.1 mol/L acetate buffer, citrate buffer, phosphate buffer, 0.04 mol/L BR buffer and the 0.05 mol/L solution of HCl were tested as the supporting electrolytes. To study electrochemical behavior of analyte, different voltammetric techniques were applied including CV, SWV and DPV and after recording voltammograms for blank, measurements were done in the presence of quercetin (2-30 mg/L).

Cyclic voltammograms of quercetin in different supporting electrolytes showed one oxidation peak in the potential range from +0.65 V in 0.1 mol/L phosphate buffer pH 7 to +0.80 V in 0.1 mol/L acetate buffer pH 4, with no reduction peaks in reversed scan.

SWV performed in tested electrolytes showed one well-defined oxidation peak in the potential range at similar values as obtained by CV (+0.59V - +0.73 V), while second protracted oxidation peak (+1.23 V) was observed only in 0.05 mol/L HCl.

Similar behavior of quercetin was observed by applying DPV, with one well-defined oxidation peak (+0.55 - +0.65 V), and one protracted oxidation peak (+1.05 - +1.15 V), whereas in phosphate buffer only the first oxidation peak was notable. Considering that the shape and intensity of the first peak were much better for all studied electrolytes, this peak would be more suitable for quantification of quercetin.

Linear relationships between the current for first oxidation peak and studied concentration range in tested electrolytes for SWV and DPV measurements are showed on Figure 1. Good linearity was obtained for all studied electrolytes with both SWV and DPV techniques with correlation coefficients higher than 0.9900. From Fig.1 it is evident that the values for analytical signal were much higher by applying SWV than DPV, therefore this technique was recommended as more suitable for quantification of quercetin in real samples. Obtained slopes and intercepts for calibration curves indicated the highest sensitivity by using citrate and BR buffers.

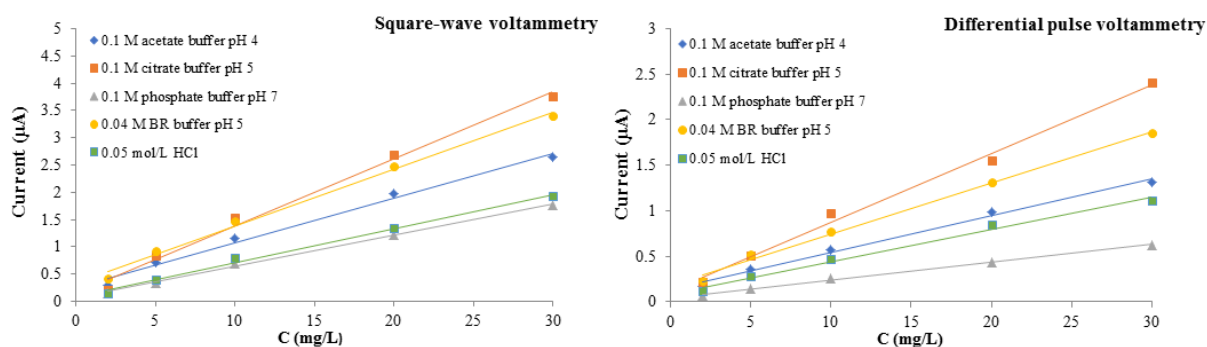


Figure 1. Plots between peak current vs. concentration of quercetin obtained using SWV and DPV.

Conclusion

In this study preliminary results for voltammetric determination of quercetin by using boron-doped diamond electrode as a working electrode were presented. Voltammetric behavior of quercetin was investigated by CV, SWV and DPV in different supporting electrolytes. For

developing a voltammetric method a well-defined oxidation peak at the potential of about +0.70 V was selected. The analytical signal of SWV was much higher than for DPV, therefore this technique would be more suitable for further optimization and validation of analytical method for quercetin determination in real samples. Although good linearity was obtained for all studied supporting electrolytes, the best sensitivity was expected to obtain for citrate and Britton-Robinson buffers. Based on these preliminary results, further experiments will be focused on the optimization of pH value and concentration of the buffer, as well on optimization of the instrumental parameters of the SWV.

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