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APPLICATION OF THE MODIFIED CARBON PASTE ELECTRODES FOR DETERMINATION OF CATECHIN

Stojanović, Z.¹, Đurović, A.¹, Kravić, S.¹, Suturović, Z.¹, Brezo, T.¹, Richtera, L.^{2,3},
Bytešniková, Z.^{2,3}, Grahovac, N.⁴

¹University of Novi Sad, Faculty of Technology, Department of Applied and Engineering Chemistry, Novi Sad, Serbia

²Mendel University in Brno, Department of Chemistry and Biochemistry, Brno, Czech Republic

³Brno University of Technology, Central European Institute of Technology, Brno, Czech Republic

⁴Institute for Field and Vegetable Crops, Department for industrial plants, Novi Sad, Serbia

Abstract

Catechin is a flavonoid compound with polyphenolic structure naturally occurring in plants, fruits, tea, red wine and cacao products. Many beneficial effects are associated with catechin consumption such as antioxidant, anticarcinogenic, anti-inflammatory, antiatherogenic, antibacterial and antiviral activity. Determination of catechin is typically based on the use of high-performance liquid chromatography, but also methods such as spectrophotometry and capillary electrophoresis are reported.

In this work we investigated the use of different modifications of a carbon paste electrode (CPE) for voltammetric determination of catechin. The reason for introducing a modifier into the carbon paste was to increase the sensitivity of the voltammetric techniques, due to the catalytic effect of the modifier on the electrode processes. Multi-walled carbon nanotubes (MWCNTs), antimony(III) oxide and bismuth nanoparticles are investigated as bulk modifiers for preparation of CPE with concentration of 5% (w/w). Electroanalytical measurements are performed in 0.1 M phosphate buffer pH 7.0 using cyclic voltammetry and square wave voltammetry, in the concentration range from 1 to 20 mg/dm³ of catechin.

Two oxidation peaks of catechin are observed for all studied modified CPEs and bare CPE, with significantly higher intensity of the first peak. The results also showed improvement of sensitivity by using the modified CPEs in comparison to unmodified CPE. The application of MWCNTs as a modifier contributed to the highest sensitivity for catechin determination in relation to the other modifiers. These preliminary results show that MWCNTs modified CPE can be used as a very sensitive sensor for catechin determination in real samples.

Key Words: catechin; carbon paste electrode; modification; voltammetry.

Introduction

In recent years, polyphenols have been attracting great attention due to their antioxidant properties and probable role in the prevention of various diseases associated with oxidative stress, such as cancer, cardiovascular and neurodegenerative diseases. Catechin is a flavonoid which belongs to naturally polyphenolic compounds and is ubiquitous constituent of various fruits, vegetables, teas and wines. Consumption of food rich in catechin has many beneficial effects on human health such as strong antioxidant, anti-carcinogen, anti-inflammatory, anti-mutagenic, anti-microbial effects (Yao et al., 2015).

In terms of human health, determination of catechin in different plants has attracted increasing interest. High-performance liquid chromatography (HPLC) is one of the most frequently used technique for determination not only catechin but also other flavonoids together (Li et al., 2012). However, even reported HPLC methods are very precise and accurate, their implementation requires expensive equipment and the procedures may be tedious and time-consuming. In recent years, the identification and characterisation of catechin by electrochemical methods have drawn attention due to many advantages over conventional methods (Masek et al., 2015). Electrochemical methods are relatively simple, very accurate, and sensitive, and they are low-cost and require only a short analysis time.

In this work, bare carbon paste electrode (CPE) and different modified CPE were compared for electrochemical determination of catechin. Introduction of modifiers were done in order to improve sensitivity of voltammetric response of the prepared sensor. Obtained results demonstrated enhanced detection by using modified CPEs in comparison to bare CPE.

Materials and methods

Chemicals

Catechin ((+)-catechin, $\geq 98\%$ purity), multi-walled carbon nanotubes (thin, $<5\%$ Metal Oxide (TGA)), paraffin oil, antimony(III) oxide, potassium dihydrogen phosphate and dibasic potassium phosphate were purchased from Sigma-Aldrich (St. Louis, Missouri, USA). Stock solution of catechin (2.9 g/dm^3) is prepared by diluting the pure substance with ethanol in the normal vessel covered with aluminium foil as a protection from the light, and is kept in the refrigerator. Working solutions are prepared by diluting to the desired concentration with the supporting electrolyte. 0.1 mol/dm^3 phosphate buffer pH 7.0 that is used as a supporting electrolyte is prepared by mixing equi-molar solutions (0.1 mol/dm^3) of KH_2PO_4 and K_2HPO_4 in doubly distilled water. Desired pH value is adjusted by using drops of 0.1 mol/dm^3 HCl.

Preparation of the working electrodes

Unmodified CPE is prepared by mixing 0.5 g of expanded graphite with 0.3 cm^3 of paraffin oil using pestle and mortar for 30 minutes until a homogenized paste is obtained. The prepared paste is packed in the home-made carbon paste electrode holder with copper wire at the back to provide electrical contact. The electrode surface is smoothed by polishing on a teflon board by applying a slight manual pressure. After performing a set of experiments the surface of the electrode is renewed by extrusion of approximately 0.5 mm of the carbon paste from the holder and by addition of the fresh paste into the holder.

Modified CPEs are prepared by mixing 0.475 g of expanded graphite, 0.025 g of the modifier and 0.3 cm^3 of paraffin oil. After 30 minutes of mixing the same procedure is used as for the unmodified CPE.

Apparatus

PalmSens 4 potentiostat (GA Houten, Netherlands) connected to a personal computer using the PSTrace 5.4 software and with a three-electrode system is used for voltammetric measurements. Unmodified or modified CPEs are used as a working electrode, platinum wire as a counter electrode, and an Ag/AgCl (3.5 mol/dm^3 KCl) as a reference electrode. All electrochemical measurements were carried out in a process glass vessel (50 cm^3) with tapered bottom. Electrical stick stirrer was used to stir the analysed solution. All potentials in the paper are referred to Ag/AgCl (3.5 mol/dm^3 KCl) reference electrode.

General procedure

For performing the electroanalytical analysis, 20 cm^3 of the supporting electrolyte is transferred into the process glass, cyclic voltammetry (CV) and square-wave voltammetry (SWV) are used as voltammetric procedures. Voltammograms are recorded in the potential range from -0.3 to $+1.4 \text{ V}$. The experimental parameters for CV were step potential 0.05 V , scan rate 0.3 V/s , while step potential of 0.005 V , amplitude of 0.025 V and frequency of 50 Hz are applied for performing SWV. All measurements are performed at room temperature.

Results and discussion

Cyclic voltammetry of catechin showed two oxidation peaks and one reduction peak. The first oxidation peak occurred at peak potentials range from +0.25 to +0.3 V, the second in the range from +0.599 to +0.699 V, while reduction peak appeared at the same potential for all studied working electrodes +0.15 V. Similar behavior of catechin is observed by other authors (Janeiro and Oliveira Brett, 2004; Corrêa Ribeiro et al., 2019). Oxidation peaks are associated with functional OH groups attached to ring structure, however more detail study has to be performed for investigating the exact mechanism of this reactions.

SWV is also used as an electroanalytical procedure for investigation of the linearity by using different working electrodes. Voltammograms are recorded for concentration range of catechin from 1 to 20 mg/dm³. As can be seen from the Figure 1, the intensity of the first oxidation peak was much higher than for the second. Therefore, it would be more suitable for quantification purposes in real samples.

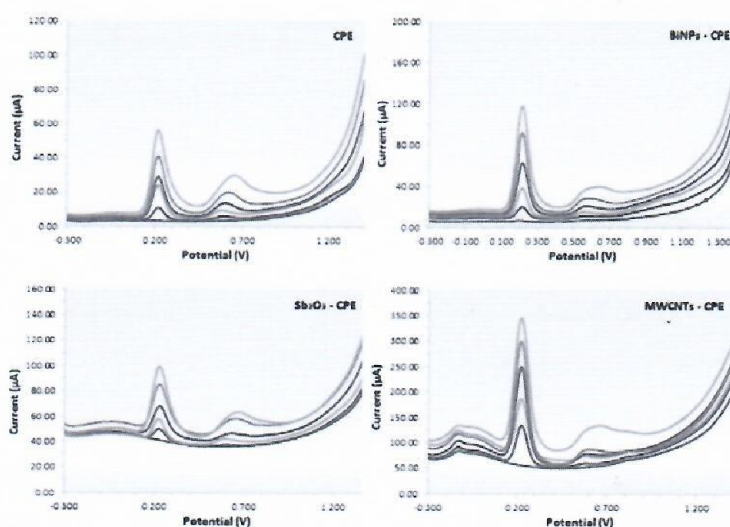


Figure 1. SW voltammograms obtained at different CPEs recorded in 0.1 mol/dm³ phosphate buffer pH 7.0 with increasing concentrations of catechin with blank at the bottom.

The linear relationships between the first oxidation peak current and the concentrations are presented on Figure 2. Obtained equations illustrated that the peak current varied linearly with concentration with regression coefficient from 0.9936 to 0.9947.

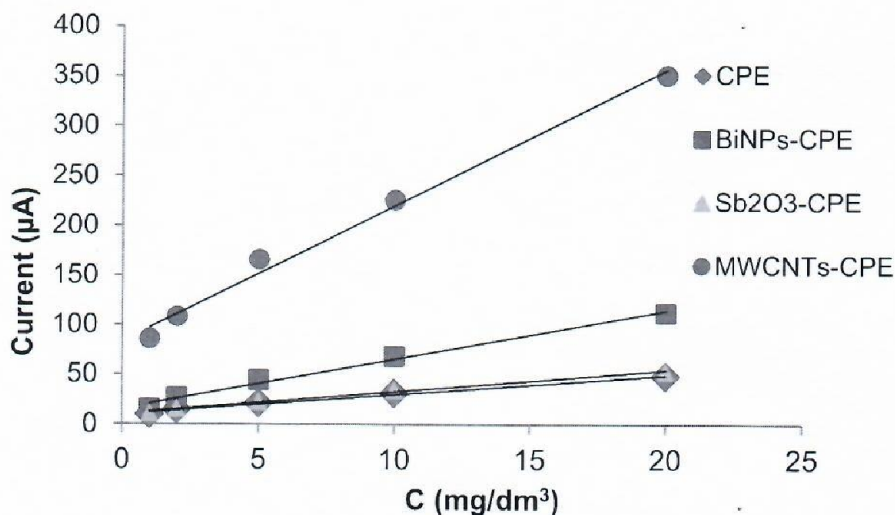


Figure 2. Plots between peak current vs. concentration of catechin obtained using different CPEs.

The sensitivity of SWV using different CPEs is determined based on values obtained for detection and quantification limit. The LOD is calculated using equation $3 \cdot s/m$, while LOQ is calculated using $10 \cdot s/m$, where s is the standard deviation of the blank, and m is the slope of the regression line. Calculated values of LOD and LOQ are presented in the Table 1.

Table 1. Calculated values of LOD and LOQ for bare CPE and modified CPEs.

(mg/dm ³)	CPE	BiNPs-CPE	Sb ₂ O ₃ -CPE	MWCNTs-CPE
LOD	0.92	0.35	0.72	0.25
LOQ	3.08	1.17	2.41	0.82

By comparing results obtained by using different CPEs, it is obvious that modified CPEs showed better sensitivity in comparison to bare CPE. In the case of modified electrodes the highest sensitivity is achieved by using MWCNTs, while somewhat lower sensitivity is achieved using BiNPs and Sb₂O₃ as a modifier.

Conclusions

The aim of this study was to investigate and compare the sensitivity of different CPEs for voltammetric determination of catechin. The obtained results showed that modified CPEs showed better sensitivity for catechin determination in comparison to unmodified. The best results in terms of linearity, sensitivity are achieved with MWCNTs as a modifier. The results shown in this study are preliminary and further experiments will be directed towards the optimization of experimental and instrumental parameters in order to increase the sensitivity, and that developed method could be used for catechin quantification in real samples.

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