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Poly(Phenol Red)-Based Voltammetric Sensor for the Simultaneous Quantification of Hydroxycinnamic Acids

Anastasiya Zhupanova * and Guzel Ziyatdinova

Analytical Chemistry Department, Kazan Federal University, Kremleyevskaya, 18, 420008 Kazan, Russia; Ziyatdinovag@mail.ru
* Correspondence: zhupanova.nastya@mail.ru

Abstract: Hydroxycinnamic acids are one of the most widely distributed class of natural phenolics in plants. Their coexistence requires selective methods for quantification. Voltammetry on chemically modified electrodes is one of the approaches to solve this problem. Electrodes based on the electropolymerized triphenylmethane dyes give sensitive and selective response to natural phenolic antioxidants of different classes. In this work, combination of polyaminobenzene sulfonic acid functionalized single-walled carbon nanotubes (f-SWCNTs) and poly(phenol red) has been used as electrode surface modifier. The polymeric coverage has been obtained by potentiodynamic electropolymerization which conditions have been optimized on the basis of voltammetric response of hydroxycinnamic acids mixture. Poly(phenol red)-based electrode provides well-resolved peaks of caffeic, ferulic, and *p*-coumaric acids and significant increase of the oxidation currents compared to bare glassy carbon (GCE) and f-SWCNTs-modified electrodes. Simultaneous voltammetric quantification of caffeic, ferulic, and p-coumaric acids has been performed for the first time. Two linear dynamic ranges of 0.10–2.5 μM for all acids and 2.5–100 μM for caffeic acid and 2.5–50 μM for ferulic and *p*-coumaric acids have been achieved using differential pulse voltammetry in Britton-Robinson buffer pH 2.0. The limits of detection are 47.6, 22.4, and 38.0 nM for the caffeic, ferulic, and *p*-coumaric acids, respectively.

Keywords: voltammetry; modified electrodes; electropolymerization; triphenylmethane dyes; natural phenolics; hydroxycinnamic acids; simultaneous quantification

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1. Introduction

Hydroxycinnamic acids (*p*-coumaric, caffeic, ferulic, 5-hydroxyferulic, and sinapic acids) are one of the most widely distributed class of natural phenolics in plants [1]. Biosynthesis pathways leads to the coexistence of this acids in the plants, fruits, vegetables, and whole grains [1,2]. Therefore, sensitive and selective methods for the quantification of hydroxycinnamic acids are required. Various types of chromatography [1,3] and capillary electrophoresis [4,5] are traditionally used to solve this problem. Nevertheless, these methods are often needed in the preliminary extraction of the hydroxycinnamic acids as well as are characterized by tedious procedures, high consumption of organic solvents and relatively expensive equipment.

Electrochemical methods are simple, cost-effective, and sensitive but insufficient selectivity of response of structurally related compounds is the major limiting factor. This problem is partially solved using chemically modified electrodes that allow simultaneous determination of hydroxycinnamic acids in binary and even ternary mixtures [6]. Thus, carbon nanofiber-based screen-printed electrode allow simultaneous determination of ferulic and caffeic acids [7], glassy carbon electrode (GCE) modified with multi-walled carbon nanotubes and electropolymerized sunset yellow has been developed for the simultaneous quantification of chlorogenic and ferulic acids in coffee [8]. WS_2 flakes/catechin-capped Au nanoparticles/carbon black-based nanocomposite sensor successfully provide full resolution of the oxidation peaks of caffeic, sinapic, and *p*-coumaric acids [9]. The analytical characteristics achieved are sufficient for the quantification of hydroxycinnamic acids in real samples. Further development of modified electrode for the voltammetric analysis of ternary mixtures of hydroxycinnamic acids is of practical interest.

Novel chemically modified electrode has been developed in current work for the simultaneous quantification of caffeic, ferulic, and *p*-coumaric acids (Figure 1) for the first time. Combination of polyaminobenzene sulfonic acid functionalized single-walled carbon nanotubes (f-SWCNTs) and electropolymerized phenol red has been used as electrode surface modifier.

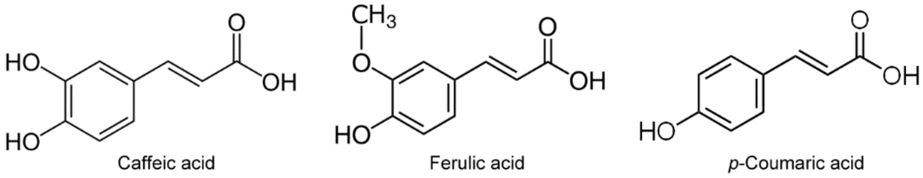


Figure 1. Hydroxycinnamic acids under investigation.

2. Materials and Methods

Caffeic (98%) and 98% *p*-coumaric acids from Sigma (Steinheim, Germany), 99% ferulic acid from Aldrich (Steinheim, Germany) have been used. Their standard 10 mM solutions were prepared in ethanol (rectificate). Phenol red (ACS grade purity) was purchased from Sigma-Aldrich (St. Louis, MO, USA). It's 10 mM solution was prepared in ethanol (rectificate). Exact dilution was applied for the preparation of less concentrated solutions.

f-SWCNTs ($d \times l$ is 1.1 nm×0.5-1.0 μm) were purchased from Sigma-Aldrich (Steinheim, Germany). Their 1.0 mg mL^{-1} homogeneous suspension in dimethylformamide was prepared by sonication for 30 min in an ultrasonic bath (WiseClean WUC-A03H (DAIHAN Scientific Co., Ltd., Wonju-si, Republic of Korea).

Other reagents were c.p. grade. Distilled water was used for the measurements. The laboratory temperature was (25 ± 2 °C).

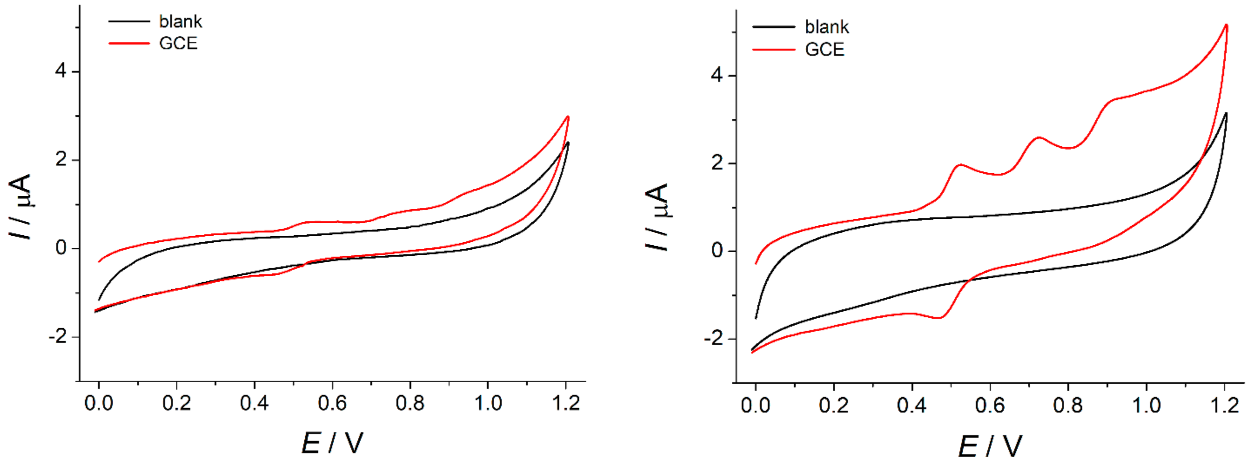
Electrochemical measurements were conducted on the potentiostat/galvanostat Autolab PGSTAT 302N with the FRA 32M module (Eco Chemie B.V., Utrecht, The Netherlands) and NOVA 1.10.1.9 software. The glassy electrochemical cell of 10 mL volume was used. The tree-electrode system consisted of the working GCE of 3 mm diameter (CH Instruments, Inc., Bee Cave, TX, USA), or a modified electrode, an Ag/AgCl reference electrode, and a platinum wire as the auxiliary electrode.

pH measurements were carried out using the "Expert-001" pH meter (Econix-Expert Ltd., Moscow, Russian Federation) with a glassy electrode.

3. Results and Discussion

3.1. Voltammetry of Hydroxycinnamic Mixture at the Bare and Polymer-Modified Electrodes

Caffeic, ferulic, and *p*-coumaric acids are oxidized at bare GCE (Figure 2a) at 0.53, 0.76, and 0.94 V, respectively. Peak potential separation allows their simultaneous detection. Nevertheless, low oxidation currents especially for *p*-coumaric acid make this task impossible. Therefore, electrode surface modification with f-SWCNTs and electropolymerized phenol red has been performed. Application of f-SWCNTs as a support for electrodeposition of poly(phenol red) provides higher surface area available for polymer deposition as well as more uniform distribution of polymeric coverage. On the other side, f-SWCNTs increase the conductivity of the electrode that is important for the effective electron transfer in the case of non-conductive polymeric coverages that are usually formed from phenolic moiety containing triphenylmethane dyes [10,11].



(**a**) (**b**)

Figure 2. Cyclic voltammograms of 5.0 µM mixture of caffeic, ferulic, and *p*-coumaric acids in Britton-Robinson buffer pH 2.0: (**a**) at bare GCE; (**b**) at poly(phenol red)/f-SWCNTs/GCE. Potential scan rate is 100 mV s^{-1}.

Potentiodynamic electropolymerization of phenol red has been performed in 0.1 M NaOH (Figure 3) as far as electron detachment proceeds easier in basic medium. The oxidation peak at 0.63 V is decreased on the second and following cycles up to full disappearance at 10th cycle that confirms formation of non-conductive polymer that agrees well with phenol red electropolymerization at the GCE in phosphate buffer pH 7.4 [12].

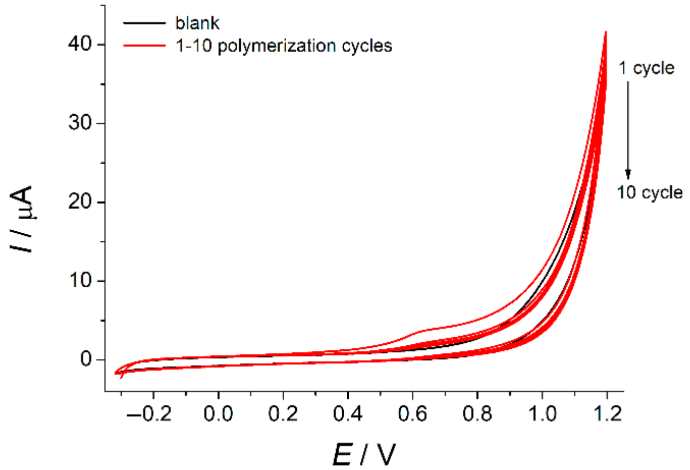


Figure 3. Electropolymerization of 75 µM phenol red at the f-SWCNTs/GCE in 0.1 M NaOH. Potential scan rate is 75 mV s^{-1}.

Electropolymerization conditions strongly affect the properties of final polymeric coverage and its response to target analytes. Therefore, monomer concentration, number of cycles, and electrolysis parameters (potential scan rate and polarization window) have been optimized on the basis of voltammetric response of hydroxycinnamic acids mixture. The best voltammetric characteristics of hydroxycinnamic acids mixture (Figure 2b) have been obtained at the polymeric coverage from the 75 µM phenol red after 10 cycles in the polarization window from –0.3 V to 1.2 V at the potential scan rate of 75 mV s^{-1}. Statistically significant increase of the caffeic, ferulic, and *p*-coumaric acids oxidation currents at the polymer-modified electrode confirm improvement of the sensitivity of detection.

On the basis of cyclic voltammetry data for individual acids at various pH of the Britton-Robinson buffer and potential scan rate, diffusion-controlled electrooxidation with proton transfer has been proved. Diffusion coefficient equal to $(3.9 \pm 0.1)\times10^{-5}$, $(2.1 \pm 0.3)\times10^{-5}$, and $(4.6 \pm 0.2)\times10^{-5}$ cm^2 s^{-1} for the caffeic, ferulic, and *p*-coumaric acids, respectively. Two electrons are involved in the electrooxidation of all acids. Anodic transfer coefficients of 0.62, 0.46, and 0.40 have been calculated for caffeic, ferulic, and *p*-coumaric acids, respectively.

3.2. Simultaneous Quantification of Hydroxycinnamic Acids

Quantification of caffeic, ferulic, and *p*-coumaric acids has been performed under conditions of differential pulse voltammetry. The effect of pulse parameters on the response of hydroxycinnamic acids mixture has been studied. The best results obtained at pulse amplitude of 50 mV and pulse time 25 ms. Peak area has been used as analytical signal which is linearly increased as caffeic, ferulic, and *p*-coumaric acids concentration grow. Two linear dynamic ranges of 0.10–2.5 μM for all acids and 2.5–100 μM for caffeic acid (2.5–50 μM for ferulic and *p*-coumaric acids) have been achieved. The detection limits at S/N =3 equal to 47.6, 22.4, and 38.0 nM for the caffeic, ferulic, and *p*-coumaric acids, respectively.

Accuracy of the method developed has been checked by added-found method. The relative standard deviation does not exceed 2% (3-5% for the low concentrations of hydroxycinnamic acids) indicating the absence of random errors of determination. Recovery values (99.2–100.6%) confirm high accuracy of the method developed.

Thus, simultaneous voltammetric determination of caffeic, ferulic, and *p*-coumaric acids has been performed for the first time. GCE modified with f-SWCNTs and poly(phenol red) gives sensitive response, reliable results, and can be applied in coffee samples screening.

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