

Voltammetric determination of dihydroxybenzene isomers using a disposable pencil graphite electrode modified with cobalt-phthalocyanine

Mihaela Buleandra¹ · Andreea Alexandra Rabinca^{1,2} · Irinel Adriana Badea¹ ·
Adriana Balan² · Ioan Stamatina² · Constantin Mihailciuc³ · Anton Alexandru Ciucu¹

Received: 10 December 2016 / Accepted: 22 February 2017 / Published online: 3 March 2017
© Springer-Verlag Wien 2017

Abstract A novel voltammetric assay for the simultaneous determination of hydroquinone (HQ), catechol (CC) and resorcinol (RS) by using an electrochemically treated pencil graphite electrode modified with cobalt-phthalocyanine is described. Differential pulse voltammetric results showed three well-distinct oxidation peaks for HQ, CC and RS at 102 mV, 203 mV and 591 mV (vs. Ag/AgCl), respectively. Thus, the method can be applied to direct simultaneous determination without previous separation. The detection limits are 3.38×10^{-7} mol L⁻¹ for HQ, 3.40×10^{-7} mol L⁻¹ for CC and 7.23×10^{-7} mol L⁻¹ for RS. The method was successfully applied to the direct determination of dihydroxybenzene isomers in tea samples, and the results were compared with chromatographic data.

Keywords Sensor · Mediator · Electrochemically treated · Electrooxidation · Simultaneous determination · Tea sample

Electronic supplementary material The online version of this article (doi:10.1007/s00604-017-2153-z) contains supplementary material, which is available to authorized users.

✉ Constantin Mihailciuc
pc_mihailciuc@yahoo.com

✉ Anton Alexandru Ciucu
anton_ciucu@yahoo.com

¹ Faculty of Chemistry, Department of Analytical Chemistry, University of Bucharest, 90-92 Panduri Avenue, 050663 Bucharest, Romania

² Faculty of Physics, 3nano-SAE Research Centre, University of Bucharest, MG38-Magurele, Bucharest, Romania

³ Faculty of Chemistry, Department of Physical Chemistry, University of Bucharest, 4-12 Regina Elisabeta, 030018 Bucharest, Romania

Introduction

Hydroquinone (HQ), catechol (CC) and resorcinol (RS), isomers of dihydroxybenzene, are important organic intermediates for the products of industry and agriculture, considered highly toxic to both environment and human even at very low concentrations [1, 2]. They are used to produce food additive agents, hair dyes, antioxidants, plastics, synthetic fibers, and in pharmaceutical industry. CC is a natural compound that widely exists in higher plants such as teas, vegetables, fruits, and tobaccos. The taste of tea is affected and can be improved by changing the content of catechol and related compounds [3, 4]. Different analytical methods have been established to determine dihydroxybenzene isomers, such as high performance liquid chromatography [5], fluorescence [6], electrochemiluminescence [3], spectrophotometry [7], and gas chromatography/mass spectrometry [8].

Electrochemical methods are of prime importance for detecting various phenolic compounds and number of works addressed on the simultaneous electrochemical determination of HQ, CC and RS [9–18]. Having similar electroactive groups, their redox peak potentials are too close to be identified at the solid electrodes. Another main problem is the possible formation of a polymeric film on the electrode surface which blocks the electron transfer [19], so a cleaning step of the electrode surface is required before each measurement. The use of disposable electrodes eliminates this time-consuming stage.

Pencil graphite electrode (PGE) presents some advantages compared with conventional electrodes like robust oxidation capacity, the possibilities of modification due to its adsorption capacity, mechanical resistance, low-cost, and the fabrication of reproducible single-use PGEs. The suitability of PGE has been demonstrated in the literature in multiple applications [20].

Nowadays chemically modified electrodes (CMEs) are widely used in the field of electroanalytical chemistry.

Among various CMEs, metallo-phthalocyanines (MePC) modified electrodes seem to be a promising approach for dihydroxybenzene isomers determination. The sensitivity and the selectivity of the sensors towards different analytes can be greatly improved as a result of using MePC [21].

A survey of the literature reveals that there is no report regarding the electrochemical determination of CC, HQ and RS using a PGE modified with cobalt-phthalocyanine (CoPC). The present paper describes the voltammetric behavior of CC, HQ and RS at the electrochemically treated CoPC modified PGE (CoPC-PGE*). Determination of the three dihydroxybenzene isomers by a differential pulse voltammetric method was successfully demonstrated by using the CoPC-PGE*, without previous chemical or physical separations and thus a novel approach for simultaneous and selective detection of isomers was established. The method was applied to the analysis of these isomers in tea samples.

Experimental

Chemicals

Hydroquinone, catechol, resorcinol, cobalt(II) phthalocyanine, N,N-dimethylformamide (DMF) and methanol were provided by Sigma-Aldrich (<http://www.sigmaaldrich.com/>). Kalium hexacyanoferrat(III) (Merck, <http://www.merck.com/>) and potassium chloride (Sigma-Aldrich) were used to prepare a redox probe solution of $1 \times 10^{-3} \text{ mol L}^{-1} \text{ K}_3[\text{Fe}(\text{CN})_6]$ in $1 \text{ mol L}^{-1} \text{ KCl}$. The dihydroxybenzenes were dissolved with ultra-pure water to obtain $1 \times 10^{-2} \text{ mol L}^{-1}$ of standard stock solutions which were further diluted with ultra-pure water to desired concentrations immediately before use. As the supporting electrolyte, Britton-Robinson buffer (BRB) was used.

Stock solutions of 2 mg mL^{-1} CC, HQ and RS respectively, were prepared in water for HPLC studies. The working solution (0.1 mg mL^{-1}) used for the HPLC method development was prepared by dilution of each stock solution in methanol.

Equipment

Voltammetric measurements were performed with Autolab PGSTAT 128 N (Ecochemie B.V., Netherlands, www.metrohm-autolab.com) controlled by Nov. 1.8 software. Pencil graphite (PG), electrochemically treated pencil graphite (PG*), cobalt-phthalocyanine (CoPC) modified pencil graphite (CoPC-PG) and a CoPC modified and electrochemically treated pencil graphite (CoPC-PG*) were used as working electrodes. Pt wire and Ag|AgCl (3.0 M KCl) were used as an auxiliary and reference electrode, respectively. PGEs were Rotring HB pencil-leads model with a diameter of 0.5 mm and 6 cm length purchased from local bookstore. The PGEs were prepared as described elsewhere [22]. Each voltammetric recording was

carried out on a new graphite pencil lead. Chromatographic analysis was performed with a Thermo Finnigan Surveyor HPLC system (Thermo-Electron Corporation – Waltham, MA, USA, www.thermo.com) equipped with a Photodiode Array detector having a 50 mm cell length and controlled by means of the Chrom Quest software. Atomic force microscopy images were recorded with the Integrated Platform SPM-NTegra, model Prima microscope (NT-MDT trade mark, <http://www.ntmdt-si.com/>) in noncontact mode using a cantilever with silicon tip of NSG-01.

Procedures

Cyclic voltammetry studies were done in the potential range $-0.2 - +1.2 \text{ V}$, at a scan rate of 100 mV s^{-1} unless otherwise stated. Differential pulse voltammograms were recorded between $-0.2 - +1.0 \text{ V}$ for different concentrations of HQ, CC and RS solutions prepared in BRB buffer, $\text{pH} = 6.80$, under optimized instrumental parameters (scan rate 10 mV s^{-1} , pulse amplitude 25 mV , sampling width 17 ms , pulse width 100 ms , pulse period 500 ms).

The chromatographic method was based on a published paper [23] using a Hypersil GOLD C18 column ($250 \times 4.6 \text{ mm}$, $5 \mu\text{m}$). The separation was achieved under isocratic elution using a mobile phase composed by water and methanol (40%) as organic modifier. A flow rate of 1 mL min^{-1} , and an injection volume of $10 \mu\text{L}$ were used; detection was realized at 270 nm . Under the chromatographic conditions described herein the elution order was HQ, RS and CC at 3.36 min , 3.79 min and 4.43 min , respectively and the resolution between peaks was 2.16 and 2.77 , respectively. In the tea sample, each compound was identified according to its retention time and UV-VIS spectrum recorded during elution.

Preparation of the CoPC modified electrode

Initially 5 mg CoPC was dispersed under ultrasonic agitation into 5 mL DMF for 20 min [24]. The PGE was immersed in the CoPC/DMF mixture for 2 h and then left to dry. The CoPC modified PGE was electrochemically treated by performing 10 cyclic voltammetric scans from -0.2 V to $+3.0 \text{ V}$ at a scan rate of 500 mV s^{-1} , in BRB of $\text{pH} 6.80$ [2].

Tea sample preparation

To demonstrate the usefulness of the proposed activated CoPC-PGE* tea samples were analyzed. 1 g of green tea was infused with 50 mL hot ($100 \text{ }^\circ\text{C}$) de-ionized water; the infusion was cooled 20 min and then filtered. $10 \mu\text{L}$ of tea infusion was diluted with 10 mL BRB ($\text{pH} 6.80$) for DPV analysis. For HPLC analysis 0.5 mL infusion was diluted with 10 mL methanol. Injection volume was $10 \mu\text{L}$.

Results and discussion

Electrochemical characterization of PG electrodes

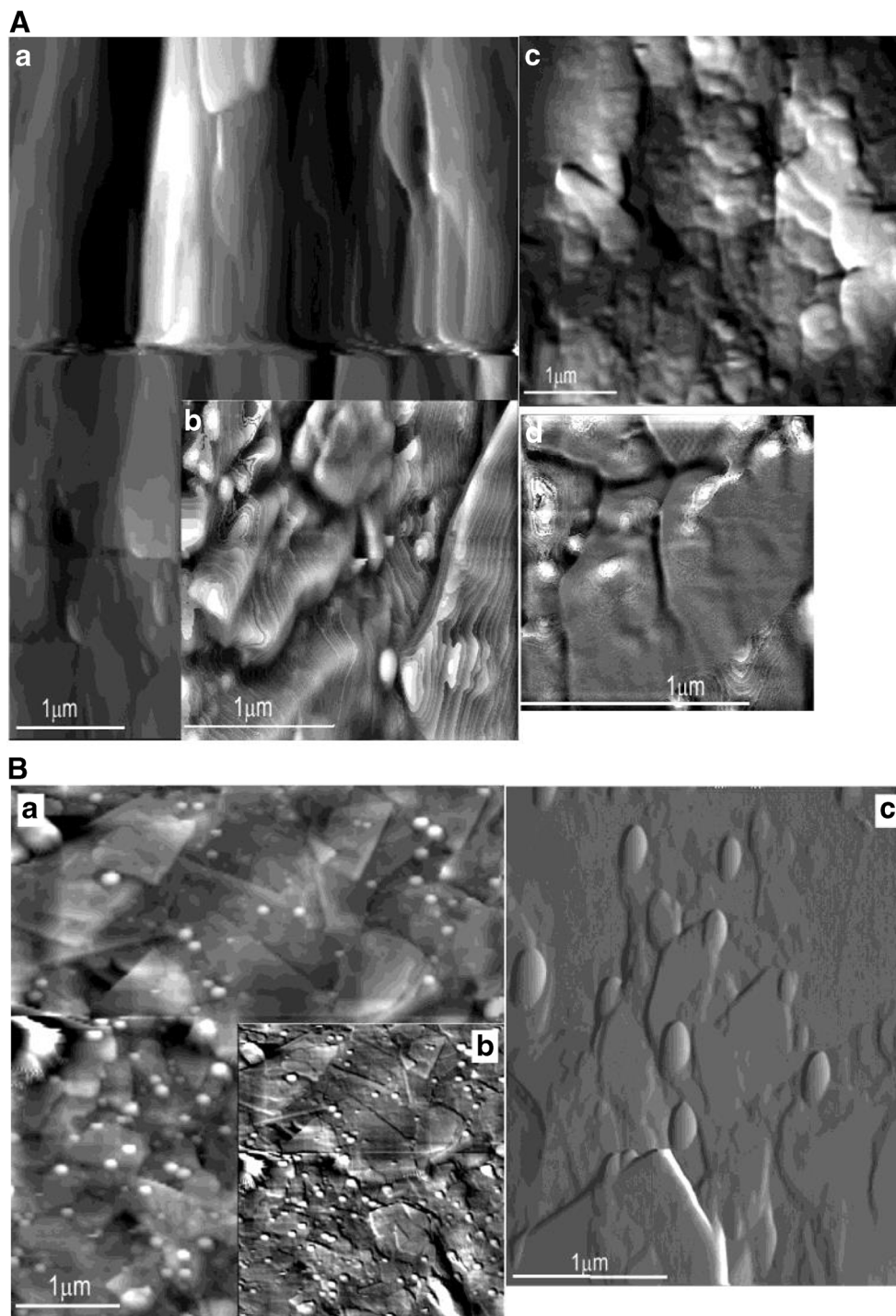
Initially, a bare PGE, an activated pencil graphite electrode (PGE*), a CoPC modified electrode (CoPC-PGE) and a CoPC modified and activated pencil graphite electrode (CoPC-PGE*) were characterized by cyclic voltammetry in $1 \times 10^{-3} \text{ mol L}^{-1} \text{ K}_3[\text{Fe}(\text{CN})_6]$ solution prepared in 1 mol

$\text{L}^{-1} \text{ KCl}$. The results are presented in the Electronic Supplementary Material (Fig. S1).

AFM studies

Non-activated/activated PGEs and non-activated/activated CoPC-PGEs were characterized using AFM. A comparison of Fig. 1a(a,b,c,d), b(a,b,c) reveals a significant morphological difference among all mentioned PGE electrode surfaces.

Fig. 1 **a** Non-activated (a) and activated (c) PGE, inset details - layer stacking in graphite (b), details of the graphite layers eroded during activation (d). **b** Non-activated CoPC-PGE (a,b) and activated CoPC-PGE* (c)



In Fig. 1a(a), (b) the morphology and texture of PGE is typical for graphite materials prepared by extrusion from a given composition. The graphite grains are stacked in flakes oriented along of the extrusion direction. In Fig. 1a(b) there are details of the local organization: stacked graphite layers in a grain of graphite. The graphite layers are stacked small pockets of graphene with well-defined edges. The electrochemical activation induces a high oxidation of the graphene layer edges in consequence the graphite grains are rounded, loose orientation, Fig. 1a(c). In Fig. 1a(d) are details related to the reducing in size, shapes and edges of the graphene layers. That is specific for oxidative process of the graphite either by chemical or electrochemical methods. The electrochemical oxidation take the advantage to induce high reactive radicals (such as $\bullet\text{OH}$), the oxidation reaction being faster than chemical route. In addition, on the graphene edges the radical species react with carbons inducing functional groups (carboxyl, hydroxyl, epoxide) which will increase the electron transfer at the interface electrode-electrolyte (observed in Fig. 1, PGE*, electronic supplementary material).

The CoPC-PGE (Fig. 1b) shows that CoPC is deposited in plate-like layers (Fig. 1b(a)) with no preferential orientation on the electrode surface. In inset, Fig. 1b(b), are detailed some features of the CoPC layers. CoPC interact only weakly with the graphite substrate and commonly adopt a square lattice with a very similar lattice constant to a bulk molecular crystal. During the drying stage, when the interactions with the graphite layers are weaker the CoPC adopt a packing in small droplets. Therefore, on the PGE substrate two forms of the CoPC co-exist. After electrochemical activation CoPC-PGE* (Fig. 1b(c)) the CoPC layers loose distinctive edges, are reduced in dimension and droplets become rounded. Due to a well-defined coverage on the PGE surface, the graphite electro-oxidation cannot be seen. However, Fig. 1 CoPC-PGE and CoPC-PGE* in electronic supplementary material clearly shows the synergic effect in the CV-peaks with high and distinctive amplification of the electron transfer at the electrode interface.

Electrochemical behaviors of dihydroxybenzene isomers at PG electrodes

Cyclic voltammetry studies of dihydroxybenzene isomers in a mixed solution ($5 \times 10^{-4} \text{ mol L}^{-1}$ of each isomer in buffer of pH 6.80) shows that for HQ a pair of well-defined redox peaks appears on CoPC-PGE* at 166 mV and 44 mV, with approximately equal anodic and cathodic peak currents and a separation between peak potentials ΔE_p of 122 mV (Fig. 2). For CC, the redox peak potentials are at 288 mV and 200 mV ($\Delta E_p = 88 \text{ mV}$). In case of RS, only an oxidation peak is observed at 698 mV, which proves that its oxidation is a totally

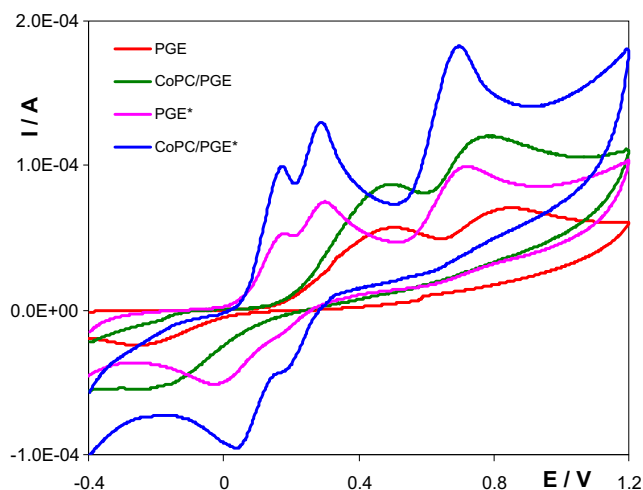


Fig. 2 Cyclic voltammograms for a mixture of HQ, CC and RS ($5 \times 10^{-4} \text{ mol L}^{-1}$ each) at PGE, CoPC-PGE, PGE* and CoPC-PGE* in BRB of pH 6.80; scan rate of 100 mV s^{-1}

irreversible electrode process. As shown in the literature [15], the electro-oxidation of RS is complex and in the first stage, non-stable phenoxy-type radicals may be generated, which further can couple with other radicals or dihydroxybenzenes to form polymers which may inactivate the electrode.

At the CoPC-PGE, although hydroquinone and catechol can be separated from resorcinol, CV responses of HQ and CC still overlap to form a wide oxidation peak at 434 mV. In cathodic range, a peak appear at about -122 mV , which represents the overlapping reductive peaks of HQ and CC. The electro-oxidation reaction of RS shows an irreversible process, because only a broad oxidation peak appeared at 757 mV.

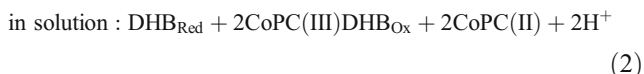
In case of using PG* and PG electrodes, a similar behavior, as presented above, is observed for the three isomers. The peak currents at electrochemically treated PGEs are separated being two times higher than those generated at untreated PGEs.

The synergistic effect of CoPC surface modification and electrochemical activation may explain the improved conductivity and electron transfer ability of the CoPC-PGE*, leading to an enhanced sensitivity of this electrochemical sensor toward dihydroxybenzene isomers.

Method optimization

The effects of pH and scan rates on the electrochemical behavior of the three dihydroxybenzene isomers in the mixed solution at CoPC-PGE* were investigated by cyclic voltammetry. Respective data and figures are given and discussed in the Electronic Supporting Material (Figs. S2, S3). In case of the oxidation processes the regression equations were $E_{pa} (\text{V}) = -0.0593\text{pH} + 0.5707$ ($R^2 = 0.9982$) and E_{pa}

(V) = -0.0628pH + 0.7373 ($R^2 = 0.9956$) for HQ and CC respectively. The linear regression equation for RS oxidation process was $E_{pa} (V) = -0.0599pH + 1.1085$ ($R^2 = 0.9926$). The three regression lines were almost parallel, implying that the anodic peak potential separation between HQ, CC and RS is constant at different pH solutions [12]. The slopes of the three regression equations were close to the theoretical value of 59 mV pH⁻¹, proving that in the electrochemical redox process of HQ, CC and RS and RS the loss of electrons is accompanied by an equal number of protons. Based on the formula [25]: $dE_p/dpH = 2.303 mRT/nF$ in which, m is the number of proton, n is the number of electron, m/n was calculated to be 1.00 and 0.85 for the oxidation and reduction process of HQ, respectively, and corresponding 1.06 and 0.86 for CC redox processes. The calculated m/n ration for RS oxidation was 1.02. Thus, the electrochemical oxidation of hydroquinone, catechol and resorcinol at the CoPC-PGE* should be a two-electron and two-proton process [16]. A mediated electrode mechanism for the oxidation of HQ, CC and RS implying $2H^+$, $2e^-$ can be expected:



where DHB_{Red} and DHB_{Ox} are the reduced and oxidized forms of dihydroxybenzene isomers. CoPC acts as a mediator to accelerate electron transfer rate for oxidation of phenols, the mediator being regenerated (Eq. (2)). Reaction 2 is reversible for HQ and CC, and irreversible for RS. This mechanism is in good agreement with that described by others [26].

The oxidation peak currents increased linearly with the square root of the scan rate, and the regression equations were $I_{pa} (\mu A) = 1.1134 v^{1/2} (mV s^{-1}) + 7.6906$ ($R^2 = 0.9942$), $I_{pa} (\mu A) = 2.1318 v^{1/2} (mV s^{-1}) + 9.1490$ ($R^2 = 0.9917$) and $I_{pa} (\mu A) = 5.3985 v^{1/2} (mV s^{-1}) - 2.5306$ ($R^2 = 0.9968$) for HQ, CC and RS, respectively. The results indicate a typical diffusion-controlled process.

In case of HQ and CC the anodic and cathodic peak potential showed a linear relationship with the decimal logarithm of scan rate. For oxidation processes of HQ and CC the linear regression equations were: $E_{pa} (V) = 0.0523 \log v + 0.2172$ ($V s^{-1}$, $R^2 = 0.9904$) and $E_{pa} (V) = 0.0704 \log v + 0.3745$ ($V s^{-1}$, $R^2 = 0.9973$), respectively. According to Laviron theory [27], the charge transfer coefficient (α) was calculated based on the equation, $K_a/K_c = \alpha/1-\alpha$, where K_a and K_c is the slope of the

straight lines for E_{pa} versus $\log v$ and E_{pc} versus $\log v$, respectively; the values for α were 0.47 HQ and 0.66 for CC. For both isomers, the calculated electron transfer number (n) was about 2. The heterogeneous electron transfer rate constant (k_s) can be calculated from eq. [27]:

$$\log k_s = \alpha \log(1-\alpha) + (1-\alpha) \log \alpha - \log \frac{RT}{nFv} - \frac{\alpha(1-\alpha)nF\Delta E_p}{2.3RT}$$

where n is the number on electrons involved in the reaction, ΔE_p is the peak potential separation ($E_{pa}-E_{pc}$), α is the charge transfer coefficient, v is the scan rate, R, T and F having their usual meaning. As the number of electrons involved in electrochemical redox process of HQ and CC is 2, the values of k_s are $0.136 \pm 0.012 s^{-1}$ for HQ and $0.302 \pm 0.070 s^{-1}$ for CC, at 298 K. These results indicate that the CoPC-PGE* can effectively promote the electron transfer and prove that the HQ and CC show a quasi-reversible electron transfer process on the CoPC-PGE* surface.

In case of RS, any increase in the scan rate causes shift in the oxidation peak potential to a positive value. A linear relationship between E_{pa} and $\log v$, was observed, in the range of 25 to 500 $mV s^{-1}$. The linear regression equation can be expressed as: $E_{pa} (V) = 0.1166 \log v + 0.8417$ ($V s^{-1}$, $R^2 = 0.9965$). According to Bard and Faulkner [28], for an irreversible anodic process α can be calculated from the following equation:

$$E_p - E_{p/2} = \frac{47.7}{n(1-\alpha)} mV$$

where $E_{p/2}$ is the potential where the current was at half the peak value. Thus, considering the number of electron n

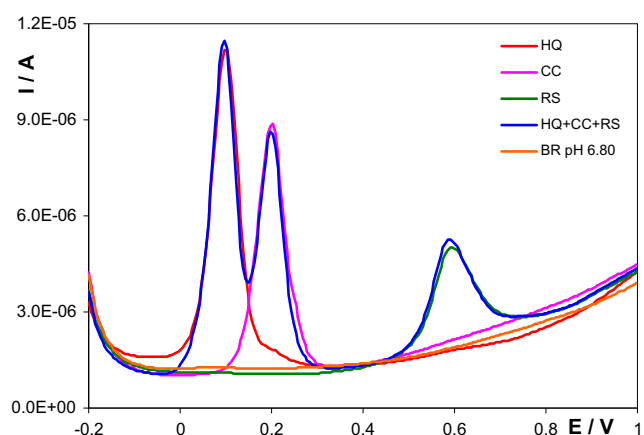


Fig. 3 Differential pulse voltammograms of $25 \times 10^{-6} \text{ mol L}^{-1}$ HQ, $25 \times 10^{-6} \text{ mol L}^{-1}$ CC, $25 \times 10^{-6} \text{ mol L}^{-1}$ RS and for a mixture of HQ, CC and RS ($25 \times 10^{-6} \text{ mol L}^{-1}$ each) at CoPC-PGE* in BRB of pH 6.80

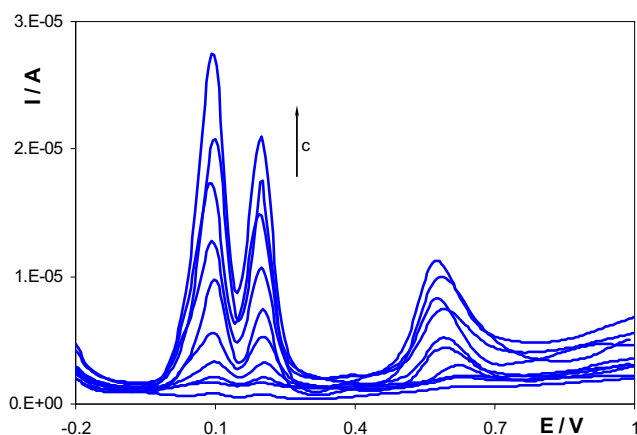


Fig. 4 Differential pulse voltammograms of HQ, CC and RS at different concentrations (from 5×10^{-7} mol L $^{-1}$ to 1×10^{-4} mol L $^{-1}$) in BRB of pH 6.80 obtained at CoPC-PGE*

transferred in the oxidation of RS equal to 2, the value of α was calculated to be 0.64.

Based on the I_{pa} vs. pH plot information and considering the determination sensitivity, a BRB of pH 6.80 was further used as the optimal supporting electrolyte for the simultaneous determination of CC, HQ and RS at a scan rate value of 100 mV s $^{-1}$.

Simultaneous determination of dihydroxybenzene isomers using DPV

DPV results in the mixed solution at CoPC-PGE* (Fig. 3) shows three well-distinguished anodic peaks for HQ, CC and RS at 102 mV, 203 mV and 591 mV, respectively, which were used for their quantification. The results indicate that the oxidation of dihydroxybenzene isomers in the mixed solution occurred independently at the CoPC-PGE*.

The oxidation peak current of each component was linear to its concentration (Fig. 4) in the range of 5×10^{-7} to 1×10^{-4} mol L $^{-1}$ for HQ ($(I (\mu A) = 0.1617 C(\mu M) + 0.0050, R^2 = 0.9973)$), 5×10^{-7} to 1×10^{-4} mol L $^{-1}$ for CC ($(I (\mu A) = 0.1202 C(\mu M) + 0.0657, R^2 = 0.9987)$) and 1×10^{-6} to 1×10^{-4} mol L $^{-1}$ ($(I (\mu A) = 0.0784 C(\mu M) - 0.2044, R^2 = 0.9966)$) for RS. The detection limits were 3.38×10^{-7} mol L $^{-1}$, 3.40×10^{-7} mol L $^{-1}$ and 7.23×10^{-7} mol L $^{-1}$ for HQ, CC and RS, respectively. The

method sensitivity is $2.18 \mu A \cdot \mu M^{-1} \cdot cm^{-2}$ for HQ, $1.62 \mu A \cdot \mu M^{-1} \cdot cm^{-2}$ for CC and $1.05 \mu A \cdot \mu M^{-1} \cdot cm^{-2}$ for RS. Therefore, for the high resolving ability and sensitivity, the modified electrode can be used for the simultaneous and sensitive determination of dihydroxybenzenes with DPV technique. Comparing the DPV results at the CoPC-PGE* with those reported in an electroanalytical method based on a glassy carbon electrode modified with multi-walled carbon nanotubes and CoPC [29], our method for direct determination of dihydroxybenzene isomers presented comparable detection limits; they are better than those presented by others [9, 10, 12, 16].

Precision of the DPV method was evaluated by repeatability (intra-day) and intermediate precision (inter-day). The repeatability of the method was assessed by repeating four experiments at 10×10^{-6} mol L $^{-1}$ of each isomer standard solutions on the same day. The intermediate precision was assessed comparing the results from three different days and the data are presented in Table 1.

Interference study

To assess the selectivity of the CoPC-PGE* an interference study in the electrode response was performed by using DPV method. Under optimal experimental conditions a mixed dihydroxybenzene solution (HQ, CC and RS, each 5×10^{-6} mol L $^{-1}$) in BRB solution of pH 6.8 was analyzed in the presence of possible interfering species. The results showed that 10-fold of ascorbic acid, phenol, o-nitrophenol, p-nitrophenol, o-aminophenol, and p-aminophenol do not interfere with the determination of HQ, CC and RS (signals change below 5%). Measurement of the peak currents for each solution was repeated three times and the average current values were calculated. All the results demonstrate that the CoPC-PGE* has good selectivity towards the mentioned interferents.

Analytical application

The applicability of the method was evaluated for the quantitative determination of HQ, CC and RS in tea infusion samples. The standard additions method was used to avoid the possible effects due to matrix. The peak currents of DPVs recorded on CoPC/PGE* before and after three standard

Table 1 Results obtained for the evaluation of the method precision for the determination of HQ, CC and RS at CoPC-PGE*

Added ($\times 10^{-6}$ mol L $^{-1}$)	Found ($\times 10^{-6}$ mol L $^{-1}$) \pm SD			Precision, RSD%		
	HQ	CC	RS	HQ	CC	RS
Intra-day precision						
10	10.08 \pm 0.37	9.93 \pm 0.37	10.13 \pm 0.40	3.63	3.68	3.98
Inter-day precision						
10	10.14 \pm 0.51	10.11 \pm 0.41	10.10 \pm 0.48	4.98	4.09	4.80

SD standard deviation, RSD% relative standard deviation

Table 2 Determination of HQ, CC and RS in tea infusion samples (*n* = 3)

	C · 10 ⁻⁶ M added	C ± SD, × 10 ⁻⁶ M found	R ± SD%	DPV content ± SD, mg g ⁻¹ tea; RSD%	HPLC content ± SD, mg g ⁻¹ tea; RSD%	r.e. %	t-value
HQ	0	3.90 ± 0.13	-	0.214 ± 0.008; 3.53	0.222 ± 0.003; 1.37	-0.036	1.63
	5	5.19 ± 0.40	102.06 ± 4.56				
	10	10.67 ± 0.07	104.81 ± 0.50				
CC	15	14.49 ± 0.09	97.32 ± 0.49				
	0	4.14 ± 0.18	-	0.228 ± 0.010; 4.32	0.227 ± 0.002; 0.98	0.003	0.10
	5	4.71 ± 0.19	96.75 ± 2.08				
RS	10	9.91 ± 0.13	99.34 ± 0.93				
	15	15.16 ± 0.07	100.84 ± 0.36				
	0	1.59 ± 0.07	-	0.088 ± 0.004; 4.32	0.084 ± 0.001; 1.21	0.052	1.84
	5	4.93 ± 0.03	99.01 ± 0.44				
	10	10.36 ± 0.04	103.11 ± 0.35				
	15	14.78 ± 0.02	98.68 ± 0.12				

SD standard deviation, RSD% relative standard deviation, *t* statistical t test

additions of dihydroxyphenol standard solutions were measured and used for recovery studies, in order to evaluate the accuracy of the method. The measurements were done in triplicate and the results are presented in Table 2. The recoveries of three added analytes to tea samples were calculated and the overall averages values were 101.39% for HQ, 98.97% for CC, and 100.26% RS (Table 2).

The presence of dihydroxyphenols in tea samples was confirmed using the HPLC method, and the statistical comparison of the results from DPV and HPLC studies is presented in Table 2. The relative errors (%) calculated as $100 \times (c_{(DPV)} - c_{(HPLC)}) / c_{(HPLC)}$ were $\leq 0.1\%$. The well-known statistical t test was applied in order to emphasize the reliability of the proposed method results. The calculated t values are smaller than the theoretical one (tabled t-value for 4 freedom degrees at 95% confidence level, two-tailed is 2.78). This means that the average values of the two methods belong to the same values population. Thus, the results using the two methods are not significantly different.

It can be summarized that the proposed voltammetric method for practical samples is accurate and reliable on the basis of the average recoveries with RSD below 5% in all cases, and can be used for the simultaneous determination of the three dihydroxybenzene isomers in tea infusion samples.

Conclusions

In this work, an electrochemically treated cobalt-phthalocyanine modified PGE and differential pulse voltammetric method were first used to determine three dihydroxybenzene isomers simultaneously and quantitatively in a mixture. Based on the good electrochemical activity and electrical conductivity of the CoPC-PGE* the determination of HQ, CC and RS with good analytical performance was achieved with good selectivity. The new DPV method is simple, rapid and was successfully applied in the direct simultaneous determination of the three isomers of dihydroxybenzene in tea samples. The DPV results using the CoPC-PGE* are in good agreement with the more laborious chromatographic ones. The problems related to the surface contamination were resolved by using a disposable electrode. At this stage, although graphite pencil electrodes demonstrate a high degree of maturity from fabrication and modification point of view, technologies are needed for mass production of modified GPEs for reliable detection of certain analytes in different matrices.

Acknowledgements This work was supported by Romanian Executive Unit for Funding Higher Education, Research, Development and Innovation (UEFISCDI), Grants numbers 251/2011, and 64/2011.

Compliance with ethical standards The authors declare that they have no conflict of interest.

References

- Hu X, Li J, Wang J (2012) Structural transformation of carbon electrodes for simultaneous determination of dihydroxybenzene isomers. *Electrochem Commun* 21:73–76. doi:10.1016/j.elecom.2012.04.031
- Buleandra M, Rabinca AA, Mihailciuc C, Balan A, Nichita C, Stamatin I, Ciucu AA (2014) Screen-printed Prussian Blue modified electrode for simultaneous detection of hydroquinone and catechol. *Sens Actuat B* 203:824–832. doi:10.1016/j.snb.2014.07.043
- Sun YG, Cui H, Li YH, Lin XQ (2000) Determination of some catechol derivatives by a flow injection electrochemiluminescent inhibition method. *Talanta* 53:661–666. doi:10.1016/S0039-9140(00)00550-6
- Lin H, Gan T, Wu K (2009) Sensitive and rapid determination of catechol in tea samples using mesoporous Al-doped silica modified electrode. *Food Chem* 113:701–704. doi:10.1016/j.foodchem.2008.07.073
- Asan A, Isildak I (2003) Determination of major phenolic compounds in water by reversed-phase liquid chromatography after pre-column derivatization with benzoyl chloride. *J Chromatogr A* 988:145–149. doi:10.1016/S0021-9673(02)02056-3
- Pistonesi M, Di Nezio M, Centurión M, Palomeque M, Lista A, Band BF (2006) Determination of phenol, resorcinol and hydroquinone in air samples by synchronous fluorescence using partial least-squares (PLS). *Talanta* 69:1265–1268. doi:10.1016/j.talanta.2005.12.050
- Nagaraja P, Vasantha R, Sunitha K (2001) A sensitive and selective spectrophotometric estimation of catechol derivatives in pharmaceutical preparations. *Talanta* 55:1039–1046. doi:10.1016/S0039-9140(01)00438-6
- Moldoveanu SC, Kiser M (2007) Gas chromatography/mass spectrometry versus liquid chromatography/fluorescence detection in the analysis of phenols in mainstream cigarette smoke. *J Chromatogr A* 1141:90–97. doi:10.1016/S0039-9140(01)00438-6
- Yin HS, Zhang QM, Zhou YL, Ma Q, Liu T, Zhu LS, Aia SY (2011) Electrochemical behavior of catechol, resorcinol and hydroquinone at graphene-chitosan composite film modified glassy carbon electrode and their simultaneous determination in water samples. *Electrochim Acta* 56:2748–2753. doi:10.1016/j.electacta.2010.12.060
- Dong JP, Qu XM, Wang LJ (2008) Electrochemistry of nitrogen-doped carbon nanotubes (CNX) with different nitrogen content and its application in simultaneous determination of dihydroxybenzene isomers. *Electroanalysis* 20:1981–1986. doi:10.1002/elan.200804274
- Wang ZH, Li SJ, Lv QZ (2007) Simultaneous determination of dihydroxybenzene isomers at single-wall carbon nanotube electrode. *Sens Actuat B* 127:420–425. doi:10.1016/j.snb.2007.04.037
- Han L, Zhang X (2009) Simultaneous voltammetry determination of dihydroxybenzene isomers by nanogold modified electrode. *Electroanalysis* 21:124–129. doi:10.1002/elan.200804403
- Zhang X, Duan S, Xu XM, Xu S, Zhou CL (2011) Electrochemical behavior and simultaneous determination of dihydroxybenzene isomers at a functionalized SBA-15 mesoporous silica modified carbon paste electrode. *Electrochim Acta* 56:1981–1987. doi:10.1016/j.electacta.2010.11.048
- Huang KJ, Wang L, Liu YJ, Gan T, Liu YM, Wang LL, Fan Y (2013) Synthesis and electrochemical performances of layered tungsten sulfide-graphene nanocomposite as a sensing platform for catechol, resorcinol and hydroquinone. *Electrochim Acta* 107:379–387. doi:10.1016/j.electacta.2013.06.060
- Zhu S, Gao W, Zhang L, Zhao J, Xu G (2014) Simultaneous voltammetric determination of dihydroxybenzene isomers at single-walled carbon nanohorn modified glassy carbon electrode. *Sens Actuat B* 198:388–394. doi:10.1016/j.electacta.2013.06.060
- Cui Y, Zhu Y, Li Y, Wang W, Xu F (2014) Electrochemical behavior of dihydroxybenzene isomers at MWCNTs modified electrode and simultaneous determination in neutral condition. *Res Chem Intermed* 40:3153–3162. doi:10.1007/s11164-013-1161-9
- Wang Y, Qu J, Li S, Dong Y, Qu J (2015) Simultaneous determination of hydroquinone and catechol using a glassy carbon electrode modified with gold nanoparticles, ZnS/NiS@ ZnS quantum dots and L-cysteine. *Microchim Acta* 182:2277–2283. doi:10.1007/s00604-015-1568-7
- Liu L, Ma Z, Zhu X, Alshahrani LA, Tie S, Nan J (2016) A glassy carbon electrode modified with carbon nano-fragments and bismuth oxide for electrochemical analysis of trace catechol in the presence of high concentrations of hydroquinone. *Microchim Acta* 183:3293–3301. doi:10.1007/s00604-016-1973-6
- Saravanan KR, Sathyamoorthi S, Velayutham D, Suryanarayanan V (2012) Voltammetric investigations on the relative deactivation of boron-doped diamond, glassy carbon and platinum electrodes during the anodic oxidation of substituted phenols in room temperature ionic liquids. *Electrochim Acta* 69:71–78. doi:10.1016/j.electacta.2012.02.077
- Akanda MR, Sohail M, Aziz MA, Kawde AN (2016) Recent advances in nanomaterial-modified pencil graphite electrodes for electroanalysis. *Electroanalysis* 28:408–424. doi:10.1002/elan.201500374
- Balan I, David IG, David V, Stoica AI, Mihailciuc C, Stamatin I, Ciucu AA (2011) Electro-catalytic voltammetric determination of guanine at a cobalt phthalocyanine modified carbon nanotubes paste electrode. *J Electroanal Chem* 654:8–12. doi:10.1016/j.jelechem.2011.02.002
- David IG, Bizgan AMC, Popa DE, Buleandra M, Moldovan Z, Badea IA, Tekiner TA, Basaga H, Ciucu AA (2015) Rapid determination of total polyphenolic content in tea samples based on caffeic acid voltammetric behavior on a disposable graphite electrode. *Food Chem* 173:1059–1065. doi:10.1016/j.foodchem.2014.10.139
- Zaidan LEMC, Napoleão DC, Guimarães G, Barbosa CMBM, Benachour M, Silva VL (2013) Validation methodology for identification and measurement of phenolic compounds in oil refinery effluent by HPLC. *Braz J Petroleum and Gas* 7:95–106. doi:10.5419/bjpg2013-0008
- Moraes FC, Cabral MF, Machado SAS, Mascaro LH (2008) Electro-catalytic behavior of glassy carbon electrodes modified with multiwalled carbon nanotubes and cobalt phthalocyanine for selective analysis of dopamine in presence of ascorbic acid. *Electroanalysis* 20:851–857. doi:10.1002/elan.200704107
- Laviron E (1974) Adsorption, autoinhibition and autocatalysis in polarography and in linear potential sweep voltammetry. *J Electroanal Chem* 52:355–393. doi:10.1016/S0022-0728(74)80448-1
- Mobin SM, Sanghavi BJ, Srivastava AK, Mathur P, Lahiri GK (2010) Biomimetic sensor for certain phenols employing a copper(II) complex. *Anal Chem* 82:5983–5992. doi:10.1021/ac1004037
- Laviron E (1979) General expression of the linear potential sweep voltammogram in the case of diffusionless electrochemical systems. *J Electroanal Chem* 101:19–28. doi:10.1016/S0022-0728(79)80075-3
- Bard AJ, Faulkner LR (2001) *Electrochemical methods fundamentals and applications*, 2nd edn. John Wiley & Sons Inc., New York, p 236
- Cesarino I, Moraes FC, Ferreira TCR, Lanza MRV, Machado SAS (2012) Real-time electrochemical determination of phenolic compounds after benzene oxidation. *J Electroanal Chem* 672:34–39. doi:10.1016/j.jelechem.2012.03.006