



Original article

Simultaneous determination of dihydroxybenzene isomers utilizing a thiadiazole film electrode



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ABSTRACT

The present study reports a sensitive electro-analytical method for the simultaneous determination of dihydroxybenzene isomers by using a thiadiazole film electrode, which was readily prepared by electropolymerization of 2,5-dimercapto-1,3,4-thiadiazole on a glassy carbon electrode with cyclic voltammetry. The functionalized electrode has a distinguishable and sensitive response to dihydroxybenzene isomers. Under the optimized conditions, the linear stripping peak currents showed good linear relationships with hydroquinone, catechol and resorcinol at concentration ranges 0.50–120, 0.50–110 and 1.00–110 $\mu\text{mol/L}$, and the detection limits are 0.1, 0.1 and 0.3 $\mu\text{mol/L}$, respectively. The proposed method is applicable to the simultaneous determination of dihydroxybenzene isomers in real samples with the relative standard deviations of less than 5.7% and the recovery rates of 95.6%–106%. The constructed electrode is characterized by simple preparation, good selectivity, and high sensitivity advantages.

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1. Introduction

Dihydroxybenzene, an important industrial bulk and processed material, is widely used in cosmetics, dyes, tanning, chemical and pharmaceutical industry. Dihydroxybenzene has three isomers, which are identified as hydroquinone (HQ), catechol (CA) and resorcinol (RE). The dihydroxybenzene isomers widely exist in the environment as harmful pollutants, since CA and HQ are significant air pollutants, RE damages human skin and causes poisoning due to absorption. Because they are toxic to humans and difficult to degrade in the ecological environment, it is very necessary to develop a simple and rapid analytical method for simultaneous determination of dihydroxybenzene isomers based on comprehensive consideration of industrial production and pollution prevention. However, dihydroxybenzene isomers have similar structures and characteristics, and consequently, are difficult to separate by physical or chemical means, and can create problems in quantitative analysis.

In recent years, electrochemical methods for the simultaneous determination of dihydroxybenzene isomers, especially the technique of the modified electrode, have significant advantages over other methods in terms of experimental

procedure and sensitivity [1–9]. With the use of the modified electrode, the electropolymerized polymer film may be a good choice, because it can enhance both selectivity and sensitivity, improve response time, decrease the overpotential of the analytes in the redox process, and exhibits good stability [10]. Many electrodes modified with electropolymerized polymers have been used in the electrochemical analysis of dihydroxybenzene [8,9]. For instance, 2,5-dimercapto-1,3,4-thiadiazole (DMcT), a heterocyclic thiol compound, has been successfully used for the electrode modification and electrochemical analysis of biological samples and heavy metals [11,12]. As a conducting polymer films, *p*-DMcT, is a promising material in modified electrodes for monitoring dihydroxybenzene isomers because of its high stability, uniformity, and reproducibility. On the basis of the previous study [12], we determined that dihydroxybenzene isomers have excellent response on the glassy carbon electrode modified by *p*-DMcT film, and so proceeded to investigate and develop a simultaneous, quantitative method for the analysis of dihydroxybenzene isomers.

2. Experimental

2.1. Chemicals and apparatus

The DMcT was purchased from J&K Chemical, Ltd. (Beijing, China). The DMcT solution (1.00×10^{-5} mol/L) was prepared by

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dissolving 15.0 mg of DMcT in absolute ethanol with 0.10 mol/L NaOH and diluting to 100-mL in a calibrated flask. The 0.1 mol/L phosphate buffer solutions (PBS) of various pH values were prepared using KH_2PO_4 and Na_2HPO_4 , according to an appropriate proportion. The isomers, hydroquinone (HQ), catechol (CA), and resorcinol (RE), were purchased from Shanghai Chemical Reagent Co., Ltd. (China). Their stock solutions were prepared by dissolving appropriate amounts of solid material in PBS and stored in brown reagent bottles. Low-concentration solutions of the dihydroxybenzene isomers for voltammetric investigations were freshly prepared from each stock solution with PBS. The standard samples of CA (GSB 07-1249-2000), RE (GSB 07-1250-2000) and HQ (GSB 07-1251-2000) were purchased from Northern Hanson Biotech Co., Ltd. (Beijing, China) and used as the three certified reference materials (CRMs). High-purity nitrogen was used for solution de-aeration and to maintain the nitrogen atmosphere within the electropolymerization process.

All other chemicals were of analytical grade or higher quality. Deionized water ($>15\text{ M}\Omega$) was used throughout the present research and acquired from a KLUP-III water treatment system (Kang ning Water Industry, China).

All voltammetric experiments were carried out using a computer-controlled electrochemical system (CHI 832B, Shanghai Chenhua Instrument, Co., Ltd., China). The standard three-electrode arrangement consisted of an Ag/AgCl reference electrode (CHI 111, Shanghai Chenhua Instrument, Co., Ltd., China), a Pt counter electrode (CHI 115, Shanghai Chenhua Instrument, Co., Ltd., China), and a modified electrode as working electrode. A solution containing 0.1 mol/L PBS of pH 5.5 and 0.1 mol/L KCl was used as the electrolyte in the voltammetric investigations.

2.2. Preparation of electropolymerized DMcT film-electrode

A glassy carbon disk electrode (GCE, 3.0 mm diameter) was first polished to a mirror-like finish with 3000-mesh emery paper, followed by 1.0- and 0.05- μm alumina slurry. The GCE was then washed successively with 1:1 nitric acid and alcohol, sonicated in a deionized water bath to remove any residual alumina, and then dried in air before use. The 1.0×10^{-5} mol/L DMcT dissolved in 0.10 mol/L NaOH was employed as precursor for electropolymerization of DMcT. The electropolymerization of DMcT on the GCE was performed between -0.40 V and 1.00 V at a scan rate of 50 mV/s . When the scanning cycle had been repeated for 30 rounds, a smooth film was obtained on the surface of the GCE. After the electrode was washed thoroughly in PBS to remove the adsorbed DMcT monomer and dried in air, a poly(2,5-dimercapto-1,3,4-thiadiazole)-modified GCE (*p*-DMcT/GCE) was obtained. From the *p*-DMcT/GCE surface, a fuscous film with isolated distribution was observed by scanning electron microscopy, suggesting that DMcT had been polymerized on the surface of the GCE to form a *p*-DMcT/GCE, as reported in the previous study [12].

2.3. Determination of dihydroxybenzene isomers

10.0 mL of PBS containing an appropriate concentration or ratio of dihydroxybenzene isomers was transferred into an electrochemical cell. After the test solution was sufficiently mixed with a small magnetic stirrer, the test solution was held at static state for 30 s at open circuit potential. Then, the voltammetric curve was recorded by applying a differential pulse voltammetry (DPV) from -0.20 V to 1.00 V . Peak currents were measured at 0.16 V for HQ, 0.27 V for CA and 0.68 V for RE. All experiments were repeated at least five times, and the mean values of measurements were presented with their relative standard deviations.

3. Results and discussion

3.1. Electrochemical responses of dihydroxybenzene isomers at *p*-DMcT/GCE

Fig. 1 showed the CVs and DPVs recorded for the mixture of dihydroxybenzene isomers in PBS at both the bare and *p*-DMcT/GCE, respectively. The oxidation peaks of only two were observed for the three isomers on the bare GCE (black curve) at 0.32 V and 0.74 V, respectively, and showed a broad, unresolved peak at ca. 0.32 V for HQ and CA. In contrast, the oxidation waves of HQ, CA and RE were clearly resolved in CV or DPV with peak potentials (E_{pa}) of 0.16, 0.27 and 0.68 V on the *p*-DMcT/GCE (red curve), respectively. As can be observed in Fig. 1, dihydroxybenzene isomers can be clearly identified, due to two larger peak potential differences (ΔE_{pa}) of 0.11 and 0.41 V between adjacent peaks. On the other hand, the peak potential of three isomers shifted negatively at *p*-DMcT/GCE, and their peak currents were larger and the peak shape was sharper, showing a higher sensibility for the responses of substrates.

3.2. Effects of pH on resolution and sensitivity

DMcT is a heterocyclic thiol compound, providing the *p*-DMcT layer on the electrode with the $-\text{SH}$ group [11]. The *p*-DMcT can form a film with a negative charge on GCE in PBS of pH 5.5 because of two aqueous pK_a values of -1.4 to 2.1 and 7.5 [13]. Both CA ($\text{pK}_a = 9.4$) and HQ ($\text{pK}_a = 10.0$) exist in their protonated forms at a

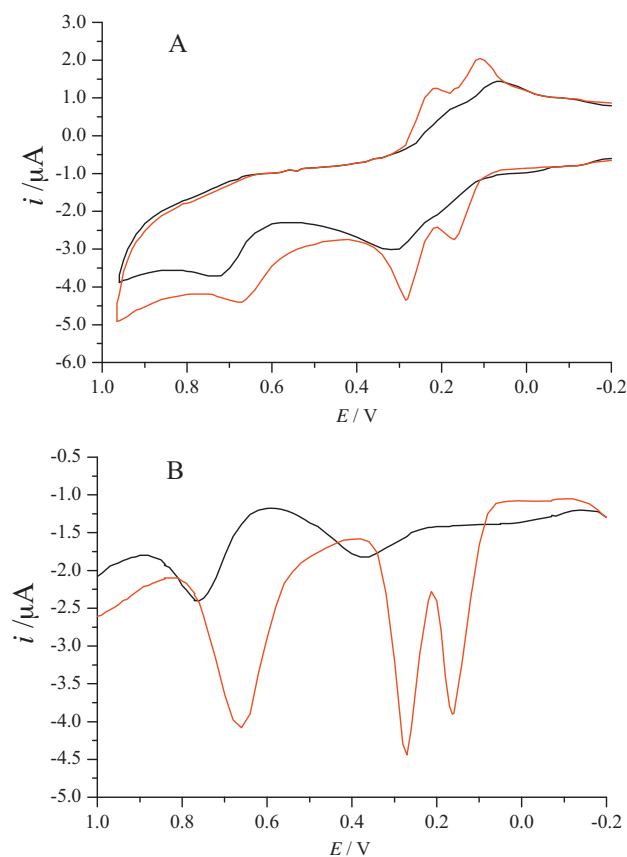


Fig. 1. (A) Cyclic voltammograms and (B) differential pulse voltammograms for the mixed solution with $70.0\ \mu\text{mol/L}$ each dihydroxybenzene isomer in PBS (pH 5.5) at bare GCE (black curve) and *p*-DMcT/GCE (red curve). Conditions for DPV were: incr. E, 0.004 V ; pulse amplitude, 0.05 V ; pulse width, 0.06 s ; pulse period, 0.2 s . (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

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