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Original Article

Voltammetric determination of chlorogenic acid in pharmaceutical products using poly(aminosulfonic acid) modified glassy carbon electrode

Mingyong Chao[*], *Xinying Ma*

Department of Chemistry and Chemical Engineering, Heze University, Heze 274015, PR China

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ABSTRACT

In this work, a poly(aminosulfonic acid) modified glassy carbon electrode was fabricated and the electrochemical behavior of chlorogenic acid (CGA) was studied by cyclic voltammetry. Compared with a bare glassy carbon electrode, the modified electrode exhibits excellent catalytic effect on the electrochemical redox of CGA. Utilizing this catalytic effect, a sensitive and selective electrochemical method for the determination of CGA was developed. The analytical parameters were optimized. Under the optimized conditions, the oxidation peak current is linearly proportional to the concentration of CGA in the range from 4.00×10^{-7} to 1.20×10^{-5} mol/L and the detection limit is 4.00×10^{-8} mol/L. Further, the performance of the proposed method has been validated in terms of linearity ($r = 0.9995$), recovery (96.3–102.8%), reproducibility (RSD < 4.0%, $n = 6$) and robustness. The developed method has been successfully applied for the determination of CGA in a variety of pharmaceutical products.

1. Introduction

Cholorogenic acid (CGA), an ester of caffeic acid and quinic acid, is a naturally occurring phenolic compound with a structure as shown in Fig. 1 [1]. CGA is a potent antioxidant found in many foods and drinks, most notably in coffee. Clinical investigations have implied that consumption of CGA can have anti-hypertension and anti-obesity effects [2,3]. CGA also can serve as anti-inflammatory, antitumor, antimutagenic and anticarcinogenic agent [4,5]. As a bioactive compound that has many therapeutic effects, CGA can be found in more than 170 kinds of traditional Chinese pharmaceutical products such as tablets, capsules, and herbal injections. Therefore, fast and convenient determination of CGA in pharmaceutical products is of great importance.

Various methods for the determination of CGA have been developed, namely, near-infrared spectroscopy [6–8], capillary electrophoresis [9,10], nano-liquid chromatography-electrospray ionization mass spectrometry [11], high-performance liquid chromatography [12–18], ultra-performance liquid chromatography [19], liquid chromatography-mass spectrometry [20,21], chemiluminescence [22,23], and electrochemical

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[*] *Corresponding author*. Department of Chemistry and Chemical Engineering, Heze University, Heze 274015, PR China.
E-mail address: chaomingyong@foxmail.com (M. Chao).

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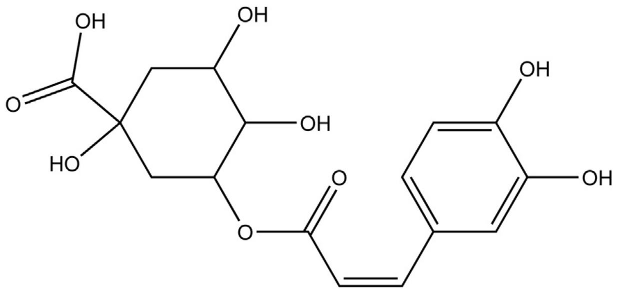

Fig. 1 – Molecular structure of chlorogenic acid.

methods [24–27]. Among these reported methods, near-infrared spectroscopy requires expensive equipment and resource-intensive calibrations. Capillary electrophoretic analyses are not very sensitive. Chromatographic methods require expensive equipment, large amounts of organic solvents, and are time-consuming. Electrochemical methods are obviously better due to their convenience, speed, higher sensitivity, and reproducibility [28–34]. For electrochemical determination of CGA, modified electrodes with modifiers such as ionic liquid containing iridium nanoparticles and polyphenol oxidase [25], horseradish peroxidase, DNA and silica–titanium composite [26], bean sprout homogenate and chitosan microspheres composite [27], and tetranuclear copper(II) complex [24] have been reported.

In recent years, electrically conductive polymers have been used as electrode modifiers due to their unique properties such as strong adherence to the electrode surface, more active sites and good chemical stability [35,36]. When fabricating polymer modified electrodes, polymer films are often electropolymerized to the surface of an electrode [37,38].

In the present work, a poly(aminosulfonic acid) modified glassy carbon electrode (PASA/GCE) for the determination of CGA was fabricated through electropolymerization and the fabricated electrode was characterized by scanning electron microscopy (SEM) and voltammetry. The electrochemical behavior of CGA at the PASA/GCE was investigated in detail by cyclic voltammetry and the polymer film showed an excellent electrocatalytical effect on the redox of CGA. Further, a novel voltammetric method for the determination of CGA in pharmaceutical products was established and validated. The fabrication conditions of the PASA/GCE and the analytical parameters were optimized. The results of CGA determination obtained using the PASA/GCE were compared with those obtained by other electrochemical methods reported in the literature.

2. Experimental methods

2.1. Chemicals

All chemicals were of A.R. grade and were used as received without any further purification. CGA was purchased from Shanghai Fortune bio-tech Co., Ltd. (Shanghai, China). Aminosulfonic acid and all other chemical reagents were obtained from Beijing Chemical Reagent Company (Beijing, China). A 8.0×10^{-3} mol/L CGA stock solution was prepared by dissolving 0.147 g of CGA in 50.00 mL of absolute ethanol. Phosphate buffers (pH = 2.2 ~ 8.0) were prepared by mixing the stock solutions of 0.2 mol/L Na_2HPO_4 and 0.1 mol/L citric acid. All aqueous solutions were prepared using double-distilled water.

2.2. Apparatus

A CHI 660C Electrochemical Workstation (Chen-hua, Shanghai, China) was used for voltammetric measurements. A three-electrode system was employed with a bare GCE or PASA/GCE (3.8 mm in diameter) as the working electrode, a platinum wire electrode as the counter electrode, and an Ag/AgCl electrode as reference electrode. A field emission SEM Sirion 200 (FEI, Hillsboro, Oregon, USA) was used for recording the SEM image of the polymer film at the surface of the modified electrode. Acidity was measured using a PHS-3B Precision pH meter (Shanghai, China) and sonication was performed using a KQ-100 ultrasonic cleaner (Kunshan, China).

2.3. Fabrication of the PASA/GCE

The polymerization solution was prepared by mixing 10.00 mL of pH 8.0 phosphate buffer, 0.50 mL of 8.0×10^{-3} mol/L aminosulfonic acid solution and 9.50 mL of double-distilled water. The GCE was pretreated by polishing its surface successively with an abrasive paper (grit 1000) and an aqueous slurry of alumina powders (0.05 μm) on a polishing cloth, and then rinsed successively with 1:1 HNO_3, absolute ethanol, and distilled water to give a smooth and clean electrode surface. Then, the electrode was ultrasonicated in distilled water for about 30 seconds, and finally allowed to dry under an infrared lamp. Using the pretreated GCE as working electrode, an Ag/AgCl electrode as the reference electrode and a platinum electrode as the counter electrode, PASA/GCE was prepared by cycling the potential between −1.0 and 2.4 V for 12 cycles in the polymerization solution (prepared as described) at a scan rate of 120 mV/second. After polymerization, the modified electrode was rinsed with double-distilled water and dried in air at room temperature to give a PASA/GCE.

2.4. Sample preparation

2.4.1. Qingkailing injection and Mailuoning injection samples

Ten vials of each injection from different batches were mixed and analyzed directly without any pretreatment.

2.4.2. Honeysuckle samples

The traditional Chinese herbal medicine honeysuckle was carefully ground to a fine powder and sieved through a 600-mesh screen, then 5.0 g of the powder was extracted with 30 mL of ethanol for 30 minutes with ultrasonic agitation. The resulting mixture was filtered and the residue was similarly extracted twice. All filtrates were transferred into a 100 mL volumetric flask and diluted to scale with ethanol.

2.5. Electrochemical measurement

Cyclic voltammetry measurements were made in an unstirred, nondeaerated pH 4.0 phosphate buffer and all potentials