



Simultaneous determination of ascorbic acid and rutin in pharmaceutical preparations with electrochemical method based on multi-walled carbon nanotubes–chitosan composite film modified electrode

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ABSTRACT

In this paper, the simultaneous voltammetric determination of ascorbic acid (AA) and rutin (Ru) has been achieved at an acetylene black paste electrode modified with multi-walled carbon nanotubes–chitosan composite film (denoted as MWCNTs–CHIT/ABPE). Compared with bare electrode, the peak currents of AA and Ru at MWCNTs–CHIT/ABPE increased greatly and the anodic peak potential difference (ΔE_{pa}) between AA and Ru are up to 342 mV, which is undoubtedly attributed to the unique characteristics of AB and MWCNTs such as excellent electric conductivity, high surface area and strong adsorptive abilities, resulting in higher accumulation efficiency to AA and Ru. The influences of some experimental conditions on the oxidation of AA and Ru were tested and the calibration plot was examined. Under the optimized condition, a good linearity was obtained in the concentration range of 1 μ M–0.4 mM for AA in the presence of 10 μ M Ru and 20 nM–10 μ M for Ru in the presence of 1 mM AA. The detection limits ($S/N=3$) of AA and Ru are 0.8 μ M and 10 nM, respectively. The proposed method was successfully applied to the simultaneous determination of AA and Ru in pharmaceutical samples with reliable recovery.

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1. Introduction

Recently, the biological, pharmacological, and medical properties of plant polyphenols, specifically bioflavonoids have been extensively researched. Rutin (3',4',5,7-tetrahydroxyflavone-3 β -D-rutinoside, Ru) is one of the flavonoids and naturally occurs in the plant kingdom and generally present in the common human diet. It has been reported that Ru possesses various biological activities, such as antitumor, antibacterial, enzyme inhibitory, and pro- or antimutagenic properties [1]. Also, Ru has a direct construction action on the capillary bed and decreases the permeability and fragility of the blood vessels [2]. Therefore, Ru has been used clinically as the therapeutic medicine and various preparations containing Ru are registered as drugs worldwide [3]. Ascorbic acid (AA), also known as Vitamin C, is a vitamin soluble in water, which interferes with oxidative-reductive and other metabolic processes in an organism, is important for the activity of enzymes, keeping the balance among some enzymatic groups and has great importance for physiological permeability of capillaries [4]. Some works have claimed better results from the use of Ru in combination with AA than from Ru alone. It has been suggested that these substances could be classed as vitamins, particularly of the 'Vitamin P'. What is more, AA is present as a natural co-existence

with Ru in plants. For this reason, they will interfere with each other during determination. So, the establishment of a fast, simple, sensitive and selective analytical method to detect AA and Ru segregately or simultaneously in various matrices will be of great significance.

At present, the main techniques for the separation and determination of AA and Ru are ultra-violet spectrophotometry with dual-wavelength technique [5], sequential injection analysis with solid phase extraction [4], high performance liquid chromatography [6], capillary electrophoresis with electrochemical detection [7,8] and capillary electrophoresis with ultra-violet detection [9]. Some of the methods above usually take a long time to make previous separation for mixture sample or need complicated chemometrics treatments to analytical signals, some require complicated instrument and skilled operator, which make them less convenient in practice. In contrast, electrochemical method is simple and rapid. Since AA and Ru are both electroactive compounds, various electrochemical methods for the individual determination of AA [10–12] and Ru [13–16] have been described. However, for simultaneous determination of AA and Ru, there are a great number of challenges. One major difficulty is that voltammetric peaks corresponding to the oxidation of AA and Ru are largely overlapped in many cases. In addition, the oxidation and adsorption competition of the two compounds at the electrode surface makes the relationship between the voltammetric response and concentration in the mixture is nonlinear. To solve these problems, many materials were used to modify electrodes.

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Single-walled carbon nanotubes modified carbon ionic liquid electrode [17], pyridinium-based ionic liquid modified carbon paste electrode [18] and gold nanoparticles/ethylenediamine/carbon nanotube modified glassy carbon electrode [19] have been fabricated and applied in the selective determination of Ru in the presence of a certain concentration of AA. However, according to our knowledge, simultaneous determination of AA and Ru by electrochemical methods has not been reported in any literature. Therefore, the search of a reliable material for the electrode modification is of considerable interest for the simultaneous determination.

Since their discovery in 1991 [20], with their exceptional electrical, chemical and mechanical properties, carbon nanotubes (CNTs) have become extremely attractive over the past years in the task of chemical sensors and biosensors [21–23]. However, the nano size, high symmetry and high aspect ratio of CNTs lead aggregations in solutions due to strong intertubular attraction. It is very important and essential that to disperse carbon nanotube bundles and ropes for the modification of electrodes. Chitosan (CHIT), a poly(aminosaccharide) prepared by deacetylation of natural chitin, has proven to be a promising functional material due to its excellent membrane-forming ability, biodegradability, nontoxicity, biocompatibility and high mechanical strength [24]. In previous reports, CHIT was found to be a perfect dispersant to disperse CNTs and the resulting CNTs–CHIT suspension was very homogeneous and stable [25,26]. Based on this, CNTs–CHIT composite film modified electrodes were fabricated and the voltammetric measurements of some substances at these electrodes were greatly enhanced, which make them extremely attractive [25–29]. Acetylene black (AB), a particularly pure form of graphitic carbon black pigment, is formulated by the controlled combustion of acetylene in air under pressure. On account of its excellent electric conductivity, large specific surface area, and strong adsorptive ability, AB has been widely used in electrochemistry and electroanalysis [30–32]. However, the fabrication of CNTs–CHIT composite film modified acetylene black paste electrode for analytical application has not been reported in any literatures.

As far as we are aware no work on simultaneous determination of AA and Ru by electrochemical methods has been reported previously, this paper describes the construction, performance and application of a multi-walled carbon nanotubes–chitosan composite film modified acetylene black paste electrode (MWCNTs–CHIT/ABPE) for the simultaneous determination of AA and Ru. In comparison with the poor responses of AA and Ru at conventional paste electrode made of carbon powder, the signals for AA and Ru at the modified electrode were apparently improved, and the oxidation peaks for AA and Ru were separated with the peak potential difference (ΔE_p) of 342 mV, which indicated that AA and Ru could be identified entirely at the modified electrode. Moreover, this electrode exhibited attractive performances for simultaneous determination of AA and Ru, such as fast voltammetric response, wide linear concentration range, low detection limit, excellent reproducibility and good stability. The sensor has been successfully applied to the determination of AA and Ru in pharmaceutical formulations with good recovery in the range of 98.3–103.5% and 101.6–102.5%, which suggested that it has great potential for practical applications.

2. Experimental

2.1. Chemicals and solutions

Ascorbic acid (AA) and rutin (Ru) were purchased from Sinopharm Chemical Reagent Co., Ltd., China. Multi-walled carbon nanotubes (MWCNTs) (8–15 nm in diameter, about 50 μm in

length and about 95% in purity) were supplied by Chengdu Organic Chemicals Co., Ltd., Chinese Academy of Sciences, China. Acetylene black (AB, purity >99.99%) was supplied by STREM Chemicals, USA. Chitosan (95% deacetylation) was obtained from Shanghai Biochemical Co., Ltd., China. Pharmaceutical formulations (compound rutin tablets with the specified amount of 20 mg Ru and 50 mg AA per tablet) served as real samples (sample 1: Shanxi Linfen Qilin Pharmaceutical Co., Ltd., China; sample 2: Shanghai Fuxing Zhaohui Pharmaceutical Co., Ltd., China; sample 3: Shanxi Yunpeng Pharmaceutical Co., Ltd., China). Other chemicals were in analytical reagent grade from Shanghai Chemical Reagent Co., Ltd., China and used as received.

Standard solutions of AA (1.0×10^{-2} M) and Ru (1.0×10^{-3} M) were prepared from weighted amounts of AA and Ru, and dissolved in water and ethanol, respectively. Fresh standard solutions were always prepared to avoid the oxidation of AA and hydrolysis of Ru in the stock solution. The dilute solutions were freshly prepared from the stock solution when needed. A chitosan solution (0.5 wt%) was prepared by dissolving 0.05 g of chitosan in 10 mL 1% acetic acid aqueous solution. The supporting electrolyte was 0.1 M hydrochloric acid aqueous solution. All solutions were prepared with doubly distilled water.

2.2. Apparatus

All the electrochemical experiments were performed using a model JP-303 polarographic analyzer (Chengdu Instrument Factory, Chengdu, China). A conventional three-electrode system was used throughout. The working electrode was the MWCNTs–CHIT/ABPE, the counter electrode was a platinum wire electrode and a saturated calomel electrode (SCE) was used as reference electrode. A digital pH meter pHs-3c model (Shanghai Leichi Instrument Factory, China) was used for the preparation for buffer solutions in electrochemical experiments. All potentials in this paper were quoted with respect to the SCE. The morphologies of the modified electrode were studied on a JEOL JSM-6610LV scanning electron microscope (Tokyo, Japan) at an accelerating voltage of 20 kV. The ultraviolet (UV) absorption spectra were recorded in the wavelength range 200–450 nm at room temperature on a UV-2501PC spectrophotometer (Shimadzu Co., Japan) with 1 cm matched quartz cells.

2.3. Preparation of the MWCNTs–CHIT/ABPE

The ABPE was prepared by thoroughly mixing 1.20 g AB powder with 0.30 g solid paraffin and ground for at least 0.5 h by hand in a small mortar, and then the mixture was heated for about 5 min until a homogeneous paste was obtained. A portion of the paste was packed into a glass capillary (inner diameter: 1.0 mm) immediately, in which a copper wire was inserted to establish electrical contact. The electrode surface was polished manually on a piece of tracing paper until it had a shiny appearance. A 0.5 wt% CHIT solution was prepared by dissolving CHIT solid in 1% acetic acid aqueous solution. Then 2 mg of carboxylated MWCNTs was dispersed with the aid of ultrasonic agitation in 1 mL of CHIT solution to give a 2 mg mL⁻¹ black suspension, then a 2 μL of this MWCNTs dispersion was cast on the electrode surface with a micro-syringe and the solvent was evaporated at room temperature in the air to obtain the MWCNTs–CHIT/ABPE. The chitosan modified ABPE (CHIT/ABPE) was prepared in a similar way by casting 2 μL 0.5 wt% CHIT solution onto the surface of ABPE but without MWCNTs. In order to show the unique properties of AB, a conventional carbon paste electrode (CPE) made of carbon powder was also prepared for comparison in a similar way by thoroughly mixing 1.20 g carbon powder with 0.30 g solid paraffin.

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