



Rapid voltammetric detection of kojic acid at a multi-walled carbon nanotubes screen-printed electrode



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ABSTRACT

A differential pulse voltammetric method for the determination of kojic acid (KA) was developed. The electrochemical behavior of KA at a multi-walled carbon nanotubes modified screen-printed electrode (MWCNTs-SPCE) was explored. A single irreversible oxidation peak was observed at a potential of 0.791 V and 0.989 V on the MWCNTs-SPCE and screen-printed carbon electrode (SPCE), respectively. Under the optimized conditions, the anodic peak current of KA recorded by differential pulse voltammetry varies linearly with KA concentration in the range 0.02–5 mM with a detection limit of 0.016 mM. The MWCNTs-SPCE was used for quantitative analysis of KA in food samples and the results indicate the feasibility of the amperometric method for KA analysis in routine detection.

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1. Introduction

Kojic acid (KA), 5-hydroxy-2-(hydroxymethyl)-4-pyranone, one of the oldest identified natural antibiotics produced by filamentous fungi and bacteria of many species of *Aspergillus*, *Penicillium* and *Acetobacter* [1], has been considered as a therapeutic agent and for the prevention of pigmentation [2]. In food production, KA has been used as an antioxidant, an additive for its preservative actions against both chemical and microbial degradation [1,3], to preserve food color, to inhibit tyrosinase, which is the essential enzyme for melanin formation, by chelating the copper in enzyme structure [4,5], and as an inhibitor of nitrosopyrrolidine formation in fried food [6–8]. In addition, KA is a by-product of some fermentation and plays an important role in monitoring fermentation processes [4,9]. For example, KA is a by-product in the fermentation process of malting rice for making rice wines, sweet beverages, and distilled liquors [6]. KA is used in the production of a number of foodstuff, including soy bean paste, soy sauce and sake [1,6]. However, because the 4-pyrone in KA molecules has aromaticity like benzene, it is not clear whether KA in all kinds of foodstuffs have side effects on human health [10]. Although consumption of KA at low levels does not present a concern for safety [1], some

studies showed that continuous overuse of KA may have adverse effect on human health and is possible to be a carcinogenic and tumorigenic [11]. The Japanese Ministry of Health, Labor, and Welfare re-evaluated the use of kojic acid in the food and personal care industries due to concerns of its possible carcinogenicity [7,12], and furthermore the United States Food and Drug Administration has not approved kojic acid for use in over-the-counter pharmaceutical products [7,13].

Therefore, the development of a convenient, economical, rapid and sensitive method for the determination of KA in different samples is important. To date, spectrometric [14], fluorimetric [15], flow injection [16], stopped-flow [17], ion-pair liquid chromatography [18], high-performance liquid chromatography [2,19–21], and capillary electrophoresis [22] techniques have been employed for the identification and determination of KA. Unfortunately these techniques require expensive instruments, skilled operators, and are complicated procedures.

Electrochemical detection of KA [5,7,23] is an alternative method which has attracted attention due to its fast response, low-cost instrument, simple and time saving operation, high sensitivity and overall, an affordable cost per sample. Kinetics of KA oxidation at conventionally carbon electrodes is slow and so a relatively high overpotential is required. In electrochemical analysis, the key component is electrode modification, which requires the selection of suitable material to improve the determination performance. Chemically modified electrodes (CMEs) have attracted consider-

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able interest over the past decades as researchers attempted to exert more direct control over the chemical nature of an electrode surface. Accordingly, many efforts have been made to lower the overpotential of KA oxidation by using CMEs [4,9,16,24–28]. Each electrode of these methods needs to be carefully regenerated after each measurement, this process being time-consuming and which may not be suitable for routine or on-site uses.

Screen-printed electrodes (SPEs) have attracted much more interest and challenged the conventional three-electrode system due to its various advantages such as simple fabrication, small size, disposability and easy mass production at low cost [29–31]. In recent years, introducing nanomaterials like carbon nanotubes (CNTs) to electrode modification is a hot topic owing to their unique structure, high surface-to-volume ratio, high specific surface area and excellent electronic conductivity. Electrodes modified with carbon nanotubes (CNTs) have been employed for the improved detection of either inorganic or biological molecules. Such modified electrodes are expected to have improved electrocatalytic activity toward electrochemical analytical applications in comparison to the bulk electrode, which may be attributed to their electronic structure, high electrical conductivity, and active sites [31–33].

A simply voltammetric method based on multi-walled carbon nanotubes modified screen-printed carbon electrode (denoted throughout as MWCNTs-SPCE) for the determination of KA in apple and rice vinegar samples has been developed. The MWCNTs-SPCE presented the advantages such as mass production and rapid response time without artificial modification. To our knowledge, there is no literature for the direct voltammetric detection of KA in food samples using MWCNTs-SPCE. The proposed electrochemical method offers significant advantages such as fast speed without the complicated pretreatment steps, low cost per analysis, and small sample volume (50 μL) which are associated to disposable sensor. In view of optimization and validation results as well as applicability to real samples, the voltammetric method could be considered as a good alternative for routine analysis of KA in foodstuffs.

2. Experimental

2.1. Reagents and solutions

KA was provided by Sigma-Aldrich. All other chemicals employed were of analytical reagent grade (Merck or Sigma) and they were employed without further purification. Doubly distilled water was used in all solution preparations. For voltammetric studies stock standard solution (1×10^{-3} M) of KA was daily prepared in double distilled water. The working solutions were prepared just before use by diluting each stock standard solution with supporting electrolyte (0.12 M BRB of pH 2.21). For study of pH effect Britton-Robinson buffer (BRB) solutions of pH 2.21–10.38 were used, whereas for all other experiments, BRB of pH 2.21 was used.

For spectrometric studies a stock standard KA solution of 1000 $\mu\text{g mL}^{-1}$ was prepared. A 5 M solution of sulfuric acid was prepared in double distilled water. Further, suitable volumes of stock solutions containing 100 $\mu\text{g/mL}$ KA and 1 mL H_2SO_4 5 M were placed into the 5 mL volumetric flasks and brought to volume with double distilled water.

2.2. Apparatus

All voltammetric measurements were performed with an AUTOLAB electrochemical analyzer (PGSTAT 128N Ecochemie B.V., Netherlands). The terminals of the working (WE), reference (RE) and counter electrodes (CE) of the AUTOLAB electrochemical analyzer were connected to the respective terminals of the disposable SPE system via standard connectors and all data processing and

experimental controls were driven through the Nova 1.8 software installed on a computer interfaced with the electrochemical analyzer.

Commercially available screen-printed carbon electrodes and screen-printed carbon electrodes modified with multi-walled carbon nanotubes were utilized sourced from Dropsens (Ovideo, Spain) which are produced exclusively on ceramic substrates. The planar screen-printed electrode 3.4 cm \times 1.0 cm \times 0.05 cm (length \times width \times height), as specified by producer, consists of three main parts which are a carbon working electrode unmodified (SPCE, ref.110) or modified with multiwalled carbon nanotubes (10 nm diameter and 1–2 μm length) containing approximately 5% ratio of carboxylic groups (SPCE-MWCNT, ref. 110CNT), a graphite counter electrode and a silver pseudo-reference electrode. The carbon working screen printed surface for both SP electrodes is 4 mm in diameter, which resulted in an apparent geometric area of 0.125 cm². Further details about disposable multi-walled carbon nanotube screen printed sensors can be obtained from the supplier's website www.dropsens.com. All experiments were carried out at room temperature (20–23 °C) using a new electrode for each assay.

The absorbance spectra were recorded on a Jasco V-530 spectrometer provided with matched 1.0 cm quartz cuvettes cells (volume, 5 mL). The suitable wavelength at which the derivative spectrum crosses the zero-line was linearly approximated from two neighboring measurements. Suitable settings were: slit width 1 cm, scan speed 100 nm/min.

Chromatographic experiments were performed with an Agilent 1260 Infinity series LC/MWD (Agilent Technologies) system, consisting of the following modules: quaternary pump (Quant Pump – G1311B), automated injector (ALS – G1329B), column thermostat (Infinity TCC – G1316C), and a multi-channel UV–vis detector (MWD VL – G1365D). System control and data acquisition were made with the Agilent Chemstation for LC 3D, version 04.03(16).

The topography and morphology of the working electrode surface (SPCE and MWCNTs-SPCE) was characterized by atomic force microscopy (AFM). AFM images were recorded with the Integrated Platform SPM-NTegra, model Prima microscope (NT-MDT trade mark) in noncontact mode using a cantilever with silicon tip of NSG-01 (NT-MDT). The surface of the working electrode was scanned in several locations to identify specific fingerprints of the nanocarbon material. The details of the topography were recorded on a down-scale from 1 μm to 100 nm to show specific fingerprints before and after coating with KA.

2.3. Electrochemical behavior of KA at SPCE and MWCNTs-SPCE

The SPCEs were connected to the respective terminals of the AUTOLAB electrochemical analyzer for measuring voltammetric response. In all such experiments, 50 μL drop of analyte solution in BRB pH=2.21 were dispensed on the SPCEs covering the three electrodes to connect the electrochemical cell.

Cyclic voltammetric (CV) experiments were performed in the potential range 0.0 V to +1.2 V with a scan rate of 100 mV s^{-1} unless otherwise stated. Differential pulse voltammograms (DPVs) were recorded between 0.0 and +1.2 V for different concentrations of KA solutions prepared in BRB, pH=2.21. Differential pulse voltammetric (DPV) recordings were carried out in the potential range +0.4 to +1.2 V under following instrumental parameters: scan rate of 10 mV s^{-1} , pulse amplitude 25 mV, sampling width 17 ms, pulse width 100 ms, pulse period 500 ms. The oxidation peak of KA at +0.791 V obtained in DPV was used for quantification. All experiments were carried out at room temperature (22 ± 2 °C). All the applied potentials mentioned in the paper are referred to the internal Ag pseudo-reference electrode of the SPCEs. The KA quantitation was achieved by measuring the peak current and the

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