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Sensors and Actuators B 119 (2006) 135–142

SENSORS AND ACTUATORS B CHEMICAL

www.elsevier.com/locate/snb

Electrocatalytic oxidation and amperometric determination of BHA at graphite–wax composite electrode with silver hexacyanoferrate as electrocatalyst

D. Jayasri, S. Sriman Narayanan *

Department of Analytical Chemistry, University of Madras, Guindy Campus, Chennai 600 025, India

Received 17 July 2005; received in revised form 28 November 2005; accepted 29 November 2005

Abstract

A graphite–wax composite electrode chemically modified with silver hexacyanoferrate (AgHCF) as a redox mediator was fabricated. Cyclic voltammetry was used to study the redox property of the AgHCF modified graphite–wax composite electrode. Various experimental parameters influencing the electrochemical behavior of the modified electrode were optimized by varying the background electrolytes, scan rates and pH. The electrochemical rugosity of the modified electrode at various scan rates was calculated from the anodic wave of the cyclic voltammogram. The feasibility of using the AgHCF modified electrode to measure butylated hydroxyanisole (BHA) was investigated. The modified electrode showed an excellent electrocatalytic activity towards the oxidation of BHA in 0.1 M KNO_3 at pH 6. The analytical utility of the electrode as an amperometric sensor for the determination of BHA in a flow system was evaluated by carrying out hydrodynamic and chronoamperometric studies. Under optimized conditions amperograms were recorded and it was found that the oxidation current increased linearly with successive addition of BHA in the concentration range of 7.4×10^{-6}–8.3×10^{-4} M. The limit of detection was found to be 3.7×10^{-6} M. For 10 successive determination of BHA at a concentration of 1.79×10^{-4} M, the relative standard deviation (R.S.D.) was 1.3%. The electrode showed a good electrochemical response in terms of sensitivity, stability and reproducibility. The proposed sensor was applied to the determination of BHA in spiked samples of dehydrated potato flakes.

Keywords: Silver hexacyanoferrate; BHA; Graphite–wax composite electrode; Amperometric sensor; Electrocatalytic oxidation

1. Introduction

Butylated hydroxyanisole (BHA) is a potent chemical antioxidant used as a preservative in food, food packaging, animal feed, cosmetics, pharmaceutical preparation, in rubber and petroleum products and it is also a stabilizer for vitamin A. BHA has been added to edible fats and fat containing foods for its antioxidant properties; it prevents food from becoming rancid and developing objectionable odors. It is widely used in the food industry because of its high thermal stability and its ability to remain active in baked and fried foods, as its properties are not lost during cooking. The detection and determination of BHA in various preparations become essential in view of its importance in diverse context. The products in which BHA has been analyzed include food, cosmetic and pharmaceutical [1], plastic [2], fat [3] and drugs [4]. Robards and Dilli [5] have reviewed the various techniques for the determination of synthetic food antioxidants including BHA.

Various voltammetric procedures have been reported for the determination of BHA using Hg [6], Pt [7] and carbon [8] as working electrodes. However, the detection limit was not sufficient for traces of this important compound to be determined and these methods were found to be less sensitive and irreproducible due to the surface fouling. Wang and Freiha [9] described a method involving preconcentration of BHA at a carbon paste electrode prior to voltammetric measurement. A flow injection method based on the oxidation of BHA at a glassy carbon electrode has been described by Pingarron and co-workers [10]. One of the promising approaches to improving the kinetics of the reaction and facilitating the determination is through the use of electrocatalytic process at chemically modified electrodes

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* Corresponding author. Tel.: +91 44 22351269; fax: +91 44 22352494.
E-mail address: sriman55@yahoo.com (S.S. Narayanan).

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doi:10.1016/j.snb.2005.11.064

(CMEs). The electrochemical behavior of CMEs offers various advantages in comparison with other electrochemical methods. The deliberate modification of the solid phase component of an electrode/solution interface provides properties of the modified electrode that differ from those of the bare surface. The desired redox reaction at the bare electrode involves slow electron transfer kinetics and therefore occurs at an appreciable rate only at potentials substantially higher than its thermodynamic redox potentials. Such reactions can be catalyzed by attaching a suitable electron transfer mediator to the surface [11]. The function of the mediator is to facilitate charge transfer between the analyte and electrode, thereby enhancing the sensitivity and selectivity of analysis. A number of modification strategies have been employed which are based on only a few approaches, by direct adsorption of the modifier onto the bare electrode surface [12,13], by covalent binding of the modifier to a specific surface site [14,15], by physical coating of the electrode surface with a polymer that contains the modifier grouping [16–19] and by bulk modification of carbon materials [20,21]. To our knowledge, reports on determination of BHA using CMEs are restricted to a single electrocatalyst in the literature [22]. We report here on the use of a silver hexacyanoferrate (AgHCF) modified graphite–wax electrode as an amperometric sensor for the electrocatalytic oxidation and determination of BHA, and describe the applicability of the modified electrode for the determination of BHA in samples in which it may be used as preservative.

2. Materials and methods

2.1. Instrumentation

A Fourier transform infrared (FT-IR) spectrum for the AgHCF complex was obtained using a Perkin-Elmer Spectrum-I Model Spectrometer. Elemental analyses were performed using a Perkin-Elmer-Optima 5300 DV ICP-Optical Emission Spectrometer. All electrochemical measurements were made using a potentiostat/galvanostat EG & G PAR Model 263A equipped with GPIP (IEEE-488) interface port in conjunction with a three-electrode system and a personal computer. The saturated calomel electrode (SCE), platinum wire and graphite–wax electrodes (with and without AgHCF) served as the reference, counter and working electrode, respectively. All the experiments were performed in solutions deoxygenated by pure nitrogen and at room temperature (25 °C).

2.2. Reagents and solutions

High purity graphite powder, silver nitrate and potassium hexacyanoferrate(II) were purchased from Merck. Butylated hydroxyanisole (BHA) was obtained from Hi-media. All other chemicals were of analytical grade. The BHA stock solution was prepared using 10% methanol solution and further dilutions were made using water. Doubly distilled water was used for solution preparation and conducting voltammetric experiments.

2.3. Preparation of silver hexacyanoferrate complex

Silver hexacyanoferrate complex was prepared as reported [23] by drop wise addition of an equimolar amount of silver salt to the potassium ferrocyanide solution and the precipitate was washed and dried at ambient temperature. The formation of the complex was confirmed by FT-IR spectroscopy. The composition of the complex was determined as follows: a known amount of the complex was decomposed at 500 °C and digested with concentrated HNO_3 and with suitable dilution used for elemental analysis. The compositions of K, Ag and Fe in the complex were found to be 6.8%, 56.3% and 9.7%, respectively, corresponding to a molecular formula $KAg_3[Fe(CN)_6]$.

2.4. Fabrication of modified electrode

The AgHCF graphite–wax electrode was prepared by thoroughly mixing 0.650 g of graphite powder and 0.050 g of AgHCF particles in an agate mortar for at least 10 min. This powder was added to 0.300 g melted paraffin wax. The liquid paste was mixed thoroughly, pressed into a glass tube with 4 mm inner diameter and 4 cm length, and then packed tightly in the tube. After solidification and removal from the tube, the electrode was obtained in the form of a rod and it was insulated with molten paraffin. The insulation was removed at both ends, at the top for making electrical connection and at the bottom to provide a sensor surface. The modified electrode consisted of 5% mediator. Similarly electrodes with 2%, 10% of the mediator and without mediator were also prepared. The electrode without the mediator was used as a bare electrode. Before each measurement, the electrode surface was polished on white paper and rinsed with bidistilled water.

2.5. Treatment of commercial food sample

BHA in spiked samples of commercially available dry potato chips was analyzed. The samples were crushed in an agate mortar. About 1 g of the powdered sample was spiked with a known amount of the standard solution of BHA and placed into a 20 ml centrifuge tube. The extraction was carried out with 10 ml of a 10% methanol–water solution. The mixture was mechanically shaken for 20 min, and after centrifugation at 3000 rpm for 20 min, the supernatant extract was collected. Five millilitres of the supernatant extract were added to 0.1 M KNO_3 in the electrochemical cell and BHA was analyzed voltammetrically by a standard addition method. Similar procedure was extended for other samples of the potato chips.

2.6. Procedure

The AgHCF modified electrode prepared by the graphite–wax composite method was characterized by cyclic voltammetry. The electrode was scanned between the potential 0.0 and 1.0 V in a 0.1 M KNO_3 medium. The effects of scan rate, various supporting electrolytes, their concentration and pH of the medium on the performance of the modified electrode was also studied. The electrochemical rugosity of the modified