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Analytical Methods

Flow injection analysis of BHA by NiHCF modified electrode

S.J. Richard Prabakar, S. Sriman Narayanan *

Department of Analytical Chemistry, School of Chemical Sciences, University of Madras, Guindy Campus, Chennai, TN 600 025, India

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ABSTRACT

Flow injection method is described for the determination of the antioxidant *tert*-butylhydroxy anisole (BHA) based on its catalytic oxidation at a nickel hexacyanoferrate (NiHCF) surface modified graphite wax composite electrode fabricated using a new approach. The electrochemical characteristics of the modified electrode were studied using cyclic voltammetry. The voltammetric response of BHA at the modified electrode showed current densities remarkably higher than the bare graphite electrode and occurred at a reduced over voltage of 200 mV. Linear calibration graphs were obtained in the range of 1.2×10^{-6}–1.07×10^{-3} M. A detection limit of 6×10^{-7} M was obtained with a correlation coefficient of 0.9983 based on S/N = 3. Reliable results were obtained by applying the proposed flow injection method to determine BHA spiked in dehydrated potato flakes. Results suggest that the developed method can be effectively employed for the determination of BHA from food samples.

1. Introduction

Antioxidants have extensive use in the food industry, being added to a wide variety of foods in order to improve their stability and especially to prevent rancidity in products containing lipids or fats. They also find their use in food packaging, animal feed, cosmetics, pharmaceutical preparation, in rubber and petroleum products. Lipid oxidation can be retarded by oxygen removal or by using antioxidants. The latter are mostly phenolic compounds, such as *tert*-butylhydroxyanisole (BHA), propyl gallate (PG) and BHT (Hudson, 1990) that provide the best results in combination with a chelating agent. Recently, people have found that these artificial antioxidants may cause loss of nourishment and even produce toxic substances to harm human health. The concentration of these additives present in a particular food is limited by legislation in many countries (Furia, 1980). The most widespread trend is to reduce the use of these compounds. As the potential harmful effects of these compounds on health have been extensively discussed (Grice, 1988; Witschi, 1986). It has become important to determine their contents in those materials that are used by people. It is reported that it is more effective to use a mixture of two or more antioxidants rather than a single compound in practical use (Robards & Dilli, 1987).

Several methods, usually involving separation steps, have been proposed for the determination of phenolic antioxidants. In the past few years, few electroanalytical methods have been described. Generally, chromatographic methods are often used for the analysis of these compounds (Delgado-Zamarren, Gonzalez-Maza, Sanchez-Perez, & Carabias Martınez, 2007; Lee, Lin, Li, & Tsai, 2006). Determination of BHA by preconcentration on a carbon paste electrode has been reported (Wang & Freiha, 1983). HPLC methods with an electrochemical detector have been reported for the determination of BHA (Andrikopoulos, Brueschweiler, Feber, & Taeschleer, 1991). Even though they appear to be sensitive tool for the determination of phenolic antioxidants, these methods are time consuming. Chemically modified electrodes pave way for the reliable and time effective determination of these compounds with greater sensitivity.

The use of conventional electrodes for electrochemical detection has a number of limitations. The limitations are low sensitivity and reproducibility, slow electron transfer reaction, low stability over a wide range of solution composition, surface fouling and high overpotential. The use of mediators showing electrocatalytic activity to modify electrode surfaces constitutes an interesting approach to fabricate sensing surfaces for analytical purposes. In operation, the redox active sites shuttle electrons between the analyte and the electrodes with significant reduction in activation overpotential. A further advantage of the chemically modified electrodes is that they are less prone to surface fouling and oxide formation compared to inert substrate electrodes. A wide variety of compounds have been used as electron transfer mediators for modification of electrode surfaces with various procedures. Metal hexacyanoferrates show interesting redox chemistry that is accompanied by changes in their electrochromic behaviour and have been potentially applied in solid-state batteries, electrode materials, electroanalytical, ion exchange and electrocatalytic purposes (Chen, 1996a, 1996b; Honda & Hayashi, 1987; Kubota & Tamamushi, 1995; Lin & Bocarsly, 1991).

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* Corresponding author. Tel.: +91 44 22202717; fax: +91 44 22352494.
E-mail addresses: sriman55@yahoo.com, sriman55@gmail.com (S. Sriman Narayanan).

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The modification of electrode surfaces with metal hexacyanoferrate is possible in different ways such as electrodeposition, adsorption, entrapping into a polymer matrice, electroless deposition, mechanically attaching the insoluble metal-hexacyanoferrate or by the reaction between metal hexacyanoferrate with self-assembled monolayer of an organosulfur compound on a gold electrode (Cai, Ju, & Chen, 1995; Gao, Wang, Li, & Zhao, 1991; Golabi & Noor Mohammadi, 1998; Mortimer, 1997; Pournaghi-Azar & Razmi-Nerbin, 1998; Reddy, Dostal, & Scholz, 1996; Xu, Wang, & Chen, 2000). The electrochemical deposition process that leads to the formation of the metal hexacyanoferrate (MHCF) on the electrode surface needs to be carefully controlled and hence it is pertinent to develop a simple and reliable method to fabricate stable MHCFs in short time. Most of the research activities use Au (Cox, Jaworski, & Kulesza, 1991), Pt, or Glassy Carbon (Lin & Bocarsly, 1991) as matrices for the preparation of modified electrodes in electroanalytical studies. These matrices may be replaced by a low cost and better anchoring functionalized surfaces because in this case the attachment of some transition metals, on these surfaces may be performed using a simple chemical method.

Very few reports are available for the determination of BHA using modified electrodes. A nickel pthalocyanin modified carbon paste electrode and a polymer coated glassy carbon electrode for the amperometric determination of BHA were reported (Ruiz, Blazquez, & Pingarron, 1995; Ruiz, Calvo, & Pingarron, 1994;). The simultaneous determination of BHA and TBHQ (tert-butylhydroquinone) at a polypyrrole electrode modified with a nickel pthalocyanin complex is also reported (De La Fuente, Acuna, Vazquez, Tascon, & Batenero, 1999). Our previous works include the use of Silver Hexacyanoferrate, Manganese Hexacyanoferrate modified graphite electrode used for the amperometric determination of BHA (Jayasri & Sriman Narayanan, 2006, 2007). Another new technique was adopted for the fabrication of cobalt hexacyanoferrate electrode using an amine adsorbed graphite powder as the substrate, which was used for the amperometric determination of BHA (Richard Prabakar & Sriman Narayanan, 2006). A similar modification procedure is adopted in the present work for the fabrication of a Nickel Hexacyanoferrate surface modified graphite wax composite electrode (GWCE). The modified electrode was found to have excellent mediation properties and was able to catalyze BHA oxidation effectively.

The present paper describes a method involving the coordination of nickel on a amine adsorbed graphite surface as an electrode matrix and the chemical derivatization of nickel anchored on the electrode to nickel hexacyanoferrate (NiHCF) film. The modification was achieved by adsorbing p-phenylenediamine onto graphite, which was used for making a graphite wax composite electrode. The electrode served as the base over which Ni^{2+} ions were coordinated to the adsorbed amine. It was followed by derivatization of the metal to its stable hexacyanoferrate thin film on the electrode surface. The NiHCF film was effectively used for the amperometric determination of BHA as it was found to have excellent catalytic activity over the oxidation of BHA. Differential pulse voltammetry (DPV) and flow injection technique were effectively used for the determination of the analyte from commercially available potato chips samples spiked with BHA. An amperometric method for the determination of Hydrazine from industrial wastewater samples using the electrode has been reported by us (Richard Prabakar & Sriman Narayanan, 2008).

2. Experimental

2.1. Chemicals and reagents

Graphite powder (1–2 μm) was purchased from Aldrich chemicals, Germany. All other reagents were of analytical grade. All aqueous solutions were prepared using doubly distilled water. Studies on effect of pH were carried out by adjusting the pH using 0.1 M HCl and 0.1 M NaOH solutions. *p*-Phenylenediamine solution (PPD) (10 mM) and $NiCl_2$ solution (0.01 M) were prepared by dissolving appropriate quantity in dry DMF and dry ethanol, respectively. All measurements were done after carefully degassing the solutions with pure nitrogen.

2.2. Flow injection procedure

A custom-built single channel flow cell was used in this work. A solution of 0.1 M $NaNO_3$ in phosphate buffer (pH 7.0) was used as the carrier (C) at a flow rate of 4.0 mL min^{-1}. The solution contained in the sample loop was injected and transported by the carrier stream after the baseline had reached a steady state value.

2.3. Treatment of commercial food sample

BHA spiked in commercially available potato chips (containing no BHA as the preservative) was analysed. The commercial sample was powdered in a mortar and pestle. 1 g of the powdered sample was weighed and spiked with a calculated amount of BHA. About 1 g of the spiked sample was placed in a centrifuge tube. To this 5 mL of 10% methanol solution was added and mechanically shaken for 20 min. The supernatant was collected after centrifuging. This extraction was repeated three times with 5 mL aliquots of 10% methanol solution and the supernatants were added together and concentrated to one third of its volume. The resulting extract was then diluted to the required concentration using the carrier solution (C). The same extract solution was used for differential pulse voltammetric determination and flow injection technique. Similar procedure was extended for other potato chips samples.

2.4. Apparatus

Electrochemical measurements were done using an Electrochemical workstation [CH Instruments (660B)] interfaced to an IBM personal computer with standard three-electrode configuration. The surface modified NiHCF graphite wax composite electrode was used as the working electrode. A platinum wire served as the counter with standard calomel electrode as the reference. Solutions were deoxygenated by bubbling high-purity nitrogen for 5 min prior to electrochemical experiments and all experiments were carried out at 25 °C.

FIA was done using a high pressure Michlins peristaltic pump PP10 (India) and a Rheodyne (Cotati, CA) model 7725 injection valve equipped with a 20 μL loop, coupled to a custom built radial flow cell with a platinum wire counter electrode and a Ag/AgCl ($E_{Ag/AgCl}$ = 0.1939 V vs. SHE) reference electrode connected to Electrochemical workstation CH Instruments (660B) controlled by an IBM personal computer for data acquisition. The reference electrode was filled with 3 M KCl solution. Working electrode was a 3 mm diameter NiHCF graphite paraffin wax composite electrode. The measurements made were converted to the standard calomel electrode values.

2.5. Electrode preparation

The fabrication of the surface modified NiHCF electrode involves four main steps as reported in our previous work (Richard Prabakar & Sriman Narayanan, 2008). In short, a graphite wax composite electrode was prepared using the p-phenylenediamine adsorbed graphite powder. An optimised composition was followed for the preparation of the electrode. The electrode was polished and surface was dipped in $NiCl_2$/EtOH to coordinate the metal cation (Ni^{2+}) to the adsorbed amine. The irreversibly bound metal