Voltammetric Sensor for the Determination of TBHQ in Coconut Oil

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Abstract A sensitive voltammetric method for the determination of *tert*-butylhydroquinone (TBHQ), a widely used synthetic phenolic antioxidant in oils and fats, using multiwalled carbon nanotube modified gold electrode (MWCNT/GE) was developed. In 0.10 M phosphate buffer solution (PBS) of pH 2, TBHQ gave redox peaks at $E_{pa}=$ 258 mV and $E_{pc}=228$ mV on MWCNT/GE. Diffusion-controlled electrooxidation of TBHQ was found to be perfectly reversible with the involvement of two electrons and two protons. The anodic peak currents varied linearly with concentrations of TBHQ in the range 4.0×10^{-6} to 1.00×10^{-4} M. The limit of detection achieved for the developed sensor was 3.20×10^{-8} M (5.31 ng mL^{-1}). Developed sensor was used for the determination of TBHQ in commercially available coconut oil. The results obtained from the developed method were in good agreement with the standard method (HPLC-UV).

Introduction

Antioxidants are substances used to preserve food by retarding deterioration, rancidity or discolouration due to oxidation (Food and Drug Administration). *tert*-Butylhydroquinone (TBHQ) is one of the commonly used synthetic antioxidants in food. Due to high thermal stability and anti-lipid peroxidation activity shown by TBHQ in comparison to other antioxidants, it is widely used in fats and oils (Shahidi 2000; Gharavi et al. 2007).

In 1972, TBHQ was first approved as a food additive in the USA (Robards and Dilli 1987). In contrast to the beneficial effects of TBHQ, there is a possibility of a number of problems in a complex matrix like food. Studies demonstrate that excess use of TBHQ, added to foodstuff, may cause a loss of sustenance, produce toxic substances that harm human health (Guan et al. 2006) and even carcinogenicity (Saad et al. 2007). The acceptable daily intake (ADI) recommended by the Joint FAO/WHO Expert Committee on Food Additives (JECFA 2007) is 0–1.40 mg of additive per kilogram body weight for TBHQ, while the Scientific Committee for Food (SCF) established a value of 0.50 mg/kg (Andrea et al. 2010). Plastics and wrapping materials frequently contain antioxidants capable of migrating into the enclosed food (Crompton 1979). Obviously, the concern for "total" or "free" antioxidant is therefore an important question.

Several analytical methods are available for the determination of TBHQ. These include high-performance liquid chromatography (Li et al. 2009; Tagliabue et al. 2004), gas chromatography (Guo et al. 2006; Gonzalez et al. 1998) and electrokinetic capillary chromatography (Guan et al. 2006). Though the above-mentioned methods are appropriate, time-consuming analyte extraction and sample cleanup is required. Electrochemical methods such as voltammetry are alternatives. Its wide application is attributed with relatively cheap and portable instrumentation, very good sensitivity with wide linear concentration range, rapid analysis (in seconds) and on site analysis without sample cleanup. Determination of TBHQ by polarographic (Cortes et al. 1994; De la Fuente et al. 1999) and voltammetric methods (Araujo et al. 2011; Goulart et al. 2014) using different electrodes are reported.

Carbon nanotubes have been at the fore front of novel nanoscale investigations owing to their unique structure-

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dependent electronic and mechanical properties (Balasubramanian and Burghard 2008; Jos et al. 2012). The performance of multiwalled carbon nanotube (MWCNT) modified electrodes has been found to be superior to the performance of conventional carbon electrodes in terms of electron transfer rate, reversibility, conductivity and adsorptivity (Britto et al. 1996; Zhao et al. 2002).

Voltammetric determination of TBHQ using modified gold electrode is not yet reported. In continuation to the sensors for food additives reported from our group (Thomas et al. 2012; Rasheed et al. 2014; Vikraman et al. 2013; Chandran et al. 2014), the present investigations involve modification of gold electrode with MWCNT. It aims at the development of a quantitative electroanalytical method for the determination of TBHQ at multiwalled carbon nanotube modified gold electrode (MWCNT/GE), based on cyclic voltammetry (CV) and square wave voltammetry (SWV). It also aims at the application of proposed method for TBHQ determination in coconut oil.

Materials and Methods

Reagents

All reagents and solvents used for the investigations were of analytical grade and Millipore water was used throughout the studies. MWCNT, Nafion, alumina and TBHQ were purchased from Sigma-Aldrich Co., USA. Ethanol, sodium dihydrogen orthophosphate and disodium hydrogen orthophosphate were purchased from Merck, Germany. Except MWCNT, other chemicals were used as received. All other common reagents were obtained from S.D. Fine-Chem Ltd., Mumbai, India.

Instruments

Electrochemical measurements were performed on an electrochemical analyser (CH instruments, USA) with a conventional three-electrode system. A gold electrode with suitable modifications as working electrode, Ag/AgCl as reference electrode and a platinum wire as the auxiliary electrode constituted the three-electrode system. A Metrohm pH meter was used to carry out the pH measurements. SEM images were recorded using JOEL 6390 LV. An ultrasonicator (Oscar Ultrasonics Pvt. Ltd., Mumbai) and HPLC-UV (LC-20AT, SPD-20A, Shimadzu) were also used.

Fabrication of MWCNT Modified GE

The GE was mechanically polished with aqueous slurries of alumina (1 μm) on a flat pad prior to modification. Polished GE was rinsed ultrasonically with water

and absolute ethanol to remove residual alumina particles from the surface, then with a piranha solution (H_2O_2:H_2SO_4=1:3 v/v) for 10 min when required. The mechanical cleaning followed an electrochemical cleaning process which included the performance of cyclic voltammetry from 0 to 1500 mV in 0.50 M sulphuric acid solution at a scan rate of 100 mV s^{-1} until a stable cyclic voltammogram was obtained.

MWCNT was refluxed in conc. HNO_3 for 48 h to cause segmentation and carboxylation (Tsang et al. 1994; Issac and Kumar 2009). Five milligrams of the acid-treated MWCNT was dispersed in 13 % (v/v) Nafion–water solution (2.30 mL) to give a 0.22 % black homogenous suspension. Five microliters of the MWCNT suspension was dropped on the clean GE surface, and the solvent was evaporated to get the modified GE.

Analytical Procedure

A suitable amount of the stock solution of TBHQ (1×10^{-3} M) in methanol was transferred to the electrochemical cell and diluted to 10 mL with the supporting electrolyte. The cyclic voltammograms and square wave voltammograms were recorded from −400 to 1000 mV at a scan rate of 100 mV s^{-1} with the three-electrode system. All experiments were carried out at room temperature (~25 °C).

Treatment of Coconut Oil Sample

Five grams of the commercially available coconut oil sample was placed in a 100-mL Erlenmeyer flask (with a screw cap), and pure methanol (10 mL) was added. The mixture was then shaken vigorously for 30 min, transferred to a 25-mL centrifuge tube and centrifuged at 3000 rpm for 10 min. After a settling time of 2 min, the extracts were transferred to a sample bottle. A 100 μL aliquot of this sample was analysed by the voltammetric procedure.

HPLC-UV as the Standard Method

The chromatographic conditions for the determination of TBHQ using methodologies previously proposed by Lin et al. (2013) was used with some modifications. An HPLC instrument equipped with UV–Vis detection at 280 nm was used. The mobile phase was a combination of (A) methanol and (B) 1 % orthophosphoric acid. A gradient was developed as follows: the solution A (v/v) ratio was varied from 40 to 80 % during 0–15 min, 100 % during 15–20 min. The flow rate was kept at 1 mL min^{-1}, and under these conditions, the retention times was 13.99 min for TBHQ. Each sample solution (20 μL) was injected, and the concentrations were calculated on the basis of peak area.

Results and Discussion

Electrocatalytic Action of MWCNT on the Electrochemical Behaviour of TBHQ

Electrochemical behaviour of TBHQ (5×10^{-5} M) was studied at bare GE and MWCNT/GE using cyclic voltammetry (CV) and square wave voltammetry (SWV), in 0.10 M PBS at a scan rate of 100 mV s^{-1}. The results are compared in Fig. 1. Using CV, bare GE could hardly sense the redox nature of TBHQ (E_{pa}=466 mV, i_{pa}=0.66 μA), but under similar experimental conditions, TBHQ gave redox peaks at E_{pa}=258 mV and E_{pc}=228 mV (i_{pa}=6.45 μA and i_{pc}=10.55 μA) on MWCNT/GE. This shows the electrocatalytic role played by MWCNT towards the reversible oxidation of TBHQ. A difference of about 30 mV was obtained between the peak potentials. According to equation, $\Delta E_p = E_{pa} - E_{pc} = \frac{59\,mV}{n}$ (Anson et al. 1983; Gan et al. 2012), the number of electrons involved in the reversible reaction was found to be 2.

SWV was also employed to explore the electrochemical behaviour of TBHQ (Fig. 1). In the case of bare gold electrode, TBHQ (5×10^{-5} M) gave an oxidation peak at E_{pa}= 432 mV with a small current (0.85 μA). It was observed that the current decreases with multiple cycles. This is due to adsorption of oxidative products on the surface of the electrode. Higher conductivity, more active sites, larger surface area and topological defects on the MWCNT surface (Xu et al. 2003) helped in enhancing the sensitivity of the modified electrode, MWCNT/GE. This resulted in lowering the peak potential of oxidation of TBHQ to 220 mV with an enhanced current (24.47 μA) at MWCNT/GE.

Evidences for Electrode Modification—Surface Area of MWCNT/GE

The Randles–Sevcik equation (Randles 1948) was used to calculate the surface area of bare GE and MWCNT/GE.
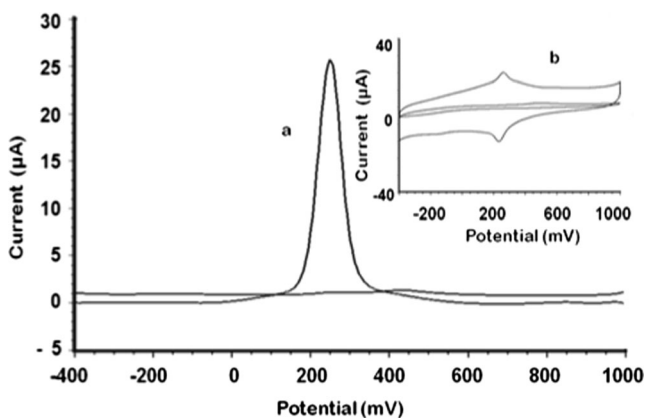

Fig. 1 Comparison of the response of TBHQ (5×10^{-5} M) on bare GE and MWCNT/GE using **a** SWV and **b** CV

CVs were recorded with GE and MWCNT/GE at different scan rates by measuring microscopic areas of the electrodes with a probe of 2×10^{-3} M K$_3$[Fe(CN)$_6$]. For a reversible system, the anodic peak current i_p is linear to the square root of scan rate, $\nu^{1/2}$ as follows

$$i_p = \left(2.687 \times 10^{-5}\right) n^{3/2} \nu^{1/2} D^{1/2} A\, C$$

where n is the number of electrons transferred (n=1), D is the diffusion coefficient D=7.6×10^{-6} cm^2 s^{-1}, A is the surface area of the electrode, C is the concentration of K$_3$[Fe(CN)$_6$] and ν refers to the scan rate.

The plot of i_p vs. $\nu^{1/2}$ follows the linear regression equation i_p=2.28 $\nu^{1/2}$−2.37 and i_p=7.51 $\nu^{1/2}$−5.41 for the bare and modified electrodes, respectively. Thus from the slope of the plot, effective surface areas of bare GE and MWCNT/GE were calculated to be 0.5604 and 1.8398 cm^2, respectively. The 3.28-fold increase in the surface area of MWCNT-modified GE compared to bare GE enhanced the response of the electroactive species. SEM images of bare GE and MWCNT/GE given in Fig. 2 give further evidences for surface modification.

Performance Characteristics of the Developed Sensor

#### *Choice of the Supporting Electrolyte and the Effect of pH*

In order to choose the most suitable supporting electrolyte for the voltammetric determination of the antioxidant TBHQ, its electrochemical behaviour was compared in various supporting electrolytes of 0.10 M PBS, citrate buffer solution, acetate buffer solution, hydrochloric acid, sulphuric acid, sodium hydroxide, potassium chloride and potassium nitrate. Of all the electrolytes tested, PBS gave better shaped reversible voltammetric peaks with relatively high sensitivity. Thus, PBS was chosen as the suitable medium for TBHQ determination.

The Effect of pH

Figures 3 and 4 show the relationships between the peak potentials and peak currents with pH values, respectively At a constant scan rate, peak potentials shifted towards negative values with increasing pH, in the range of 2–8, suggest the involvement of protons in the redox reaction of TBHQ (Ghoreishi et al. 2012). However, when the pH exceeded 8, the electrode response became unstable.

From Fig. 3, it is clear that E_{pa} shows a linear relation with pH (R^2=0.993) with a slope of −58.71. The slope is in agreement with the theoretical value (59 mV/pH), indicating that the oxidation of TBHQ occurred with the involvement of
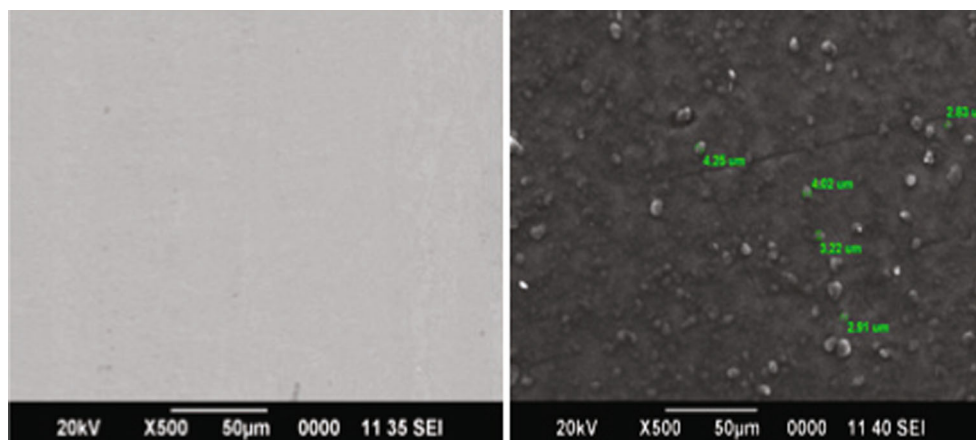
equal number of electrons and protons (De la Fuente et al. 1999).

From pH 2 to 6, the anodic and cathodic peak currents decreased gradually (Fig. 4), and the reversibility of the reaction became worse. It is apparent that both the electron transfer kinetics and the redox potential for this oxidation are pH dependent. This can be attributed to the involvement of protons in the electron transfer reactions; the two-electron oxidation requires the removal of two protons, and the two-electron reduction requires the addition of two protons. Therefore, lowering the pH (increasing the proton concentration) facilitates the reduction, but hinders the oxidation, and hence, the peaks in the CV are shifted to more positive potentials. The well-shaped peaks and larger current was the reason to select pH 2 for the following studies.

Effect of MWCNT Film Thickness

Influence of thickness of the film formed by MWCNT–Nafion suspension on the redox peaks of TBHQ was studied using CV by changing the dropping volume of MWCNT–

Nafion suspension (2.17×10^{-6} g μL^{-1}) on the bare electrode from 1 to 6 μL. From 1 to 5 μL, peak currents increased significantly, decreased on changing the volume to 6 μL, insulating nature of Nafion towards electrons (Nafion acts as a cation exchange resin) (Gryger et al. 2002) and hampering of electron transfer by excess amount of MWCNT (Lonappan et al. 2011) may be the reason. Thus, 5 μL of MWCNT–Nafion suspension was fixed for further studies.

Effect of Potential Scan Rate

The effect of the potential scan rates on the peak currents of the antioxidant TBHQ (5×10^{-5} M), at the MWCNT/GE was also investigated in 0.1 M PBS (pH 2.0). Resulting peak currents are plotted against the scan rate (Fig. 5) which demonstrates that the redox peak currents of TBHQ was proportional to the square root of the potential scan rate in the range of 20–140 mV s^{-1} with linear regression equations (E_{pa}=1.45 $\nu^{1/2}$−1.68 and E_{pc}=−1.00 $\nu^{1/2}$+2.93) (R^2>0.99). This indicated that the redox reaction of TBHQ at the surface of
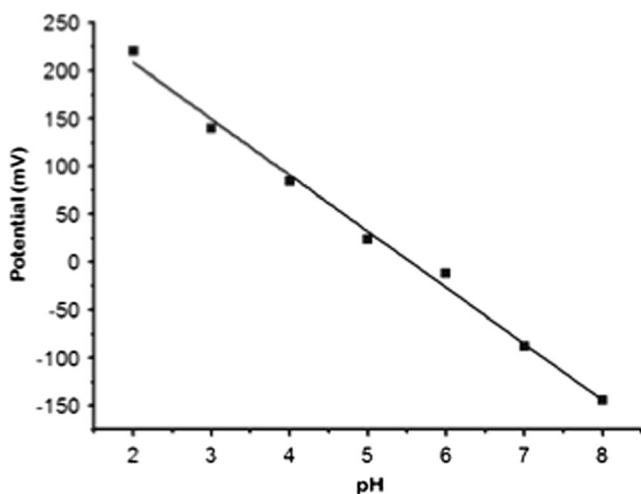

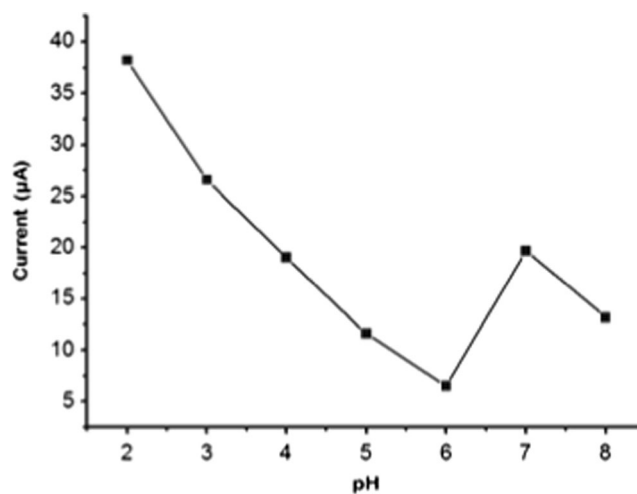Fig. 3 Variation of peak potential of TBHQ oxidation with pH

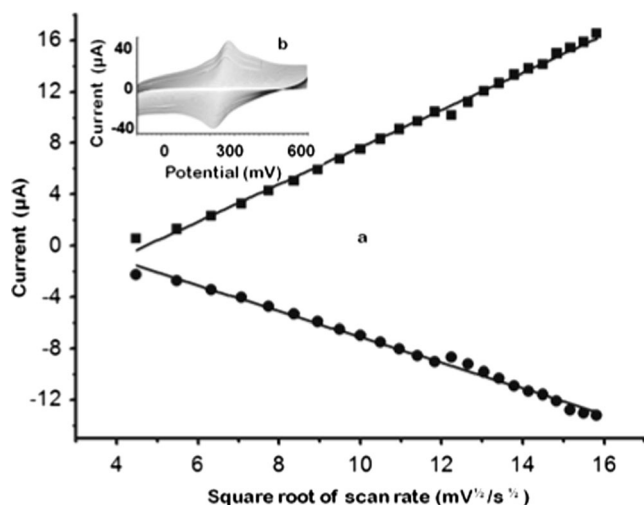Fig. 4 Relationship between anodic peak current and pH of the medium

Fig. 5 **a** Plot of anodic and cathodic peak currents as a function of potential scan rate (20–250 mV s^{-1}) and **b** cyclic voltammograms of 5×10^{-5} M TBHQ at varying potential scan rates

MWCNT/GE was controlled by diffusion mechanism (De la Fuente et al. 1999; Bond 1980).

Also, the shift of peak potential (Fig. 5) as a function of the scan rate indicated that with increasing scan rate, the anodic and cathodic peak potentials for TBHQ shifted in positive and negative directions as shown; this suggests that the electron transfer rate was not fast at higher scan rate, and the electrochemical reactions gradually became less reversible (Wang et al. 2011).

Mechanism of the Electrochemical Redox Reaction of TBHQ

From the earlier sections, it can be seen that electrochemical redox reaction of TBHQ is perfectly reversible with two-electron transfer. From the plot of pH with anodic peak potential, it is clear that equal number of electrons and protons are involved in the redox reaction of TBHQ. Thus, the possible mechanism of electrochemical redox reaction of TBHQ is given in Fig. 6. TBHQ undergoes oxidation by the removal of two electrons and two protons to form *tert*-butylquinone and vice versa.
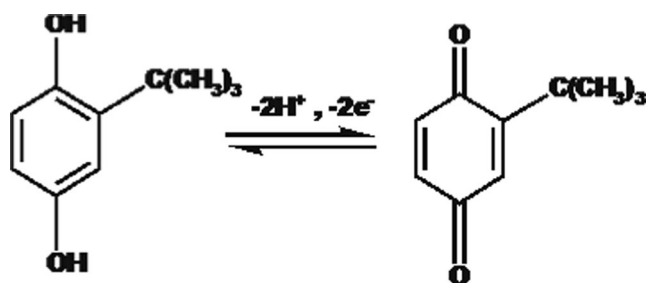

Fig. 6 Mechanism of electrochemical redox reaction of TBHQ

Linear Range and Limit of Detection

Linear range and limit of detection were determined under optimised experimental conditions using SWV in 0.10 M PBS (pH 2) (Fig. 7). The anodic peak currents showed linear relationship with concentrations of TBHQ in the range 4×10^{-6} to 1×10^{-4} M ($R^2 = 0.99$). The linear regression equation was formulated as $i_p = 3.30 \times 10^{-5}$ C + 7.52. The limit of detection achieved for the developed sensor was 3.20×10^{-8} M (5.31 ng mL^{-1}). The limit of detection of TBHQ for the proposed sensor is compared with that of the reported works (Table 1).

Interferences

Various common interfering substances such as ascorbic acid, citric acid, EDTA and common metal salts were evaluated at the MWCNT/GE under optimal experimental conditions to investigate method selectivity. The tolerance limit for the interfering species was the maximum concentration that gave a relative error of ±5 % at a concentration of 5×10^{-5} M TBHQ. The signal change produced by the interferents in the response of TBHQ is tabulated in Table 2.

Studies showed that up to twofold excess of ascorbic acid concentration had no effect on the peak currents of the analyte, but interferes when present in higher concentration. EDTA, citric acid, K$^+$, Ca^{2+}, Zn^{2+}, Cl$^-$, SO$_4^{2-}$, NO$_3^-$, CO$_3^{2-}$ and CH$_3$COO$^-$ did not interfere until a 100-fold increase in the concentration level (There were no obvious electrochemical responses for these species in the potential window between −400 and 1000 mV except the peak potential (804 mV) of EDTA which was different from the analyte) .

The possibility of interference by other antioxidants such as butylated hydroxyl anisole (BHA) and propyl gallate (PG) on
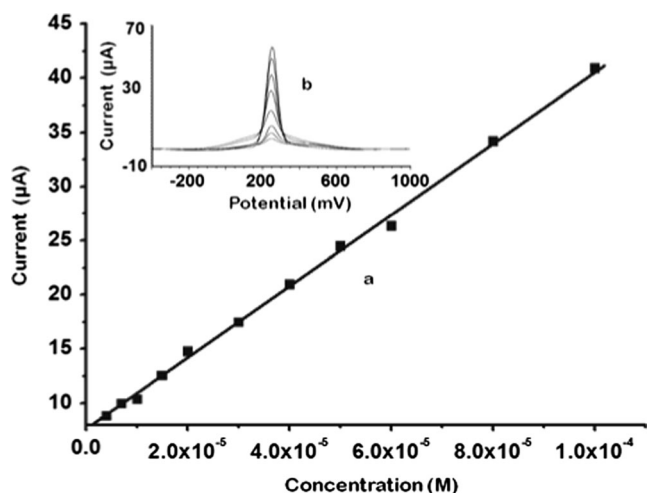

Fig. 7 **a** Calibration graph of TBHQ at MWCNT/GE and **b** square wave voltammograms of TBHQ at different concentrations from 4×10^{-6} to 1×10^{-4} M

Table 1 Comparison of the detection limit of present sensor with that of previously reported methods

Sl. no.	Method	References	Detection limit
1	Differential pulse voltammetry	De la Fuente et al. 1999	7.40×10^{-6} M
2	GC-MS	Guo et al. 2006	5.00×10^{-6} M
3	Reverse phase HPLC		6.60×10^{-8} M
4	Linear sweep voltammetry	Caramit et al. 2013	3.40×10^{-7} M
5	First derivative voltammetry	Lin et al. 2013	4.75×10^{-7} M
6	Present method	–	3.20×10^{-8} M

the determination of TBHQ was studied under similar conditions. PG gave an anodic peak at 468 mV. It was seen that TBHQ was suffering from an interference of 52.29 %, by PG but BHA do not interfere though it shows an anodic peak at 380 mV.

Repeatability and Reproducibility

Electrochemical response of TBHQ (5×10^{-5} M or 8.30 μg mL^{-1}) was determined with six modified electrodes (MWCNT/GE) prepared by the same fabrication method. The relative standard deviation (RSD) of the peak currents was calculated to be 3.8 %. This indicated that the reproducibility of the developed sensor was satisfactory. The modified electrode was repeatedly used 10 times (CV/SWV was performed at least five times in the buffer solution after each use to regenerate the electrode surface) to perform the experiment in solution containing 8.30 μg mL^{-1} of TBHQ. The RSD of these replicates obtained was 2.4 %.

Table 2 Interference study

Sl. no.	Foreign species	Signal change (%)
1	Potassium chloride	0.60
2	Sodium carbonate	−3.40
3	Potassium nitrate	1.10
4	Calcium sulphate	0.70
5	Zinc acetate	4.30
6	Citric acid	−3.90
7	EDTA	4.40
8	Ascorbic acid	−35.30
9	Butylated hydroxyanisole	1.30
10	Propyl gallate	−52.50

Table 3 Comparison of the determination of TBHQ in coconut oil using the developed method and standard method (HPLC-UV)

TBHQ added (M)	Developed method		HPLC-UV	
	TBHQ found (M ± SD)	Percent of recovery	TBHQ found (M ± SD)	Percent of recovery
5×10^{-6}	$4.82 \times 10^{-6} \pm 0.19$	96.46	$4.85 \times 10^{-6} \pm 0.11$	97.00
1×10^{-5}	$1.02 \times 10^{-5} \pm 0.24$	102.00	$0.99 \times 10^{-5} \pm 0.13$	99.00
5×10^{-5}	$5.03 \times 10^{-5} \pm 0.10$	100.60	$5.04 \times 10^{-5} \pm 0.22$	100.80

SD standard deviation

Analytical Application

To validate the developed method, proposed sensor was used for the determination of TBHQ in commercially available coconut oil. Each spiked sample solution was subjected to three parallel determinations as per the procedure discussed earlier. Experimental results are shown in Table 3. The results obtained with the developed sensor were compared with that obtained from the HPLC-UV method. The results obtained from the standard method were in good agreement with the developed method and establishes the utility of the present method.

Conclusions

A method was developed for the determination of TBHQ using a carbon nanotube modified gold electrode (MWCNT/GE). The electrochemical behaviour of TBHQ at MWCNT/GE was investigated, and it was found that on modification, the anodic peak current was shifted by 208 mV negatively. This lowering of potential indicated the electrocatalytic effect of MWCNT.

TBHQ gave best responses in 0.10 M PBS (pH 2) when 5 μL of (2.17×10^{-3} g mL^{-1}) MWCNT–Nafion suspension was used as the modifier. Under optimised conditions, a linear concentration range of 4.00×10^{-6} to 1.00×10^{-4} M TBHQ, and a detection limit of 3.20×10^{-8} M were obtained.

The developed sensor showed good reproducibility (RSD = 3.80 %) and repeatability (RSD = 2.40 %). Satisfactory quantitative results were obtained for the determination of TBHQ in coconut oil sample, and the obtained results were found to be in agreement with those from the standard HPLC method.

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