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Electrochemical determination of 8-hydroxyquinoline in a cosmetic product on a glassy carbon electrode modified with 1-amino-2-naphthol-4-sulphonic acid

Tuğba Tabanlıgil Calam^a  and Elif Begüm Yılmaz^b 

^aTechnical Sciences Vocational High School, Gazi University, Ankara, Turkey; ^bInstitute of Materials Science and Nanotechnology, Bilkent University, Ankara, Turkey

ABSTRACT

A new voltammetric method was developed for the simple, rapid and inexpensive determination of 8-hydroxyquinoline (8HQ) on a modified electrode obtained by the electrodeposition of 1-amino-2-naphthol-4-sulfonic acid (ANSA) on the surface of a glassy carbon (GC) electrode. The electrode interfacial properties were investigated by electrochemical impedance spectroscopy (EIS). The electrochemical response of the ANSA-GC electrode toward 8-hydroxyquinoline was investigated by the use of square wave voltammetry. The ANSA-GC modified electrode showed two linear plots with 8-hydroxyquinoline concentrations from 5×10^{-7} to 1.4×10^{-5} mol dm⁻³ (R^2 of 0.9984) and from 1.4×10^{-5} to 4.25×10^{-4} mol dm⁻³ with a correlation coefficient R^2 equal to 0.9967. The limit of detection was 1.6×10^{-7} mol dm⁻³. The ANSA-GC modified electrode also showed excellent stability and reproducibility for up to two weeks. The analytical application of the ANSA-GC modified electrode was investigated for the determination of 8-hydroxyquinoline in a blush cosmetic product. The results in good agreement to those obtained by spectrophotometry as a standard method.

KEYWORDS

8-hydroxyquinoline; cosmetics; spectrophotometry; square wave voltammetry

Introduction

8-Hydroxyquinoline (8HQ) also known as oxine or 8-quinolinol, is a phenolic compound used in the preparation of disinfectants, fungicides^[1] and bactericides.^[2] 8-Hydroxyquinoline widely used in industry, medicine and agriculture.^[3] Also, although its effects on living health are still being studied, it has been found to have an oncogenic potential on mice.^[4]

8-Hydroxyquinoline is widely used in the production and preservation of cosmetic products due to its potent antimicrobial properties, as well as its possible negative effects on human health.^[2] Considering that the use of cosmetic products in daily life has increased, the properties of 8-

hydroxyquinoline to humans should be investigated.^[5] According to the European Union Council Directive 76/768/EEC, 8-hydroxyquinoline cannot be used in products such as suntan cream and baby products. Also, the maximum authorized concentration of 8-hydroxyquinoline in the finished cosmetic products is 0 to 3% (w/w).^[6]

In addition to the possible negative effects of 8-hydroxyquinoline in terms of health, pharmacological studies in recent years show that 8-hydroxyquinoline can be used as an active drug ingredient to shorten the treatment process for both active and latent tuberculosis.^[7] Therefore, the determination of 8-hydroxyquinoline in commercial cosmetic products is important for checking their conformance to the current legislation and for quality control purposes.^[8]

In the determination of various organic and inorganic species, modified electrodes are preferred because they offer advantages such as high electron transfer rate, high sensitivity and excellent selectivity. For this purpose, solid electrode surfaces such as gold, platinum and glassy carbon (GC) are modified using various Schiff bases,^[9,10] thiols,^[11] triazoles,^[12,13] metal oxides,^[14] alloys,^[15] and metals.^[15] As a result of the modified GC electrodes, excellent analytical performance has been obtained for the determination of many species.

In the literature, the determination of 8-hydroxyquinoline has been reported by various analytical methods such as thin-layer chromatography,^[16] flow injection spectrophotometry^[17] and high-performance liquid chromatography.^[18–20] Compared to the analytical methods mentioned above, electrochemical procedures are environmentally friendly and cost-effective. Also, electroanalytical methods do not require pretreatment and offer advantages such as ease of use, few processing steps and short determination times.^[21]

Although the study of the electrochemical properties and determination of 8-hydroxyquinoline in the literature is limited, some studies have been reported using various working electrodes such as the carbon paste electrode,^[3] the glassy carbon (GC) electrode,^[22] the multiwalled carbon nanotube (MWCNT)/Nafion^[23] electrode, and the hanging mercury drop electrode.^[24] Also, the electrochemical response of the 8-hydroxyquinoline on an unmodified electrode is rather weak. Therefore, the use of modified electrode surfaces may be advantageous for the determination of 8-hydroxyquinoline.

Guo et al. modified the glassy carbon electrode surface with MWCNT/Nafion. They investigated the electrochemical properties of 8-hydroxyquinoline on the surface of the prepared modified electrode (MWCNT/Nafion/GC) and determined 8-hydroxyquinoline in cosmetic products.^[23] Due to the limited number of studies using the modified electrode as the

working electrode in the literature, an electroanalytical method must be developed for the sensitive and selective determination of 8-hydroxyquinoline.

In this study, 1-amino-2-naphthol-4-sulphonic acid (ANSA) was electro-polymerized on the GC electrode surface by cyclic voltammetry (CV). Electrochemical impedance spectroscopy (EIS) and CV were used to characterize the prepared ANSA-GC electrode. The electrochemical properties of 8-hydroxyquinoline on the modified electrode (ANSA-GC) were investigated.

Under the optimal conditions, the analytical performance of the ANSA-GC electrode was investigated for the sensitive and selective determination of 8-hydroxyquinoline. Comparing with the unmodified GC electrode, the ANSA-GC electrode showed a favorable voltammetric response to 8-hydroxyquinoline. The analytical applicability of the ANSA-GC electrode was also confirmed by the determination of 8-hydroxyquinoline in a blush cosmetic sample. In this study, an alternative method was reported for the electrochemical determination of 8-hydroxyquinoline.

Experimental

Instrumentation and chemicals

All voltammetric measurements were performed using a CHI 660B Electrochemical Work Station (China). A Ag/AgCl/KCl (saturated) and Ag/Ag⁺ (0.01 mol dm⁻³) electrodes in acetonitrile were used as the reference electrodes in the studies of aqueous and non-aqueous media, respectively. A platinum wire was used as a counter electrode.

The untreated GC electrode (BAS, 3 mm diameter) or modified electrode were used as the working electrode. The measurements of the pH values of buffer solutions were performed using a Thermo Orion 5 Star device. For electrode surface cleaning processes, a Bandelin Sonatax ultrasonic bath was used. All experiments were performed at room temperature.

Acetonitrile, phosphoric acid (85%), boric acid, sodium acetate, glacial acetic acid, sodium hydroxide and hydrochloric acid (37%) were purchased from Merck (Germany). ANSA was obtained from Hopkin and Williams. Sodium phosphate dibasic (anhydrous) was purchased from Carlo Erba Reagents. Perchloric acid (70%), sodium phosphate monobasic (anhydrous), tetrabutylammonium tetrafluoroborate (TBATFB), potassium chloride (KCl), potassium ferricyanide and potassium ferrocyanide were obtained from Sigma-Aldrich. All chemicals were of analytical reagent grade and used as received.

Procedure for the electrode preparation

The glassy carbon electrodes were cleaned according to our previous report.^[11] Following that procedure, the electrodeposition of the ANSA film on the unmodified GC electrode surface was performed using cyclic voltammetry in an aqueous solution containing $1 \times 10^{-4} \text{ mol dm}^{-3}$ ANSA and 0.1 mol dm^{-3} KCl for 25 cycles between -1.5 and $+2.0 \text{ V}$ using a scan rate of 0.1 V s^{-1} . The resulting modified electrode was rinsed using doubled distilled water and was ready for use.

Square wave voltammetry and cyclic voltammetry

Square wave voltammetry was used in the potential range from 0.3 to 0.9 V with a 0.040 V wave amplitude and 15 Hz frequency at room temperature for the determination of 8-hydroxyquinoline.

Cyclic voltammetry was used for the characterization of the modified electrode surface and comparison of the unmodified GC and the ANSA-GC electrode. The cyclic voltammograms were performed in 1.0 mmol dm^{-3} $\text{K}_3[\text{Fe}(\text{CN})_6]/\text{K}_4[\text{Fe}(\text{CN})_6]$ solution in the presence of 0.1 mol dm^{-3} KCl across the potential range from -0.4 to $+0.5 \text{ V}$ with 50 mV s^{-1} scan rate.

The cyclic voltammograms in 1.0 mmol dm^{-3} ferrocene were performed in acetonitrile containing 0.1 mol dm^{-3} TBATFB across the potential range from -0.2 to $+0.5 \text{ V}$ with 50 mV s^{-1} scan rate.

Measurement of electrochemical impedance spectroscopy

The electrochemical impedance spectroscopy (EIS) measurements were performed across the frequency range from 100 kHz to 1 kHz with 10 mV wave amplitude at an electrode potential of 0.215 V by applying an AC voltage of the formal potential of redox probes. The electrochemical impedance spectroscopy measurements were obtained in the presence of a 1.0 mmol dm^{-3} $\text{K}_3\text{Fe}(\text{CN})_6$ and 1.0 mmol dm^{-3} $\text{K}_4\text{Fe}(\text{CN})_6$ redox probe mixture containing 0.1 mol dm^{-3} KCl.

Analytical procedure for the electrochemical detection of 8-hydroxyquinoline

The ANSA-GC modified electrode was placed in an electrochemical cell that contains 10 mL Britton-Robinson buffer solution at $\text{pH } 2.0$ for voltammetric measurements. To obtain the desired concentration of 8-hydroxyquinoline, an appropriate volume of 8-hydroxyquinoline was added from the $1 \times 10^{-3} \text{ mol dm}^{-3}$ stock solution.

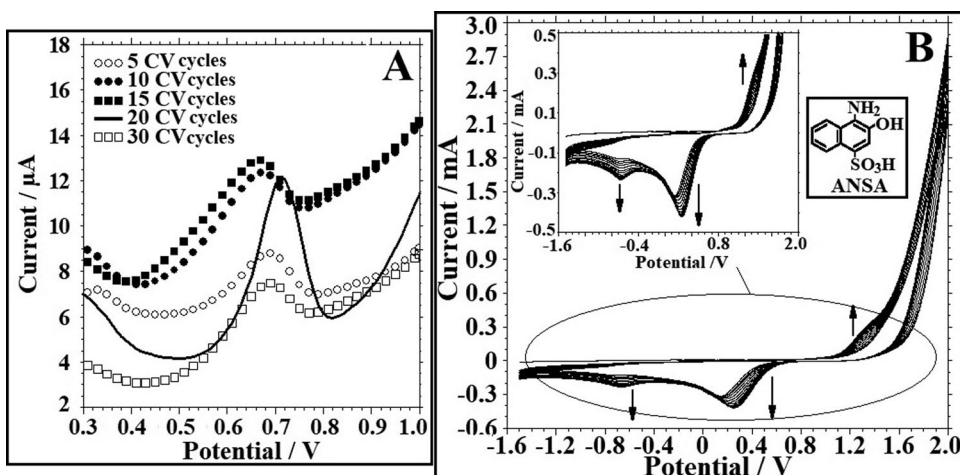


Figure 1. (A) Square wave voltammograms of $2 \times 10^{-4} \text{ mol dm}^{-3}$ 8-hydroxyquinoline in Britton-Robinson buffer solution at pH 2.0 on the ANSA-GC modified electrode prepared using 5, 10, 15, 20 and 30 electrochemical deposition cycles. (B) Cyclic voltammograms obtained in $1 \times 10^{-4} \text{ mol dm}^{-3}$ ANSA solution containing 0.1 mol dm^{-3} KCl solution on the GC electrode using a scan rate of 100 mV s^{-1} , a sweep segment of 20, and a sample interval of 1 mV.

Standard ultraviolet–visible spectrophotometric method for comparison

A standard spectrophotometric method was used to examine the accuracy of the proposed method. The spectrophotometric measurements were performed between 200 and 600 nm. The obtained peak absorbance for 8-hydroxyquinoline was at 310 nm. The calibration plot was prepared concentrations between 1.0 and $10 \mu\text{mol dm}^{-3}$ 8-hydroxyquinoline solution at 310 nm.

Results and discussion

Influence of the number of sweep segments for the preparation of ANSA-GC modified electrode

Figure 1A shows the influence of the number of sweep segments for the polymerization of ANSA upon the oxidation of $2 \times 10^{-4} \text{ mol dm}^{-3}$ 8-hydroxyquinoline using square wave voltammetry in pH 2.0 Britton-Robinson buffer solution. Sweep segment numbers of 5, 10, 15, 20, and 30 were used to determine the optimize the conditions. The oxidation peak current due to $2 \times 10^{-4} \text{ mol dm}^{-3}$ 8-hydroxyquinoline increased with the number of sweep segments from 5 to 20 and decreased at higher values. Therefore, 20 sweep segments for cyclic voltammetry were selected to be the optimum number for the preparation of ANSA-GC electrode.

The coverage of the glassy carbon surface was performed (Figure 1B) using $1 \times 10^{-4} \text{ mol dm}^{-3}$ ANSA solution in the presence of 0.1 mol dm^{-3} KCl using cyclic voltammetry between +2 V and −1.5 V with a 100 mV s^{-1}

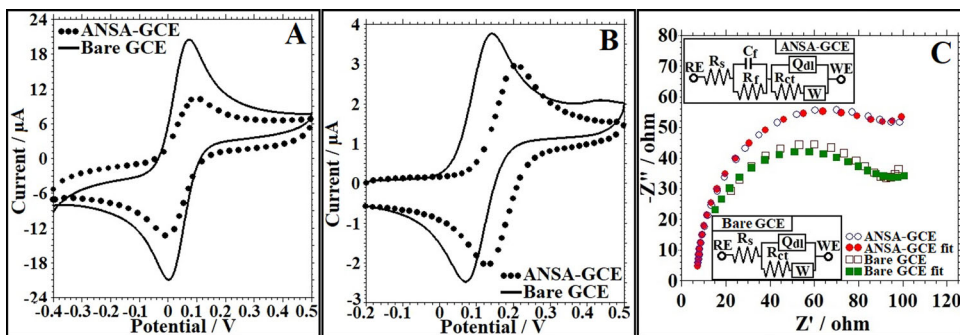


Figure 2. (A) Cyclic voltammograms of the unmodified GC and ANSA modified GC electrode in $1.0 \text{ mmol dm}^{-3} \text{ K}_3[\text{Fe}(\text{CN})_6]/\text{K}_4[\text{Fe}(\text{CN})_6]$ solution in the presence of $0.1 \text{ mol dm}^{-3} \text{ KCl}$. (B) 1.0 mmol dm^{-3} ferrocene in acetonitrile containing $0.1 \text{ mol dm}^{-3} \text{ TBATFB}$. (C) Nyquist diagram at the unmodified GC and ANSA modified GC electrode obtained in the electrochemical impedance spectroscopy measurements.

scan rate for 20 cycles. Characteristic irreversible cathodic and anodic peaks were observed in the cyclic voltammograms with maxima at approximately -0.65 , $+0.15$ and $+1.3 \text{ V}$. A gradual increase was observed on the peak current with an enhanced number of potential cycles. These results demonstrate that the ANSA film was electropolymerized upon the surface of unmodified GC electrode with each potential scan.

Electrochemical characterization of the ANSA-GC modified electrode

Blocking effect of ANSA-GC modified electrode on redox probes

In the characterization of the modified surfaces, redox probes such as ferrocene and $\text{K}_3\text{Fe}(\text{CN})_6/\text{K}_4\text{Fe}(\text{CN})_6$ are commonly used.^[25] The electrochemical properties of the redox probes on the unmodified and modified electrode surfaces were compared. $1.0 \text{ mmol dm}^{-3} \text{ K}_3\text{Fe}(\text{CN})_6/\text{K}_4\text{Fe}(\text{CN})_6$ (Figure 2A) and 1.0 mmol dm^{-3} ferrocene (Figure 2B) redox probes were employed for the voltammetric characterization of ANSA-GC.

The current peaks of the redox probes decreased following the coverage of the GC electrode surface with the ANSA molecules. These results show that the modified electrode surface conductivity was decreased. Figure 2A and B demonstrate that the peak currents of the redox probes decreased. These measurement demonstrate that the heterogeneous electron transfer rate of these probes was slightly reduced on the surface of the ANSA-GC modified electrode.^[9]

Characterization of the modified electrode by electrochemical impedance spectroscopy (EIS)

Following the modification process, electrochemical impedance spectroscopy (EIS) provides information about the impedance change of the

electrode surface and the electron transfer kinetics of the redox-probe controlled by this impedance change at the electrode interface.^[26] Figure 2C shows a Nyquist diagram (impedance plot) of the unmodified and modified GC electrodes. In addition, the inset of Figure 2C shows the experimental measurements that are fit to equivalent circuits for the unmodified and modified electrode surface analyses where R_f is the resistance of the solid electrolyte interface, R_s is the solution resistance, Q_{dl} is the double layer capacitance (constant phase element/CPE), R_{ct} is the charge transfer resistance, W is the Warburg element, and C is the capacitance in an equivalent circuit.^[27]

The semicircle diameter is equal to the charge transfer resistance (R_{ct}). After modifying the GC electrode with ANSA, the value of charge transfer resistance increased from 81 Ω (unmodified GC) to 100 Ω (ANSA-GC). As these curves demonstrate, the electrochemical impedance spectroscopy of the ANSA modified electrode displays a higher interfacial electron transfer resistance, indicating that the ANSA layer obstructed the electron transfer of the redox probe.

The relationship between the concentration of the redox probe and the charge transfer resistance is provided by:

$$k^{\circ} = \frac{RT}{R_{ct} F^2 A C n^2} \quad (1)$$

where C is equal to $1 \times 10^{-3} \text{ mol dm}^{-3}$ and is the redox probe concentration; R , equal to $8.314 \text{ J K}^{-1} \text{ mol}^{-1}$, is the ideal gas constant; A , equal to 0.07065 cm^2 , is the geometric surface area of the electrode; F , equal to 96485 C mol^{-1} , is the Faraday constant; T , equal to 298 K is the temperature; k° is the potential dependence; and n is the number of transferred electrons for the redox probe.^[27] The standard rate constant for electron transfer was determined by Equation (1).^[27] The k° values were calculated to be 4.49 cm s^{-1} and 3.63 cm s^{-1} on the unmodified GC and ANSA-GC electrodes, respectively.

This study demonstrates that a decrease in standard electron transfer rate occurred as a result of modification of the GC electrode surface with the ANSA film. Two reasons may cause the blockage of the covered film: First, the presence of the ANSA film creates a physical barrier on the electrode surface. This prevents the redox probe from accessing the GC electrode surface and charge transfer between the interfaces. Second, negative charges on the electrode surface may cause electrostatic repulsion.^[26] The increase in interfacial charge transfer resistance is caused by the electrostatic repulsion between negatively charged groups on the electrode and the negatively charged probe in the solution. The change in the impedance due to the modification process showed that ANSA molecules were attached to the GC surface. The EIS and CV results therefore agree with each other.

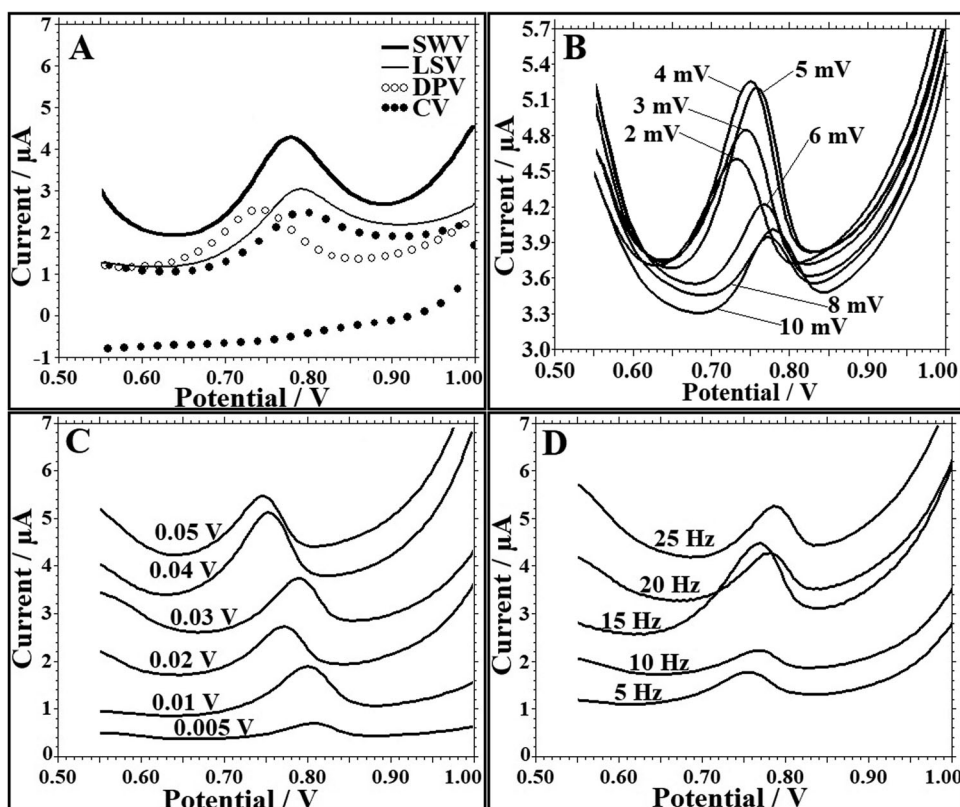


Figure 3. (A) Characterization of linear sweep voltammetry (LSV), square wave voltammetry (SWV), differential pulse voltammetry (DPV) and cyclic voltammetry (CV) for the oxidation of 8-hydroxyquinoline. (B) Optimization of the scan increment upon on the oxidation peak of $1 \times 10^{-5} \text{ mol dm}^{-3}$ 8-hydroxyquinoline for square wave voltammetry using a frequency of 15 Hz and an amplitude of 0.04 V. (C) Optimization of the amplitude on the oxidation of $1 \times 10^{-5} \text{ mol dm}^{-3}$ 8-hydroxyquinoline for square wave voltammetry using a frequency of 15 Hz and a scan increment of 4 mV. (D) Optimization of the frequency for the oxidation of $1 \times 10^{-5} \text{ mol dm}^{-3}$ 8-hydroxyquinoline for square wave voltammetry using an amplitude of 0.04 V and a scan increment of 4 mV.

Selection of the voltammetric procedure and the optimization of square wave voltammetry (SWV) for the determination of 8-hydroxyquinoline

Differential pulse voltammetry (DPV), linear sweep voltammetry (LSV), cyclic voltammetry (CV) and square wave voltammetry (SWV) were compared for determination of 8-hydroxyquinoline. Figure 3A shows the obtained voltammograms for $1 \times 10^{-5} \text{ mol dm}^{-3}$ 8-hydroxyquinoline. The oxidation peak current of 8-hydroxyquinoline was higher by square wave voltammetry than the other methods. In addition, the 8-hydroxyquinoline oxidation peak was sharper and better-defined using this method. Therefore, square wave voltammetry was selected for the determination of 8-hydroxyquinoline.

Square wave voltammetry has several advantages such as the rejection of background currents and excellent sensitivity. In addition, the use of square wave voltammetry may provide other information, including trace levels of some species as the electrode kinetics for preceding, following, or catalytic homogeneous chemical reactions.^[28]

The influence of different values of the scan increment, amplitude and frequency on the oxidation peak for $1 \times 10^{-5} \text{ mol dm}^{-3}$ 8-hydroxyquinoline was investigated and the obtained voltammograms are shown in Figure 3B, C and D, respectively. The maximum the anodic peak current value was obtained for a scan increment equal to 4 mV (Figure 3B), an amplitude of 0.04 V (Figure 3C), and a frequency of 15 Hz (Figure 3D). These optimized values were used in the subsequent square wave voltammetric measurements.

Influence of the supporting electrolyte and the pH on the oxidation of 8-hydroxyquinoline

The influence of the supporting electrolyte was investigated using square wave voltammetry and the results are shown in Figure 4A. The anodic peak of $2 \times 10^{-4} \text{ mol dm}^{-3}$ 8-hydroxyquinoline was obtained in pH 2.0 HClO_4 solution, pH 2.0 Britton-Robinson buffer, pH 4.5 acetic acid/sodium acetate buffer, pH 2.0 H_3PO_4 solution, and pH 7.0 phosphate buffer. The values of anodic peak current were determined to be 3.05, 6.14, 1.46, 2.83 and $1.70 \mu\text{mol dm}^{-3}$, respectively. Since the maximum peak current value was obtained in the Britton-Robinson buffer, this medium was selected to be the most suitable medium for the determination of 8-hydroxyquinoline.

The influence of pH upon the electrochemical response of $2 \times 10^{-4} \text{ mol dm}^{-3}$ 8-hydroxyquinoline on the ANSA-GC modified electrode was investigated using square wave voltammetry in Britton-Robinson buffer across the pH range from 1.0 to 6.0 as shown in Figure 4B. The oxidation peak current of 8-hydroxyquinoline reached a maximum value at pH 2.0. The peak current decreased gradually as the pH was increased from 2.0 to 6.0. Thus, for the determination of 8-hydroxyquinoline, pH 2.0 was selected to be the optimum value.

The relationship between the pH value and the anodic peak potential is shown in Figure 4C. The anodic peak potential shifted to more negative potential values with increasing pH. This response demonstrates that protons are directly associated with the oxidation of 8-hydroxyquinoline. The linear regression equation was described by $E(\text{V}) = -0.0623\text{pH} + 0.8447$ with a correlation coefficient R^2 equal to 0.9935. The slope value of (-0.0623 V/pH) is in close agreement with the potential shift predicted by the Nernst equation of -0.059 V/pH at 298 K.^[29] This response demonstrated that the numbers of proton and electron transferred in the oxidation process of 8-hydroxyquinoline were equal to each other.

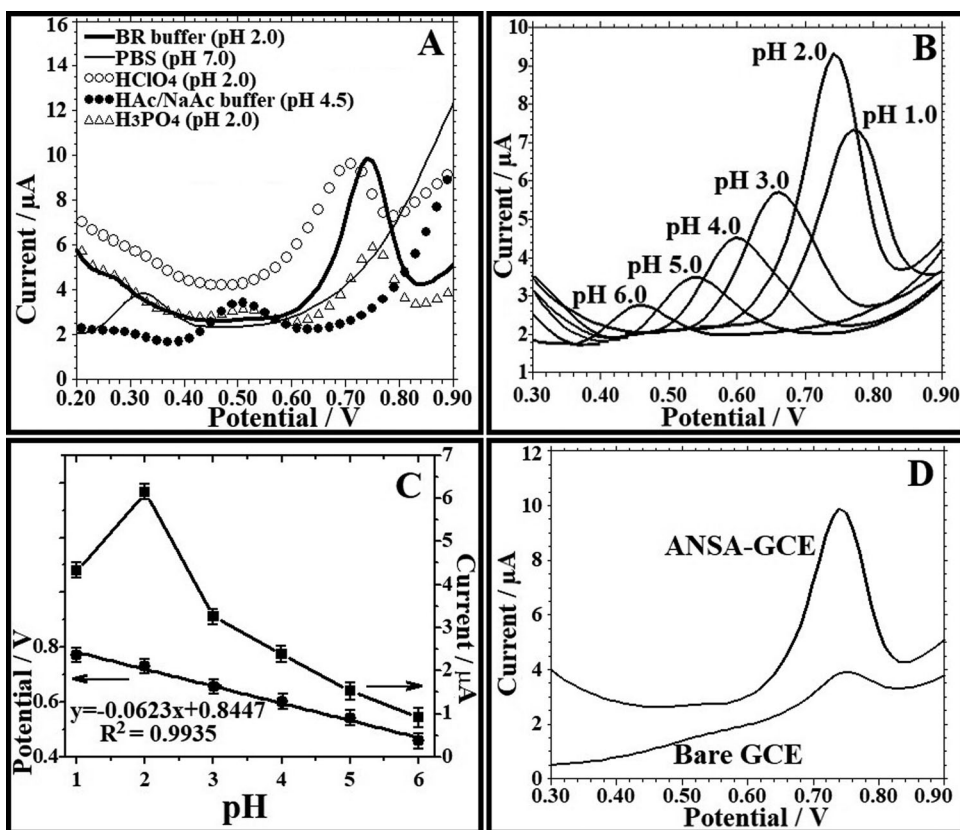


Figure 4. Square wave voltammograms of $2 \times 10^{-4} \text{ mol dm}^{-3}$ 8-hydroxyquinoline in (A) Britton-Robinson buffer at pH 2.0, phosphate buffer at pH 7.0, HClO_4 solution at pH 2.0, acetic acid/sodium acetate buffer at pH 4.5, and H_3PO_4 solution at pH 2.0. (B) Optimization of the pH for Britton-Robinson buffer at values of 1.0, 2.0, 3.0, 4.0, 5.0 and 6.0. (C) Plots of the peak potential and current values as a function of pH. (D) Voltammetric response of $2 \times 10^{-4} \text{ mol dm}^{-3}$ 8-hydroxyquinoline on the unmodified GC and ANSA-GC electrodes.

The voltammetric responses of $2 \times 10^{-4} \text{ mol dm}^{-3}$ 8-hydroxyquinoline were investigated on the unmodified GC and ANSA-GC modified electrode surfaces. The obtained voltammograms are shown in Figure 4D. The anodic peak current values for 8-hydroxyquinoline on the unmodified GC and ANSA-GC modified electrodes were equal to 1.08 and 6.15 mA, respectively. The peak current on the ANSA-GC modified electrode was 5.69 times higher than that the value obtained using the unmodified GC electrode.

Influence of the scan rate upon the electrochemical properties of 8-hydroxyquinoline on the modified ANSA-GC electrode

Important information about the mechanism of the electrochemical process may be obtained from the relationship between the scan rate (v) and the redox peak current (I) and potential.^[29] The influence of scan rate in the

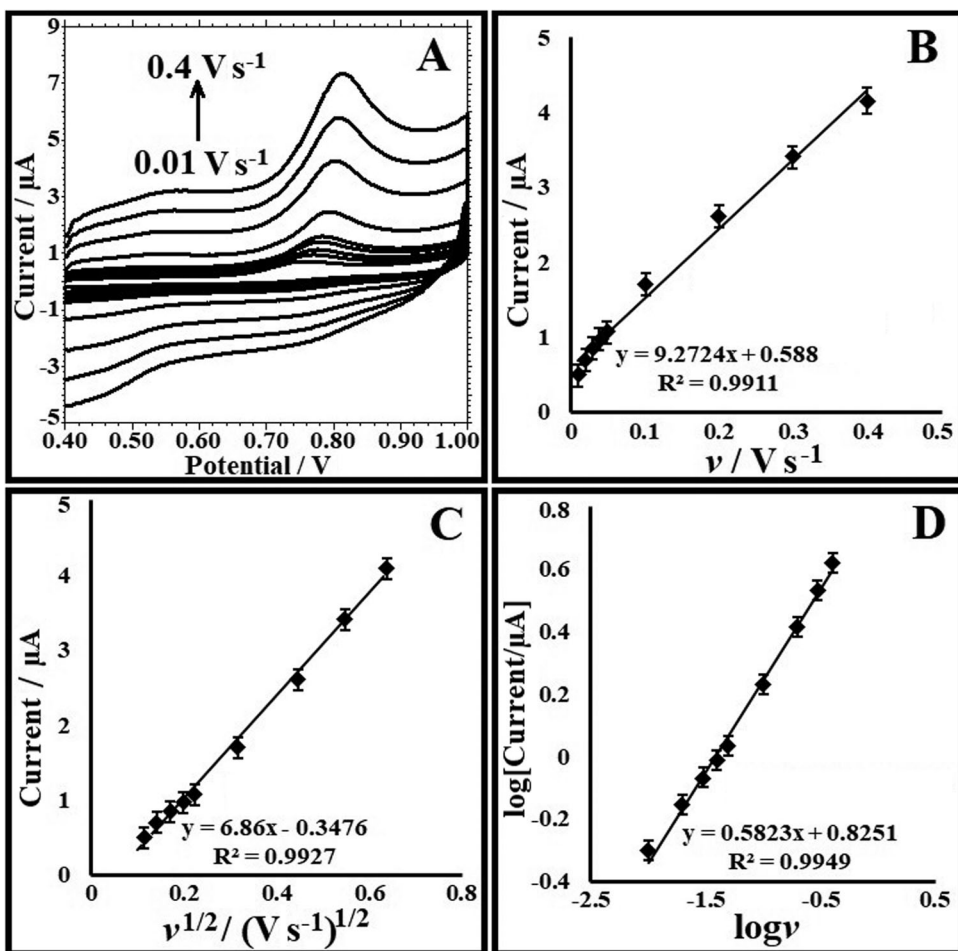


Figure 5. (A) Cyclic voltammograms of 2×10^{-4} mol dm⁻³ 8-hydroxyquinoline in Britton-Robinson buffer at pH 2.0 as a function of scan rate at values of 0.01, 0.02, 0.03, 0.04, 0.05, 0.1, 0.2, 0.3 and 0.4 V s⁻¹. (B) Plot of the peak current as a function of the scan rate v , (C) Plot of the peak current as a function of $v^{1/2}$, (D) Plot of the $\log[\text{Current}]$ as a function of the $\log(v)$.

presence of 2×10^{-4} mol dm⁻³ 8-hydroxyquinoline was investigated. When the scan rate was increased from 0.01 V s⁻¹ to 0.4 V s⁻¹ (Figure 5A), the anodic peak currents of 8-hydroxyquinoline was enhanced and the peak potential shifted to more positive values.

The plot of anodic peak current as a function of the scan rate is shown in Figure 5B. The corresponding linear equation is described by I (μA) = $9.2724v$ (V s⁻¹) + 0.588 with a correlation coefficient R^2 equal to 0.9911. The oxidation reaction on the ANSA-GC surface was an adsorption-controlled process because the peak current increased proportionally with the scan rate.^[29]

In addition, the plot of peak current versus $v^{1/2}$ is shown in Figure 5C. The corresponding linear equation is described by I (μA) = $6.86v^{1/2}$ (V s⁻¹)^{1/2} -

0.3476 with a correlation coefficient R^2 equal to 0.9927. The proportional increase in peak current (I_p) with the scan rate demonstrates that the oxidation reaction of 8-hydroxyquinoline on the surface of the modified electrode was an adsorption controlled process.^[30–32]

In addition, the linear relationship between $\log I$ and $\log v$ was described by $\log I = 0.5823 \log v + 0.8251$ with a correlation coefficient R^2 equal to 0.9949 as shown in Figure 5D. The theoretical slope values for the adsorption-controlled and diffusion-controlled processes are 1 and 0.5, respectively. For both adsorption-controlled and diffusion-controlled processes, the slope value is between 0.5 and 1.0.^[33] The slope value (0.5823) in this work was between the theoretical values of 0.5 and 1.^[34]

Analytical figures of merit of the ANSA-GC modified electrode for the determination of 8-hydroxyquinoline

Square wave voltammetry was used for the determination of 8-hydroxyquinoline because of its better detection limits and sensitivity. A linear relationship was obtained between the concentration values of 8-hydroxyquinoline and the anodic peak current values corresponding to these values. Square wave voltammograms curves of 8-hydroxyquinoline with various concentrations on the ANSA-GC modified electrode are shown in Figure 6.

A linear response was obtained in a wide concentration range from 5×10^{-7} to $1.4 \times 10^{-5} \text{ mol dm}^{-3}$ and from 1.4×10^{-5} to $4.25 \times 10^{-4} \text{ mol dm}^{-3}$ as shown in the Figure 6 inset. The resulting linear regression equations were $I_{pa} (\mu\text{A}) = 0.1200[8\text{-hydroxyquinoline}] (\mu\text{mol dm}^{-3}) - 0.0028$ with a correlation coefficient R^2 equal to 0.9984 and $I_{pa} (\mu\text{A}) = 0.0184[8\text{-hydroxyquinoline}] (\mu\text{mol dm}^{-3}) + 1.7110$ with a correlation coefficient R^2 equal to 0.9967, respectively. Moreover, the values of the limit of detection (LOD) and the limit of quantification (LOQ) were determined to be $1.6 \times 10^{-7} \text{ mol dm}^{-3}$ based on a signal-to-ratio of 3 and $5.5 \times 10^{-7} \text{ mol dm}^{-3}$ based on a signal-to-ratio of 10, respectively. The limits of detection and quantification were determined by:^[34]

$$LOD = \frac{3S}{m} \quad (2)$$

$$LOQ = \frac{10S}{m} \quad (3)$$

where m is the slope of the calibration equation and S is the standard deviation evaluated from the peak current corresponding to lowest concentration in the working range. The ANSA-GC electrode exhibited better analytical performance for 8-hydroxyquinoline using the optimized conditions.

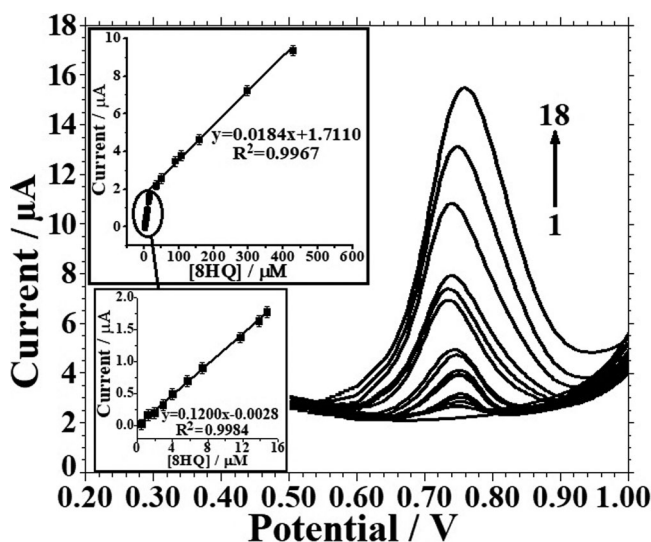


Figure 6. Square wave voltammograms for different concentrations (1→18: 0, 0.5, 1.2, 2.0, 2.9, 4.0, 5.7, 7.4, 11.7, 13.8, 14.7, 32.8, 48.4, 88.1, 106.1, 157.1, 295.8, and 425.6 $\mu\text{mol dm}^{-3}$) of 8-hydroxyquinoline in Britton-Robinson buffer at pH 2.0 on the ANSA-GC modified electrode. Upper inset: plot of peak current as a function of the higher concentrations of 8-hydroxyquinoline (2→10), Lower inset: plot of peak current as a function of the lower concentrations of 8-hydroxyquinoline (2→18).

Comparison of the reported method with similar studies in the literature

The voltammetric determination of the 8-hydroxyquinoline, which is added as a preservative to cosmetic products but has harmful effects on human health, is important. However, there are few studies in the literature related to the electrochemical determination of 8-hydroxyquinoline. A comparison of the proposed method with other studies in the literature is shown in Table 1.

The previous literature studies have reported a lower limit of detection for 8-hydroxyquinoline value than the value obtained in this study. However, a low limit of detection and a wide working range have been achieved using the ANSA-GC modified electrode. Also, the syntheses of the coating materials employed in the other studies are complicated and time-consuming.

The ANSA-GCE modified electrode is prepared in a short time and with fewer steps than the working electrodes used in other studies. The reduced number of steps in the preparation process saves time and reduces errors in the production. Therefore the ANSA-GC modified electrode has significant advantages for the determination of 8-hydroxyquinoline and is an alternative approach for this important analyte.

Stability, repeatability and reproducibility of the modified electrode

The repeatability of the ANSA-GC electrode was investigated in $1 \times 10^{-5} \text{ mol dm}^{-3}$ 8-hydroxyquinoline solution as shown in Figure 7A

Table 1. Comparison of the ANSA-GC modified electrode for the determination of 8-hydroxyquinoline by different modified electrodes.

Electrode	Technique	Limit of detection ($\mu\text{mol dm}^{-3}$)	Linear range ($\mu\text{mol dm}^{-3}$)	Reference
Multiwalled carbon nanotube/Nafion-GC electrode	Differential pulse voltammetry	0.009	0.02–10	[23]
Glassy carbon paste electrode	Differential pulse voltammetry	0.052	0.1–100	[3]
Sodium lauryl sulfate multiwalled carbon nanotube paste electrode	Cyclic voltammetry	0.11	20–350 and 400–1000	[35]
ANSA-GC	Square wave voltammetry	0.16	0.5–14 and 14–425.6	This work

and D. Ten replicate measurements using the same ANSA-GC electrode were carried out by square wave voltammetry and the relative standard deviation was shown to be 2.26%.

The reproducibility was investigated using ten identically prepared modified electrodes as shown in Figure 7B and and E. The relative standard deviation was shown to be 4.45%, demonstrating a reliable procedure for the preparation of the modified electrode.

To evaluate the stability of the modified electrode, square wave voltammograms of $1 \times 10^{-5} \text{ mol dm}^{-3}$ 8-hydroxyquinoline were obtained on the first, seventh and fifteenth days following the preparation of an ANSA-GC modified electrode. The prepared modified electrode was stored in ultra-pure water at room temperature and the results are shown in Figure 7C and F.

After seven days, the peak current of 8-hydroxyquinoline underwent a decrease of 5.38%. A reduction of 9.56% in the peak current was observed after fifteen days. These results show that the ANSA-GC electrode provided good reproducibility, repeatability and high stability for the voltammetric determination of 8-hydroxyquinoline.

Interferences

The possible presence of interferences due to other species present in cosmetic products with 8-hydroxyquinoline were investigated. NaCl, NaOH, KOH, $\text{Al}(\text{OH})_3$, phosphoric acid, ascorbic acid, citric acid, benzyl alcohol, alanine, lysine and glycerin may be present in the cosmetics. The influence of these compounds was investigated using the optimal conditions for the determination of 8-hydroxyquinoline. The results showed that 100-fold excess concentrations of NaCl, NaOH, KOH, and ascorbic acid; 30-fold excess concentrations of phosphoric acid, citric acid, alanine, and lysine; and 10-fold concentration of $\text{Al}(\text{OH})_3$, glycerin, and benzyl alcohol did not significantly influenced the peak current height, with variations of less than 5%. The effect of some ions and molecules on the peak currents of 10

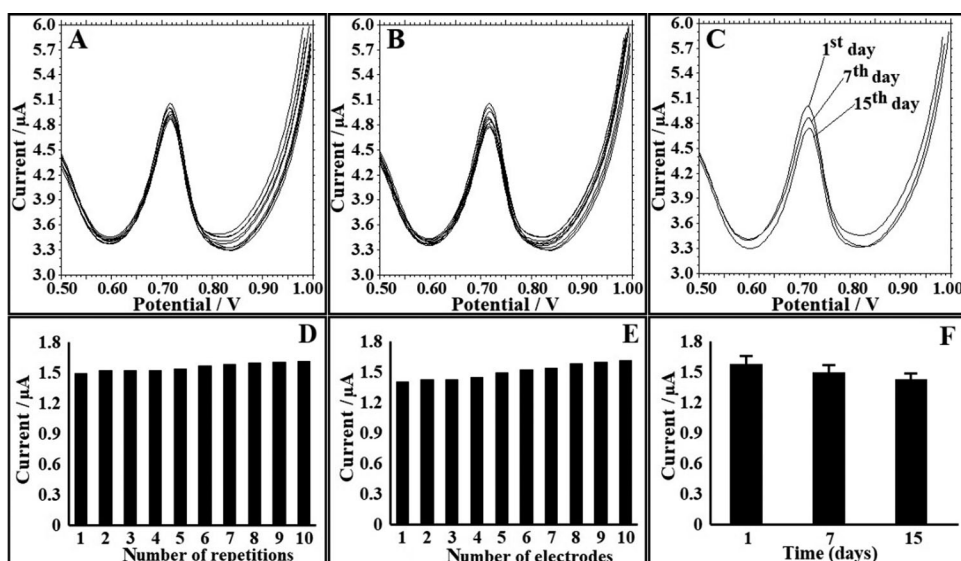


Figure 7. Square wave voltammograms of $1 \times 10^{-5} \text{ mol dm}^{-3}$ 8-hydroxyquinoline (A) at the same and (B) the different ANSA-GC electrodes. (C) Square wave voltammograms obtained following storage of the ANSA-GC electrode in ultrapure water for 7 and 15 days. Peak currents of 8-hydroxyquinoline at (D) the same and (E) the different ANSA-GC modified electrodes. (F) Measured peak currents for 8-hydroxyquinoline on the day of preparation and 7 and 15 days after preparation.

Table 2. Characterization of potential interfering species upon the determination of $10 \mu\text{mol dm}^{-3}$ 8-hydroxyquinoline.

Coexisting substance	Concentration (mM)	Change of peak current (%)
NaCl	1	+3.56
NaOH	1	−4.09
KOH	1	−4.37
$\text{Al}(\text{OH})_3$	0.1	−3.94
Phosphoric acid	0.3	+2.38
Ascorbic acid	1	+1.26
Citric acid	0.3	+3.07
Benzyl alcohol	0.1	+2.29
Alanine	0.3	+3.01
Lysine	0.3	+3.43
Glycerin	0.1	−1.12

$\mu\text{mol dm}^{-3}$ 8HQ was given in Table 2. Hence, these results show that the ANSA-GC modified electrode is selective for the determination of 8-hydroxyquinoline in the cosmetic samples.

Analysis of cosmetics for 8-hydroxyquinoline

Cosmetic blush was purchased and analyzed to investigate the suitability of the developed method for real sample analysis. 0.5 g of the blush sample was sonicated for 30 min in 15 mL of 1:1 ethanol-water. The resulting mixture was filtered and the filtrate was used to determine 8-hydroxyquinoline. Two volumes of the filtrate were added to the electrochemical cell

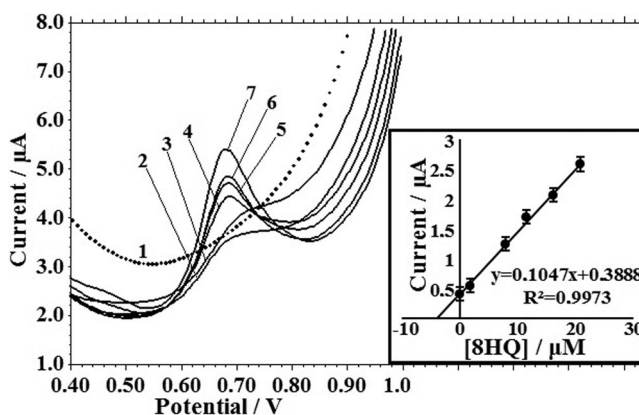


Figure 8. Square wave voltammograms obtained for the determination of 8-hydroxyquinoline in a blush cosmetic sample: (1) Britton-Robinson buffer electrolyte solution at pH 2.0, (2) the blush sample, (3) $1.9 \mu\text{mol dm}^{-3}$ 8-hydroxyquinoline, (4) $6.8 \mu\text{mol dm}^{-3}$ 8-hydroxyquinoline, (5) $11.5 \mu\text{mol dm}^{-3}$ 8-hydroxyquinoline, (6) $16.2 \mu\text{mol dm}^{-3}$ 8-hydroxyquinoline, and (7) $21 \mu\text{mol dm}^{-3}$ 8-hydroxyquinoline. Inset: plot of the peak anodic current as a function of the concentration of 8-hydroxyquinoline.

containing 10 mL of the supporting electrolyte solution to obtain two concentrations of 8-hydroxyquinoline.

The concentrations of 8-hydroxyquinoline in these solutions were determined using square wave voltammetry by the method of standard addition to be $3.747 \mu\text{mol dm}^{-3}$ and $10.317 \mu\text{mol dm}^{-3}$. A blush sample was added to the electrochemical cell containing pH 2.0 Britton-Robinson buffer as the supporting electrolyte as shown in Figure 8. Then, known volumes of the standard 8-hydroxyquinoline solutions were added and voltammograms were obtained. Figure 8 shows example voltammograms for the sample. The obtained concentration was $3.747 \mu\text{mol dm}^{-3}$ for five replicate measurements by square wave voltammetry.

For comparison purposes, the sample was also analyzed by a standard spectrophotometric procedure and values of $3.706 \mu\text{mol dm}^{-3}$ and $10.289 \mu\text{mol dm}^{-3}$ were obtained. The results are summarized in Table 3. The recovery values were 101.1% and 100.3% and relative standard deviations were 1.05% and 0.26%. The results showed that the determination of 8-hydroxyquinoline in the cosmetic sample using ANSA-GC modified electrode was performed with good accuracy and precision.

A *t*-test was performed to determine whether there is agreement between the values obtained by square wave voltammetry and the reference spectrophotometric procedure. For the two concentrations of 8-hydroxyquinoline, the *t* values were determined to be 1.95 and 2.34. When the degrees of freedom were 4 and the confidence level was 95%, the theoretical *t* value was 2.78. The calculated *t* values were lower than the theoretical *t* value. This

Table 3. Determination of 8-hydroxyquinoline in a blush cosmetic sample on ANSA-GC modified electrode in Britton-Robinson buffer solution at pH 2.0.

Sample	Square wave voltammetry ^a ($\mu\text{mol dm}^{-3}$)	Spectrophotometry ^a ($\mu\text{mol dm}^{-3}$)	Relative Standard Deviation (%)	Recovery (%)	t_{ex}^b	t_{cri}^b	F_{ex}^c	F_{cri}^c
Blush 1	3.747 ± 0.039	3.706 ± 0.024	1.05	101.1	1.95	2.78	2.64	6.94
Blush 2	10.317 ± 0.027	10.289 ± 0.020	0.26	100.3	2.34	2.78	0.54	6.94

^a $N = 5$ ^b t_{ex} calculated t value; t_{tab} reported t value from Student t -test table with 95% confidence level.^c F_{ex} calculated F value; reported F value from F -test table with 4/2 degrees of freedom and 95% confidence level.

result shows that there was no significant difference in the results by these methods applied, showing the developed method was reliable.

In addition, the F -test was also employed to determine whether significant differences are present between these two methods. For the two concentrations of 8-hydroxyquinoline, the F values were determined to be 1.052 and 1.277. When the degrees of freedom were 4 and the confidence level was 95%, the statistical value of F was 6.39. Since the calculated F values are lower than the statistical F value, there are no significant difference between standards for these methods.

Conclusion

8-Hydroxyquinoline is an important compound that is known to have harmful effects on human health and is employed as a preservative in cosmetic products. This report describes for the first time the use of an ANSA-GC modified electrode for the determination of 8-hydroxyquinoline by square wave voltammetry. A simple, new, inexpensive and rapidly prepared electrochemical sensor was successfully fabricated with ANSA on the GC electrode for the determination of 8-hydroxyquinoline.

The ANSA-GC modified electrode was characterized by electrochemical methods including cyclic voltammetry and electrochemical impedance spectroscopy. By optimizing the electrochemical conditions, a low limit of detection and a wide linear concentration range were obtained with good reproducibility and repeatability for the determination of 8-hydroxyquinoline on the ANSA-GC modified electrode. The voltammetric analysis using the ANSA-GC modified electrode provided excellent reproducibility, selectivity, stability, repeatability, reliability, and accuracy.

As a result, the determination of 8-hydroxyquinoline in the cosmetic sample was successfully performed using the ANSA-GC modified electrode.

Disclosure statement

No potential conflicts of interest are reported by the authors.

ORCID

Tuğba Tabanlıgil Calam  <http://orcid.org/0000-0002-3712-7713>

Elif Begüm Yılmaz  <http://orcid.org/0000-0001-5742-3694>

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