

Determination of hydroquinone in a square wave voltammetry procedure using a graphite-polyurethane composite electrode

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Abstract: In order to a better characterization of a graphite-polyurethane composite intended to be used as a voltammetric sensor, the performance in a square wave voltammetric procedure was investigated. Using hydroquinone (HQ) as a probe, the electrode showed to be useful in square wave voltammetry with limit of detection of $0.28 \mu\text{mol L}^{-1}$, with recoveries between 99.1 and 101.5%. The results of the proposed method agreed with HPLC ones within 95% confidence level.

Keywords: composite electrodes; polyurethane; square wave voltammetry.

Introduction

The development of electroic materials in substitution to mercury, which is limited to use in anodic potentials and due to their potentially hazards to health and environment has been a useful field of search in electroanalytical chemistry. The composite electrodes are among these materials.

According to, Tallman and Petersen [1], a composite electrode can be defined as heterogeneous material composed of at least an insulating phase mixed to at least one conducting phase. Usually the conducting phase is the graphite powder and the insulating, also called agglutinant, can be a mineral oil as proposed by Adams [2] for carbon pastes, or waxes and polymers [3].

Regarding the use of polymers as agglutinants, many composite electrodes of graphite with epoxy [4,5], polyester [6,7], PVC [8,9], polypyrrole [10,11] have been proposed for amperometric and voltammetric determinations in the quantification of different analytes.

Recently, a new composite material prepared with graphite and a castor-oil derivative polyurethane resin (PU), mixed in different compositions,

has been proposed as an alternative electrode material [12]. The electrode presented promising usefulness when compared to the glassy carbon [13,14].

Hydroquinone (HQ) was chosen a probe, since it is a compound that presents a well-known voltammetric behavior and recently [15] became one of the most used organic reducing agent, especially in the production of inhibitors of polymerization, in photographic developers, besides application in cosmetics. Due to its importance, hydroquinone has been quantified by different procedures, like flow injection with electrochemical detection [16], amperometric [17], cyclic voltammetry [18]. The most used are the chromatographic procedures [19-21], however such procedures use to be time consuming and generate considerable amount of residues. So, the development of alternative methods for hydroquinone is an important issue.

In this work, the graphite-PU electrode performance in an analytical procedure for the quantification of hydroquinone in photographic developers using square wave voltammetry (SWV) was developed. In order to obtain the best analytical response, parameters, such as frequency, pulse amplitude and step potential, were optimized.

Experimental details

Reagents and solutions

All reagents were of analytical grade and used as received. Solutions were prepared with water distilled twice in quartz stiller. Stock 1.00 mmol L^{-1} HQ (Sigma, Brazil) in 0.1 mol L^{-1} acetate buffer pH 4.5 solution was used in quantitative measurements. The photographic developer D-76 from Kodak (Brazil) was used as HQ commercial sample.

Apparatus

Voltammetric experiments were performed using an AUTOLAB PGSTAT-30 galvanostat/ potentiostat coupled to a microcomputer and controlled with a 4.9-GPES software. A three-electrode cell (25 mL total capacity) was used with an Ag/AgCl electrode and a platinum wire as the reference and auxiliary electrodes, respectively. All measurements were performed at room temperature.

Preparation of the composite electrode

The 60% (graphite, w/w) composite graphite-PU electrode was prepared as previously described [12].

Procedures

Voltammetric measurements were performed without deaeration, using the 60% (graphite, w/w) composite and the glassy carbon (GC) electrodes for comparison.

The cyclic voltammograms were obtained between -600 e 1000 mV for 5.00 mmol L^{-1} HQ with scan rate 25 mV s^{-1} .

For the measurements of square wave voltammetry (SWV) a $5.00 \cdot 10^{-5} \text{ mol L}^{-1}$ HQ in acetate buffer pH 4.5 solution was used as probe, in a potential window of $0 - 1000 \text{ mV}$, with frequency (f) of 50 s^{-1} , pulse amplitude (ΔE_p) of 50 mV and step potential (ΔE_s) of 10 mV . These parameters were optimized on the basis of multivariate calibration, using a factorial planning 2^n , where n = number of variable: f (50 and 200 s^{-1}) and ΔE_s (10 and 50 mV) under a pulse amplitude fixed at 50 mV .

The standard addition method in the photographic developer samples was performed as follows. To a well known amount of photographic developer content $1.00 \cdot 10^{-4} \text{ mol L}^{-1}$ of HQ dissolved in 0.1 mol L^{-1} acetate buffer pH 4.5, three $100 \mu\text{L}$ aliquots of $2.00 \cdot 10^{-2} \text{ mol L}^{-1}$ standard HQ solutions were added and successive voltammograms were recorded under the optimized conditions for each addition.

Comparison Method [13]

The HQ content in the commercial sample was also determined in a HPLC procedure after removing the sulfite and carbonate present in the photographic developer, by addition of barium chloride to the sample solutions. These ions probably form low soluble salts in the mobile phase, prejudicing the analytical signal.

Samples were prepared by weighing aliquots of 0.0300 g of the photographic developer, which were placed in 50 ml volumetric flasks. To the same flask it was added 0.07 g of barium chloride and the volume was completed with acetate buffer pH 4.5.

The resulting solution correspond to $2.72 \cdot 10^{-4} \text{ mol L}^{-1}$ (30.0 ppm) HQ, according to the label value, was then sonicated during 10 minutes and filtered in sinterized glass plate funnel. Finally $300 \mu\text{l}$ aliquots of the filtered solution were transferred to four different 10 ml volumetric flasks. Standard additions of 0 , 300 , 600 and $900 \mu\text{l}$ of standard 9.08 mmol L^{-1} (1000 ppm) HQ were then added to each flask and the volume completed with acetate buffer pH 4.5. The procedure was repeated at least three times.

The HPLC chromatograms were recorded in a Shimadzu LC-10AD UP chromatograph, equipped with an Aldrich RP-18 column ($150 \times 4.6 \text{ mm}$, $5 \mu\text{m}$), using methanol:water ($60:40 \text{ v/v}$) as mobile phase, flowing at 1.0 ml min^{-1} . The detection was performed at 288 nm using a photo diode array SPD-M 10A UP (HP) detector. The HQ retention time was 2 minutes according the standard addition method.

Results and Discussion

Determination of Hydroquinone

Cyclic voltammograms when compared under the same experimental conditions, suggest that the 60% (graphite, w/w) composite electrode presented low residual current and higher intensity of HQ current peak than the GC, as describe earlier [12] for other analytes.

At respect to SWV, it is a technique dependent of the frequency (f), amplitude (ΔE_p) and step potential (ΔE_s) [22,23]. The best results were obtained with $f = 50 \text{ s}^{-1}$ and $\Delta E_s = 10 \text{ mV}$ with $\Delta E_p = 50 \text{ mV}$. The resulting voltammograms are presented in Fig. 1, from which is possible to observe the HQ oxidation at c.a. 420 mV (vs. Ag/AgCl), with good definition in both forward, reverse and net curves. This suggests that the 60% (graphite, w/w)

composite electrode is a suitable tool to be used in SWV procedures, when using HQ as a probe.

Using these optimized conditions an analytical curve has been obtained in the $1.00 \cdot 10^{-6}$ to $1.00 \cdot 10^{-3}$ mol L⁻¹ range. The results are presented in Fig. 2 with an insert for lower concentrations. The curves were obtained with no need of surface renewing between successive determinations.

In the investigated interval one linear region was determined between 1 and 400 $\mu\text{mol L}^{-1}$, obeying the linear equation $I_p = -6.44 \times 10^{-8} \text{ A} + 7.10 \times 10^{-2} \text{ A mol}^{-1} \text{ l [HQ]}$, ($n = 10$, $R = 0.999_6$).

For concentrations higher than 400 $\mu\text{mol L}^{-1}$ a practically constant current was observed, suggesting a saturation of the active sites of the electrode. The limit of detection (LOD) obtained in the interval 1.00 to 400 $\mu\text{mol L}^{-1}$ was of 0.28 $\mu\text{mol L}^{-1}$, determined as three times the standard deviation of the blank (S_d) divided by the angular coefficient of straight line (b) in the region 1-10 $\mu\text{mol L}^{-1}$ [24]:

$$\text{LOD} = 3 S_d / b \quad (1)$$

An analytical curve for HQ was also obtained at the GC using the same conditions employed in the experiments with the 60%

(graphite, w/w) composite electrode.

As observed to the composite, one linear region was determined, but in the 6 to 1000 $\mu\text{mol L}^{-1}$ range, with equation $I_p = -0.200 \times 10^{-6} \text{ A} + 0.0500 \text{ A mol}^{-1} \text{ l [HQ]}$, ($n = 12$, $R = 0.998_8$). The LOD observed for HQ using GC electrode is coincident with the first signal in the linear range.

It was observed that the linear region was higher to the GC in relation to the 60% (graphite, w/w) composite, because in the composite a decrease in the sensibility of the current occurs at higher concentrations. Therefore, it was observed that the peak current is higher and the LOD is smaller to the composite when compared to the GC, since the first is 0.28 $\mu\text{mol L}^{-1}$ while for the GC is only 6 $\mu\text{mol L}^{-1}$.

Ten SWV voltammograms of $5.00 \cdot 10^{-5}$ mol L⁻¹ HQ in 0.1 mol L⁻¹ acetate buffer pH 4.5, were successively recorded at the 60% (graphite, w/w) composite electrode and revealed a repeatability of $(2.60 \pm 0.138) \mu\text{A}$, $n=10$, for the peak current. The electrode surface was renewed after each measure, as describe in the experimental section.

Standard additions of 99, 198 and 296 $\mu\text{mol L}^{-1}$ HQ to solution of the photographic developer containing $1.00 \cdot 10^{-4}$ mol L⁻¹ of HQ showed recoveries between 99.1 to 101.5%.

Table 1. Determination of HQ in the Kodak D-76 photographic developer

Hydroquinone / mg g ⁻¹				
Labeled	SWV	HPLC	E ₁ / %	E ₂ / %
50.0	49.8 ± 0.1	51.5	-0.5	3.4

E₁: SWV vs labeled (SWV-labeled/labeled) x 100%

E₂: SWV vs HPLC (SWV-HPLC/HPLC) x 100%

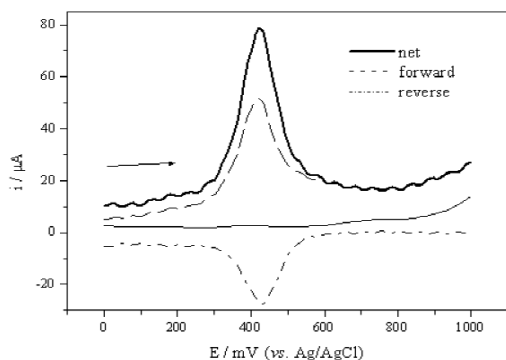


Figure 1. Voltammograms of SWV obtained for 60% (graphite, w/w) composite electrode using $5.0 \cdot 10^{-5}$ mol L⁻¹ HQ in acetate buffer pH 4.5, $f = 50$ s⁻¹, $\Delta E_p = 50$ mV, $\Delta E_s = 10$ mV.

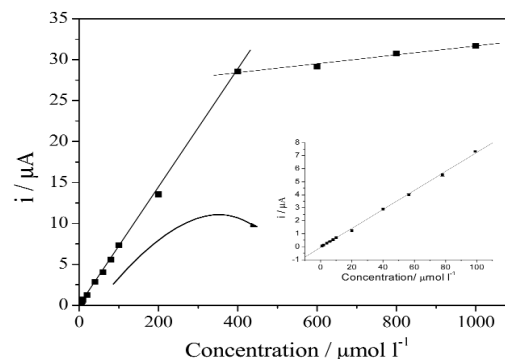


Figure 2. Peak current dependence of the HQ concentration at 60% (graphite, w/w) composite electrode, in SWV under the optimized conditions described in the text.

Application of the method

The performance of the proposed method in the determination of HQ in commercial photographic developer sample was evaluated. For the voltammetric determination of the HQ amount present in the photographic developer D-76, the successive standard addition method was used. The voltammograms were recorded at the 60% (graphite, w/w) composite electrode in SWV without surface renewing between measurements. The conditions for the determination of hydroquinone were those optimized as above.

The results obtained in the determination of HQ using the composite 60% (graphite, w/w) by SWV were compared with those obtained by HPLC and the results are presented in Table 1. These results agree in the limit of confidence of 95%, according *t*-Student test.

Comparing the results obtained with SWV and HPLC methods, it is found a LOD of 0.28 $\mu\text{mol L}^{-1}$ using the composite in SWV, for the linear response of 1.0 – 400 $\mu\text{mol L}^{-1}$ and a LOD of 0.54 $\mu\text{mol L}^{-1}$ in HPLC for the linear response of 8.17 – 825 $\mu\text{mol L}^{-1}$.

P. Cervini, E.T.G. Cavalheiro, Determinação de Hidroquinona em Voltametria de Onda Quadrada Usando um Eletrodo Compósito de Grafite-Poliuretana.

Resumo: Para uma melhor caracterização do eletrodo compósito grafite-poliuretana como um sensor voltamétrico, seu desempenho foi avaliado em voltametria de onda quadrada. Usando a hidroquinona (HQ) como uma sonda, o eletrodo mostrou-se útil em voltametria de onda quadrada, com limite de detecção de 0,28 $\mu\text{mol L}^{-1}$, com recuperações entre 99,1 e 101,5%. Os resultados do método proposto concordaram com o método comparativo HPLC, com um nível de confiança de 95%.

Palavras-chave: eletrodos compósitos; poliuretana; voltametria de onda quadrada.

Conclusions

According to these results it can be concluded that the 60% (graphite, w/w) graphite-PU composite electrode represents an interesting alternative to be used in SWV. The determination of HQ in photographic developer using this composite showed to be an efficient alternative method, allowing low cost, no need of surface renewing between measurements, long useful life, repeatability and low reagent consumption.

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