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The use of a graphite–castor oil polyurethane composite electrode for the determination of hydroquinone in photographic developers

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Abstract

The performance of a new graphite–castor oil polyurethane composite electrode in the determination of hydroquinone in photographic developers in a differential pulse voltammetric (DPV) procedure is described. The 60% (graphite, w/w) composite electrode presented good stability, repeatability and accurate response. Limit of detection of $934 \, nmol \, L^{-1}$ was observed for hydroquinone within a linear dynamic range from 66 to $530 \, nmol \, L^{-1}$. The determination of hydroquinone in a photographic developer sample showed agreement with the label values in a 95% confidence level with maximum 2% relative error and recoveries between 100.1 and 100.4%. No need of sample preparation was required since the *p*-methylaminophenolsulfate (metol) present in the developer formulation did not interfered in the measurements.
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1. Introduction

The use of solid materials, such as composite electrodes, as detectors for electrochemical analysis is commonly known [1]. A composite electrode results from the combination of two or more dissimilar materials. In general it can be defined as a material consisting of at least one conductor phase mixed with at least one insulator phase [2]. Each individual component keeps its original nature while giving the composite distinctive chemical, mechanical and physical properties, different from those shown by the individual components. These electrodes can be classified according to the way in which the conductor and the insulator are distributed within the material [3]. In particular, composite materials of graphite (carbon) present good properties for use as electrodes and sensors [4].

Carbon electrodes are suitable for analysis of the oxidation and reduction processes of both organic and inorganic compounds but are primarily employed for the investigation of electrochemical oxidation processes, because of their wide anodic polarization range and low residual current within this range. In the positive potential range carbon electrodes present several advantages over mercury and some noble metal electrodes [5]. Among the more successful types of composites is the carbon paste electrode prepared from as intimate mixture of graphite and an organic liquid. However, these electrodes have one serious disadvantage since they have limitation for use in nonaqueous solvents [6] and they have low operational stability when a long lifetime is required [7]. In this way, solid composite carbon electrodes, prepared with polymers, can be advantageous for electrochemical analysis, showing several improved properties such as polishing surface regeneration, rigidity, easiness of fabrication, economy and possibility of using in nonaqueous solvents [8]. Recently we proposed the use of a new composite prepared from castor oil derivative polyurethane (PU) and graphite as an electrode material [9].

The use of a composite prepared from graphite and polyurethane polymer obtained from vegetal oil present some advantages, as: (i) reduce risks to the environment; (ii) present

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low temperature in the curing process; (iii) is a bi-component liquid system, formed by a poliol and a pre-polymer, what confers easiness in the preparation, by simply mixing the binder with carbon and eventual modifiers; (iv) present high hydrophobicity, reducing volume variation in presence of aqueous solutions and avoiding undesirable infiltration in the electrodes; (v) resistance to many nonaqueous solvents, acid and basic solutions and (vi) it can be used in different compositions, depending on the study. Due the facility of surface renewal of composite electrodes, they can be used in determinations, of substances that can adsorb or polymerize in the sensor surface, as the phenolic species, among others.

The hydroquinone is a phenolic compound which is important in a wide number of biological and industrial processes such as coal-tar production, paper manufacturing and, specially, photographic developers, and in the aquatic environment. The determination and quantification of this analyte may be performed using different techniques, such as HPLC [10,11] with different detectors, flow injection analysis [12], kinetic spectrophotometry [13], differential pulse voltammetry [14], based on the Belousov–Zhabotinski oscillating chemical reaction [15] or biosensors [16]. Therefore, few studies involving the determination of this reducer in photographic developers has been developed [17–19]. Thus, the developing of novel procedures for direct quantification of hydroquinone in photographic developers is very important, representing an interesting test for the new graphite–PU composite electrode.

The detection limits found in the literature for hydroquinone vary in a wide range of concentrations, depending on the technique used. The lowest limits were achieved with capillary electrophoresis at $0.05 \, ng \, mL^{-1}$ level [20]. However for electroanalytical techniques the lower LOD described is $8 \, \mu mol \, L^{-1}$, with a method based in a biosensor [17] detector.

Thus, this work describes the use of a carbon–castor oil polyurethane composite electrode with the purpose of to determine hydroquinone in photographic developers, in a differential pulse voltammetric procedure. Different parameters were evaluated and optimized for this quantification. The analysis was accomplished without pre-treatment of the sample.

2. Experimental

2.1. Reagents and solution

All reagents were of analytical grade and used as received. Solutions were prepared with water bi-distilled in quartz stiller.

Hydroquinone was purchased from Sigma (St. Louis, MO, USA) and a $5.0 \times 10^{-3} \, mol \, L^{-1}$ stock solution was prepared in $0.1 \, mol \, L^{-1}$ acetate buffer of pH 4.0. Reference solutions from 6.60 to $53.0 \times 10^{-8} \, mol \, L^{-1}$ were prepared from stock solution by appropriated dilutions with the same buffer solution.

Metol were purchased from Aldrich (Milwaukee, WI, USA) and a solution was prepared in $0.1 \, mol \, L^{-1}$ acetate buffer solution (pH 4.0).

The Kodak D-76 photographic developer (São José dos Campos, SP, Brazil), was purchased from a local store and analyzed using the proposed composite electrode. No sample preparation was required.

2.2. Apparatus

Voltammetric experiments were performed in a BAS-CV 50 W potentiostat interfaced with a personal computer. The area of the 60% (graphite, w/w) composite working electrode was $0.135 \, cm^2$ [9]. A glassy carbon electrode ($\phi = 3 \, mm$) was used for comparison in the voltammetric measurements. A three-electrode cell (25 mL capacity) was used with a saturated calomel electrode (SCE) and a platinum wire as the reference and auxiliary electrodes, respectively. All measurements were performed at room temperature.

2.3. Preparation of the working electrode

The composite containing 60% of graphite and 40% of castor oil polyurethane was prepared as described in a previous work [9]. The electrode was prepared from rods of the composite (3 mm diameter) extruded in a press. Pieces 50 mm longer were cut and attached to a copper wire with the help of a silver epoxy (EPO-TEK 410 E, Epoxy Technology, Billerica, MA, USA) and let to cure for 24 h. The electrode was sealed in a glass tube using the same polyurethane resin without graphite and used after at least 24 h. After curing, the excess of polymer was removed using a 600-grit sand paper, polished with $1 \, \mu m$ alumina slurries in an APL-2 polishing wheel (Arotec, São Paulo, SP, Brazil) followed by sonication in isopropyl alcohol for 5 min. The electrode was then washed with large amount of water.

2.4. Electrochemical measurements

Cyclic voltammograms were obtained using $5.0 \times 10^{-5} \, mol \, L^{-1}$ hydroquinone solution in $0.1 \, mol \, L^{-1}$ acetate buffer pH 4.0 between -0.25 and $+0.60 \, V$ at a $25 \, mV \, s^{-1}$ scan rate at the 60% (graphite, w/w) composite and carbon paste electrodes with 3 mm of diameter.

The carbon paste was prepared by mixing 40% (w/w) graphite powder (1–2 μm particle size, Aldrich) with 60% (w/w) mineral oil (Aldrich) in a mortar. The mixture was homogenized during 20 min with a pestle and inserted a 3 mm i.d. polyethylene tube. The electric contact was achieved with a copper wire.

Differential pulse voltammograms of the 60% (graphite, w/w) composite electrode was recorded in $5.0 \times 10^{-5} \, mol \, L^{-1}$ hydroquinone solution in $0.1 \, mol \, L^{-1}$ acetate buffer pH 4.0 between -0.25 and $+0.60 \, V$ at a $5 \, mV \, s^{-1}$ scan rate 50 mV pulse amplitude. These parameters were optimized on the basis of multivariate calibration,

using a factorial planning 2^n, where n = number of variable: scan rate and amplitude searching for higher sensitivities. These variables were ranged from 5 to 50 mV s^{-1} and 10 to 50 mV respectively.

2.5. Determination of hydroquinone in photographic developers

As in the literature it was not found any official method for the hydroquinone determination in these samples, addition-recovery tests were accomplished for the quantification of this analyte in solution. For that, DPV measures were performed in the same conditions mentioned previously. Three successive additions of 125 μL of the 1.0×10^{-2} mol L^{-1} hydroquinone solution were placed into a solution containing 1.0×10^{-4} mol L^{-1} of hydroquinone, in acetate buffer pH 4.0. For each addition, four voltammetric measures were obtained without need of electrode surface renovation.

Among the constituents of the photographic developer, metol (*p*-methylaminophenolsulfate) is the unique component that could influence the determination of the analyte. In that way, a study was carried out in order to verify eventual metol interference in the analysis.

For hydroquinone sample determination, experiments of standard addition were accomplished using DPV. The additions were of 250, 500 and 750 μL of a solution containing 1.0×10^{-3} mol L^{-1} of hydroquinone to the sample without pre-treatment.

2.6. Comparison method

The HQ content in the commercial sample was also determined in an HPLC procedure after removing the sulfite and carbonate interfering species present in the photographic developer, by addition of barium chloride to the sample solutions.

Samples were prepared by weighing aliquots of 0.03 g (±0.1 mg) 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 was then sonicated during 10 min and filtered in syntherized glass plate funnel. Finally 300 μL aliquots of the filtered solution were transferred to four different 10 mL volumetric flasks, which correspond to 2.72 mmol L^{-1} (300 ppm) HQ according to the label value. Standard additions of 0, 300, 600 and 900 μL 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 mm × 4.6 mm, 5 μm), using methanol:water (60:40, 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 min according the standard addition method.

3. Results and discussion

3.1. DPV measurements and optimization of the composite electrode response

Previous studies showed that the carbon–castor oil polyurethane composite electrode containing 60% of graphite in its composition presents the best electroanalytical properties [9], based in results obtained using cyclic voltammetry and scanning electron micrographs of the composites containing between 30 and 70% of graphite (w/w).

The results obtained with the 60% (graphite, w/w), when compared with those obtained at a carbon paste electrode (CPE) of the same area under the conditions described in Section 2 revealed that, although the current density is a little higher in the CPE, the peak potentials of both oxidation and reduction process are displaced to higher values increasing the separation of the peak signals (ΔE_p). This fact suggests that the electron transfer is difficult in the CPE, probably due to the presence of the mineral oil used as agglutinant.

Differential pulse voltammetric measurements were performed for 60% (graphite, w/w) composite electrode and glassy carbon in 5.0×10^{-5} mol^{-1} hydroquinone solution in 0.1 mol L^{-1} acetate buffer pH 4.0. The comparison was performed since the glassy carbon (GC) possesses a very known response for this electroactive specie. The DPV voltammograms obtained for both electrodes are presented in Fig. 1. As can be seen, the composite electrode showed higher peak current in relation to the GC electrode, indicating that the proposed composite material has great potential in the determination of hydroquinone.
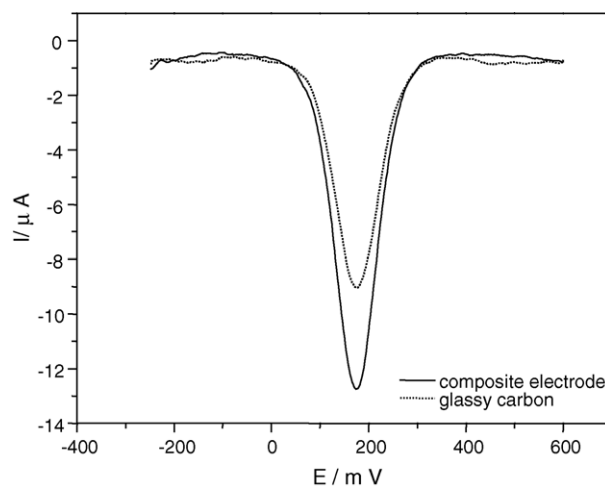

Fig. 1. Differential pulse voltammogram obtained at the 60% (graphite, w/w) composite and glassy carbon electrodes, using 5.0×10^{-5} mol L^{-1} hydroquinone in 0.1 mol L^{-1} acetate buffer solutions. Scan rate 10 mV s^{-1} and pulse amplitude 50 mV.

Based on this evidence, studies were executed for optimization of the experimental conditions, with the purpose of increasing the signal obtained for hydroquinone. The 2^n factorial planning suggested that the best parameters for DPV were $5\,mV\,s^{-1}$ and $50\,mV$ for scan rate and pulse amplitude respectively.

After optimization of the DPV experimental conditions at the composite electrode 60% (graphite, w/w), voltammetric measurements were accomplished in acetate buffer solution pH 4.0 with different hydroquinone concentrations from 1.00 to 100 $\mu mol\,L^{-1}$ ($n = 11$), with the purpose of obtaining an analytical curve for the determination of the linear range for this system. The curve was linear in the entire interval of hydroquinone concentration, obeying the following equation:

$$I_p = 2.68 \times 10^{-2}\,\mu A + 5570\,\mu A\,\mu mol^{-1}\,L\,[HQ]$$

$$(r = 0.999_7,\ n = 11) \tag{1}$$

where I_p is the peak current in μA and $[HQ]$ the hydroquinone concentration in $\mu mol\,L^{-1}$. The analytical curve was obtained measuring the peak currents for 11 different concentrations measured in triplicate for each point.

In order to evaluate the significance of the obtained data it was developed an analysis of variance (ANOVA) [21]. Such analysis presented a residual standard deviation of 1.68×10^{-8} The R-squared was 0.992 with a lack of fit 0.144 ($F_{crit} = 5.41$). The response was significant, which can be seen by a regression significance of 4013.7 against an F_{crit} of 5.32. The linearity was evaluated by residual graphic and the value calculated by ANOVA was 0.006 ($F_{crit} = 5.41$).

From these data a 934 $nmol\,L^{-1}$ detection limit was determined for hydroquinone. This was the concentration value in which the signal is three times higher than the blank $\pm$S.D. at the peak potential. The repeatability was evaluated from 10 successive measurements between which the electrode surface was renewed by polishing and sonicating as described in Section 2. The mean peak current value was $2.66 \pm 0.17\,\mu A$ ($n = 10$) for a $5.00 \times 10^{-5}\,mol\,L^{-1}$ hydroquinone in $0.10\,mol\,L^{-1}$ acetate buffer pH 4.5. The electrode is quite stable and has been used for more than 1 year in our laboratory.

3.2. Study of interference and recovery

The effect of concomitants usually found in photographic developers, such as metol, was evaluated to avoid interference in the analysis of the studied analyte.

According to the manufacturer the D-76 photographic developer used as sample contains in its formulation 1–5% of metol and 5% of hydroquinone, besides inert material. Considering such information, a study was accomplished to evaluate the possible interference of the metol in the hydroquinone determination, in this sample, using DPV measures at 60% (graphite, w/w) composite electrode. The investiga-

Table 1
Results of the addition-recovery experiment using hydroquinone with three different standard concentrations ($n = 4$)

Sample	Hydroquinone (mg mL^{-1})		Recovery (%)
	Added	Found	
D-76	0.0135	0.01353	100.2
	0.0270	0.02703	100.1
	0.0405	0.04065	100.4

tion was made using solutions containing constant concentration of hydroquinone (5%) and different metol percentages (0, 5, 10, 20, 30 and 40%). The amount of added metol surpass the relationship metol/hydroquinone mentioned by the manufacturer of the sample. In none of the solutions the interference of the metol was verified in the hydroquinone voltammetric response (results not shown). In that way, there was no need of a sample pre-treatment for elimination of the metol.

Recoveries varying from 100.1 to 100.4% of hydroquinone (Table 1) in the commercial sample of photographic developer were obtained using the 60% (graphite, w/w) composite electrode. In this study, 0.0135, 0.0270 and 0.0405 $mg\,mL^{-1}$ of hydroquinone solutions were added to each sample and the peak current was observed using DPV measurements at $20\,mV\,s^{-1}$ and $50\,mV$ of scan rate and pulse amplitude, respectively. Four DPV voltamgramms were obtained for each experiment ($n = 4$). The values obtained in the recovery studies presented a relative error lower than 0.5%. The recovery results obtained suggest an absence of the matrix effect on those determinations.

3.3. Application of the method

Determining the analyte in photographic developers checked the applicability of the method. Table 2 presents a comparison between the label values and those results obtained for three commercial samples using the proposed composite electrode. Applying a paired t-test in the results obtained by this procedure and those claimed in the labels, it was found that all results are in agreement at the 95% confidence level and with relative error lower or equal to 2%.

Table 2
Determination of hydroquinone in three aliquots of the photographic developers D-76 using the 60% (graphite, w/w) composite electrode ($n = 4$) and HPLC procedure[a]

Sample	Hydroquinone (mg g^{-1})		Relative errors (%)	
	DPV	HPLC	$\lvert E_1 \rvert$[b]	$\lvert E_2 \rvert$[c]
1	49.4 ± 0.1		1.2	4.1
2	49.0 ± 0.2	51.5 ± 0.1	2.0	4.8
3	49.9 ± 0.1		0.2	3.1

[a] Labeled value: 50.

[b] E_1: DPV vs. labeled (DPV − labeled/labeled) × 100%.

[c] E_2: DPV vs. HPLC (DPV − HPLC/HPLC) × 100%.

These results suggest that the composite electrode is suitable for the determination of hydroquinone in photographic developers.

The results obtained in the determination of HQ using the composite 60% (graphite, w/w) by DPV in three different aliquots of the same developers were compared with those obtained by one HPLC analysis. The results of such comparison are resumed in Table 2.

4. Conclusion

According to the results presented in this work the graphite–polyurethane composite possess interesting features for electroanalytical quantification of hydroquinone in photographic developers. The 60% (graphite, w/w) composite presented is of easy preparation; low cost and easy surface renovation. The statistical parameters and the recovery study data clearly indicate the reproducibility, precision and accuracy of the method, and suggested that the proposed electrode is suitable for routine analysis. Many other applications may be explored in the future using this type of sensor.

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