Possibilities Of Using A New Graphite-Castor Oil Polyurethane Composite Electrode As An Amperometric Flow Detector

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ABSTRACT

The performance of a new graphite castor oil polyurethane composite electrode is evaluated as an amperometric flow injection detector using hydroquinone (HQ) as a probe. HQ was determined in photographic developers with a minimum detectable net concentration of 100 μmol L^{-1}, and 81 determinations h^{-1}, after optimization of parameters such as the detection potential, sample loop volume, and carrier solution flow rate. Interference of SO_3^{2-} present in the developers has been observed and could be eliminated by appropriate sample preparation. Results obtained at the composite electrode agreed with those from HPLC procedure within 95% confidence level, showing that the new composite can be used as an amperometric detector for flow analysis.
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INTRODUCTION

Graphite-based electrodes as substitutes for Hg in the anodic potential range have a great interest in electroanalytical chemistry. Traditionally, carbon paste electrodes, characterized by the use of an electrochemically inert liquid such as nujol, paraffin oil, etc, as insulating phase, have been the most extensively used graphite composite electrodes[1]. However, during the last decade the development of other

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composite electrodes in which the liquid insulating phase is substituted by a solid polymer such as Teflon[2], Kel-F[3], polyethylene[4], epoxy resins[5], poly (vinyl chloride)[6], and sol-gel matrices[7], showed to be a growing interest issue in electroanalysis.

The resulting electrodes demonstrated the additional advantages of being mechanically stable and resistant to organic solvents than the carbon paste ones. Within this line, our group recently developed a new composite electrode where a polyurethane (PU) polymer obtained from castor oil was used as the binding agent[8]. This composite is described as an electrode material, with all the advantages cited above, on top of relative easiness of fabrication, surface renewing and removable vegetable source. The polymer is prepared from a bi-component liquid system, a polyol and a hardener. These components can simply be mixed with carbon, and eventually modifiers, in order to prepare the electrode material. The oily nature of the resin also produces a composite with hydrophobic character, preventing swelling effect observed for composites from epoxy resins when electrodes are used in aqueous media[8].

The HQ was chosen as a probe since it presents a simple and well-known oxidation mechanism and is commonly used in electrochemistry as a test analyte to validate new electroanalytical methods[9]. In flow analysis it presented the additional advantage of did not adsorve on the electrode surface. In addition HQ is a phenolic compound, which is important in a wide number of biological and industrial processes (coal-tar production, paper manufacturing or in the developing process in photography).

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[13,14], GC/MS chromatography[15,16], differential pulse voltammetry[17], based on the Belousov-Zhabotinski oscillating chemical reaction[18,19] or with biosensors[20] amongst others.

The detection limits found in the literature for HQ vary in a wide range of concentrations depending on the technique used, although the lowest limits are achieved with electrochemical detection systems.

In routine analysis flow injection systems are interesting because of their multiple advantages, they include the fast response, low-cost instrumentation, reproducible and accurate results, in addition to the large number of samples which can be analyzed per unit of time[21]. The combination of this technique with the electrochemical detection significantly increases the advantages offered by these systems which are at the same time highly selective and sensitive, therefore low detection limits can be achieved.

This work describes the optimization of a flow injection system with electrochemical detection for the determination of hydroquinone (HQ) in a photographic developer, in order to evaluate the performance of a new 60% graphite-PU composite electrode as an amperometric detector in a flow injection procedure. Although the electrode had been used before for the determination of HQ in static procedures, it was no used earlier as an amperometric sensor.

EXPERIMENTAL

Apparatus

All the reference or sample solutions were injected manually into the carrier stream using a laboratory-constructed three-piece injector-commutador made of Perspex®[22], with two fixed side bars and a sliding central bar, that is moved for sampling and injection. The solutions were conducted with polyethylene tubing (0.8 mm i.d, fiotubos, Brazil) and propuled with an IPC 8-channel peristaltic (Ismatec Swtizerland) pump An illustration of such system is presented in figure 1.

Potentials were measured with an AUTOLAB PGSTAT-30 (Ecochemie, The Netherlands) potentiostat/galvanostat coupled to a personal computer and controlled with a GPES 4.9 software. The measurements were performed in a three-electrode configuration flow cell (Figure 2) using the graphite-PU composite electrode 60% (graphite, *w/w*) or a glassy carbon (GC) as working electrodes. A Ag/AgCl, KCl 0.1 mol L^{-1} was used as reference electrode and a platinum disk ($\varnothing$ = 3mm) was a counter. The body of the electrochemical flow cell was fabri-
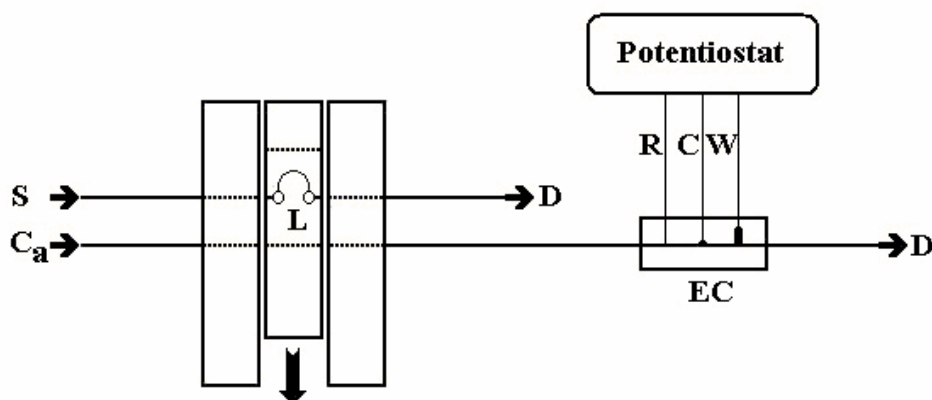
Figure 1: Scheme of the flow injection system with electrochemical detection used for the determination of HQ: S: sample, 5.0 .10^{-3} mol L^{-1} HQ solution; Ca: carrier, acetate buffer 0.1 mol L^{-1}; D, waste; L, loop; R, W, C, reference (Ag/AgCl), working (60%, graphite, *w/w*) and counter (platinum disk) electrodes, respectively; EC, electrochemical flow-through cell; Potentiostat, Autolab PGSTAT-30 potenciostate-galvanostate.

cated with the unmodified castor oil polyurethane resin (Poliquil, Brazil) and used as received[8]. The effective volume of the flow cell was of 25 μL. The detail of the electrochemical flow cell is presented in figure 2.

Reagents and Solutions

Solutions were prepared with water distilled twice in a quartz stiller. The HQ used was of analytical reagent grade (Vetec, Brazil). Stock 1.00 10^{-2} mol L^{-1} HQ in 0.1 mol L^{-1} acetate buffer pH 4.5 solution
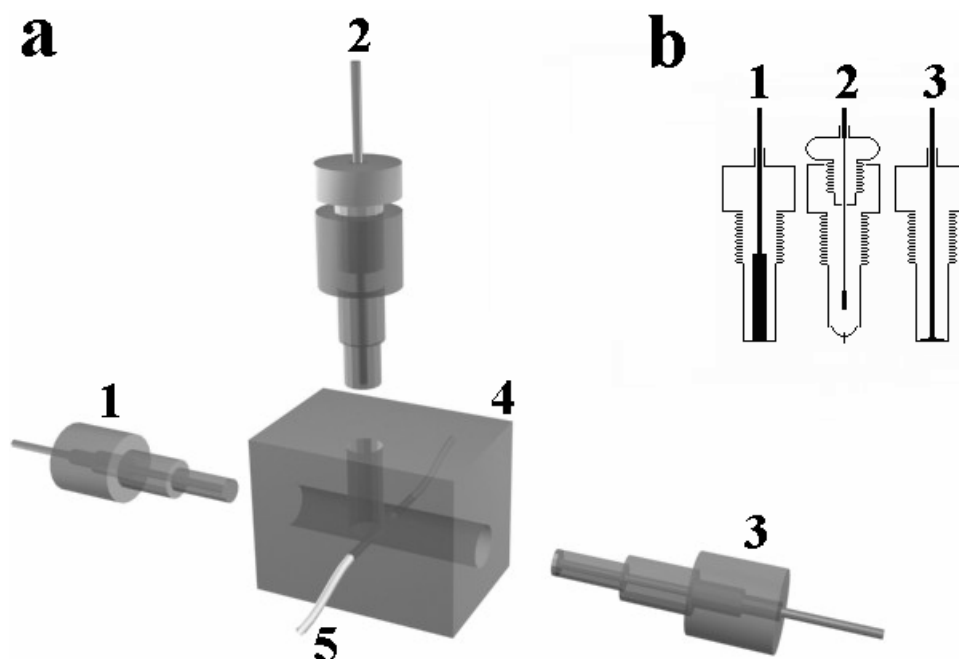

Figure 2: a: Scheme of the electrochemical cell used in the measurements in FIA system (1) Working electrode (graphite-PU), (2) Reference electrode (Ag/AgCl), (3) Counter electrode (Platinum disk), (4) Block of polyurethane resin, (5) Tube of polyethylene. b: View of the working (1), reference (2) and counter (3) electrodes.

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was used in quantitative measurements. The photographic developer D-76 from Kodak (Brazil) was used as the HQ commercial sample.

Procedures

1. Working electrode

The composite 60% (graphite, *w/w*) electrode was prepared as previously described[8]. Briefly adequate amounts of the polyol, hardener and graphite (Aldrich, USA) were mixed in a mortar for 5 minutes in order to obtain a mixture with 60% of graphite (*w/w*). The resulting mixture is inserted in a manual press and extruded as 3.0 mm diameter rods. The composite was cured for 24 h at room temperature and cutted in pieces 1.0 cm long. A copper wire (ϕ 1.0 mm) was attached to these rods with the help of a silver epoxy (EPO-TEK 410E, Epoxy Technology, USA), conducting resin in order to reach electric contact. This set was then inserted in an electrode body built up in PU resin, 5.0 mm i.d. (Figure 2) and sealed with the PU resin. The electrodes were let to cure for 24 h.

After curing, the excess of polymer was removed using a 600-grit sand paper, polished with 1 μm γ-Al_2O_3 suspension in an APL-2 polishing wheel (Arotec, Brazil), and sonicated in isopropyl alcohol during 5 min.

2. Flow injection measurements

The effect of different parameters relative to the flow system, such as carrier solution flow rate (1.4, 2.7, 4.1, 5.5 and 6.8 mL min^{-1}), detection potential (200, 300, 400, 450, 500 and 600 mV) and sample loop volume (39.3, 78.5, 117.8, 157.1 and 194.6 μL) were evaluated.

Before the measurements the electrode was placed in the voltammetric cell in contact with the carrier solution, flowing during 2 min. This showed to be enough to obtain a stable baseline.

Using the optimized conditions an analytical curve was obtained by injection of different concentrations of HQ, in increasing order from 1.00 10^{-4} to 1.00 10^{-2} mol L^{-1}, using the optimized parameters. The same procedure was repeated, but now in decreasing order to check if any memory effect was present. The injections were performed in quintuplicate.

In the determination of HQ in the photographic developer, each standard HQ solution was injected five times in the increasing order from 1.00 10^{-4} to 5.00 10^{-3} mol L^{-1}, after that, a sample of 3.00 10^{-3} mol L^{-1} HQ content in the photographic developer was injected five times. Then, the same procedure was repeated, but now in decreasing order.

Comparison method

The HQ content in the commercial sample was also determined in a HPLC procedure after removing the sulfite and carbonate interfering species present in the photographic developer, by addition of barium chloride to the sample solutions[23].

Samples were prepared by accurately weighing aliquots of ca 30 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 minutes and filtered in sinterized glass plate funnel. Finally 300 μL aliquots of the filtered solution were transferred to four different 10 mL volumetric flasks that correspond to 2.72 mmol L^{-1} HQ (300 ppm) according to the label value. Successive additions of 0, 300, 600 and 900 μL of standard 9.08 mmol L^{-1} HQ solutions (1000 ppm) 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 a RP-18 column (150 x 4.6 mm, 5 μm, Aldrich, USA), 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, USA) detector. The HQ retention time was 2 minutes according to the standard addition method.

RESULTS AND DISCUSSION

Flow injection parameters

The studied experimental parameters were: *the*

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carrier solution flow rate, a hydrodynamic factor which influences the dispersion of the sample injected; *the detection potential*, which plays an important role in the selectivity and sensitivity of the analysis and *the sample loop volume*, it that defines the amount of analyte to be detected.

## Effect of the carrier solution flow rate

The effect of the carrier solution flow rate was evaluated between 1.4 and 6.8 mL min^{-1} by successive injections of 5.00 x 10^{-3} mol L^{-1} HQ solution in acetate buffer 0.1 mol L^{-1}, pH 4.5. Figure 3 shows that the current increases up to 5.5 mL min^{-1}, remaining practically constant at 6.8 mL min^{-1}. Therefore, a flow rate of 5.5 mL min^{-1} was chosen for further studies since a lower dispersion can be achieved [21].
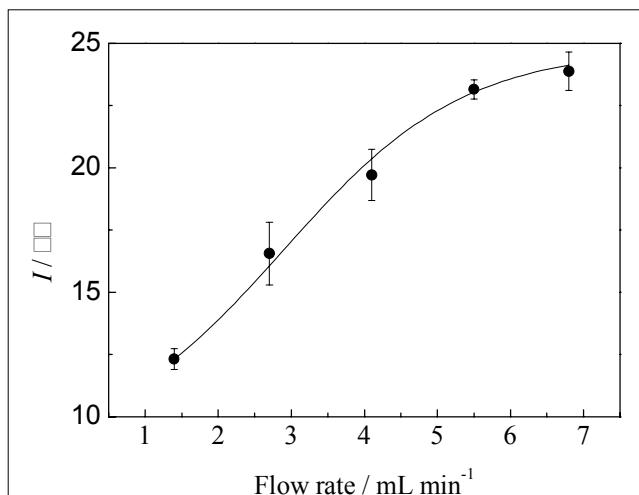
Figure 3: Effect of the carrier solution flow injection in the amperometric response of the composite 60% (graphite, *w/w*) electrode in 5.0. 10^{-3} mol L^{-1} HQ solution in 0.1 mol L^{-1} buffer acetate pH 4.5 as a carrier, using sample loop volume of 78.5 μL.

Effect of the detection potential

The effect of the detection potential was evaluated between 200 and 600 mV by successive injection of 5.00 10^{-3} mol L^{-1} HQ solution. Figure 4 shows that there is no significant difference in the currents obtained at potential values higher than 450 mV. Thus, 450 mV was chosen for further studies since it presents less standard deviation between successive measurements and lower risk of oxidizing con-
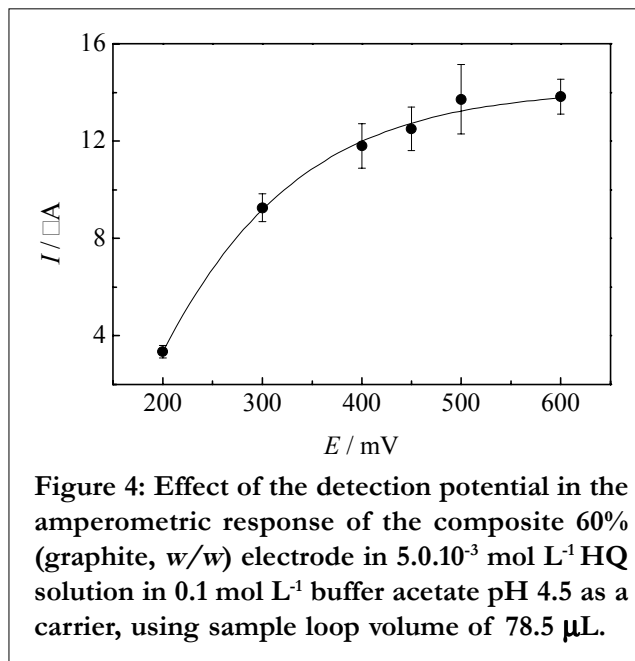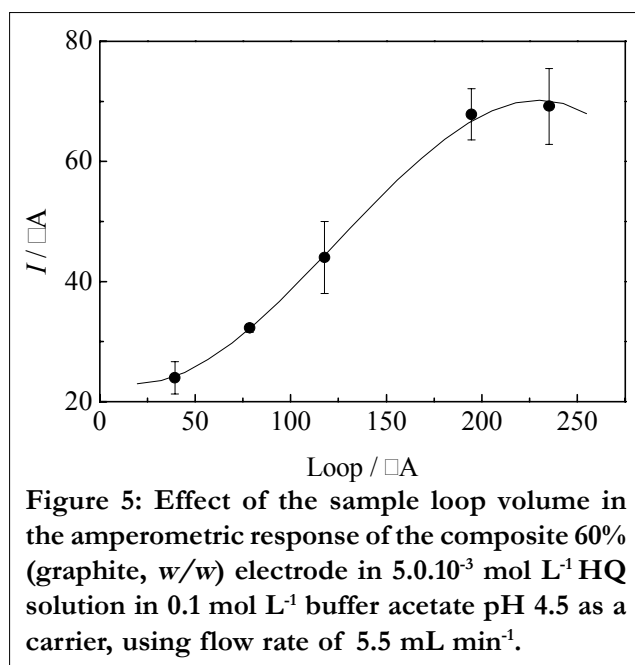

Figure 4: Effect of the detection potential in the amperometric response of the composite 60% (graphite, *w/w*) electrode in 5.0.10^{-3} mol L^{-1} HQ solution in 0.1 mol L^{-1} buffer acetate pH 4.5 as a carrier, using sample loop volume of 78.5 μL.

taminant species.

Effect of the sample loop volume

The effect of the sample loop volume in the transient signals was investigated for volumes from 39.3 to 235.6 μL using a 5.00 10^{-3} mol L^{-1} HQ solution, under a constant flow rate of 5.5 mL min^{-1} and detection at 450 mV. Figure 5 shows that the current signal increased significantly up to 194.6 μL. For higher sample loop volumes the signal remained prac-

Figure 5: Effect of the sample loop volume in the amperometric response of the composite 60% (graphite, *w/w*) electrode in 5.0.10^{-3} mol L^{-1} HQ solution in 0.1 mol L^{-1} buffer acetate pH 4.5 as a carrier, using flow rate of 5.5 mL min^{-1}.

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tically constant. So, this volume was selected.

Analytical curve

The analytical curve (Figure 6) was obtained in order to evaluate the behavior of the amperometric response of the composite 60% (graphite, *w/w*) in relation to the concentration of HQ.

Best results were obtained with a 5.5 mL min^{-1} flow rate, 25 cm (194.6 μL) sample loop and 450 mV (vs. Ag/AgCl) potential detection. Using these optimized conditions, a linear response was obtained in the $1.00\ 10^{-4}$ to $1.00\ 10^{-2}$ mol L^{-1} HQ range (Figure 6), and acetate buffer 0.1 mol L^{-1}, pH 4.5 as a carrier. The injections were realized first in the increasing and then in the decreasing concentrations to evaluate a possible memory effect. The linear region (insert in Figure 6) observed in all investigated interval, obeyed the linear equation y= 0.12 μA + 3.59 μA mmol L^{-1} [HQ], (n = 5, R =0.999$_9$). 81 determinations per hour analytical frequency was observed under the optimized conditions. The limit of detec-

tion (LOD) obtained in this interval was of 100 μmol L^{-1}, determined as three times the standard deviation of the blank (S_d) divided by the angular coefficient of straight line (b) of the region studied[24]:

$$LOD = 3\,S_d/b \tag{1}$$

This LOD is suitable for use in samples such the photographic developer and even in cosmetic formulations.

The LOD for HQ at a glassy carbon electrode used as amperometric flow detector under the same experimental conditions was 712 μmol L^{-1}, *i.e.* seven times higher.

Determination of hydroquinone in photographic developer sample

The applicability of the composite electrode 60% (graphite, *w/w*) as a FIA amperometric detector for the determination of hydroquinone was verified analyzing the photographic developer D-76 from Kodak (Brazil) following the procedure specified in the ex-
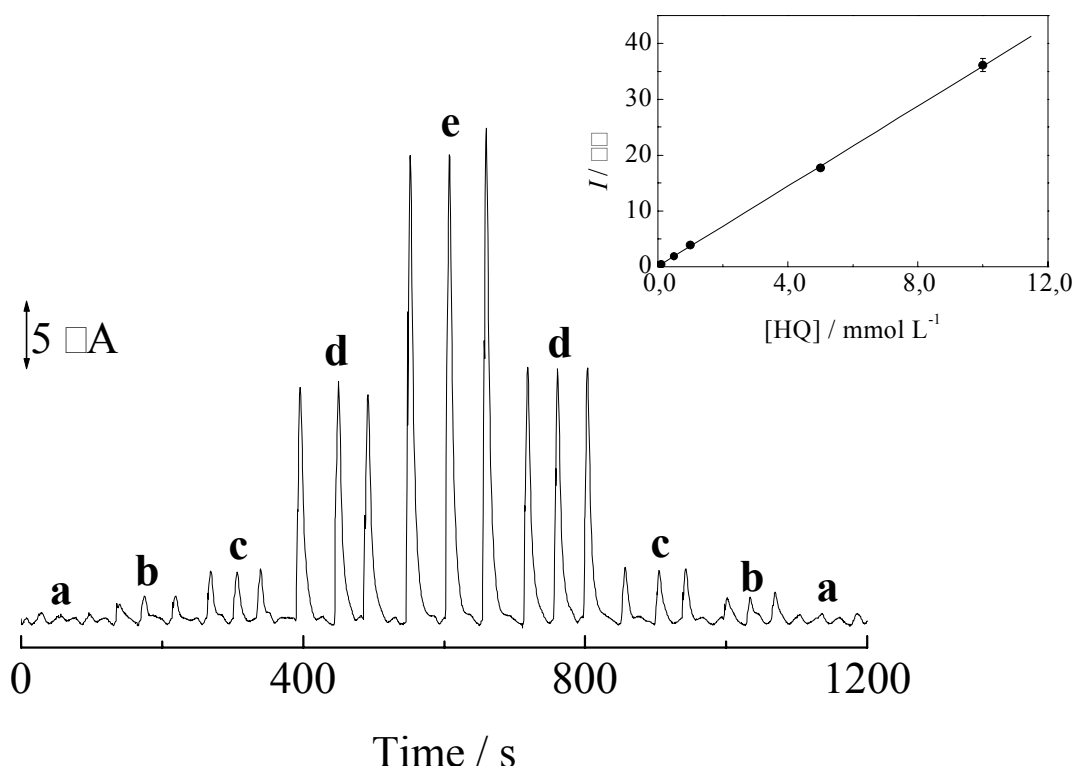

Figure 6: Transient signals obtained at the composite 60% (graphite, *w/w*) electrode using (a) 1.00.10^{-4}, (b) 5.00.10^{-4}, (c) 1.00.10^{-3}, (d) 5.00.10^{-3} and (e) 1.00.10^{-2} mol L^{-1} of HQ and 0.1 mol L^{-1} buffer acetate pH 4.5 as a carrier, flow rate of de 5.5 mL min^{-1}, detection potential of 450 mV and sample loop volume of 194.6 μL. In the detail the linear portion of the analytical curve.
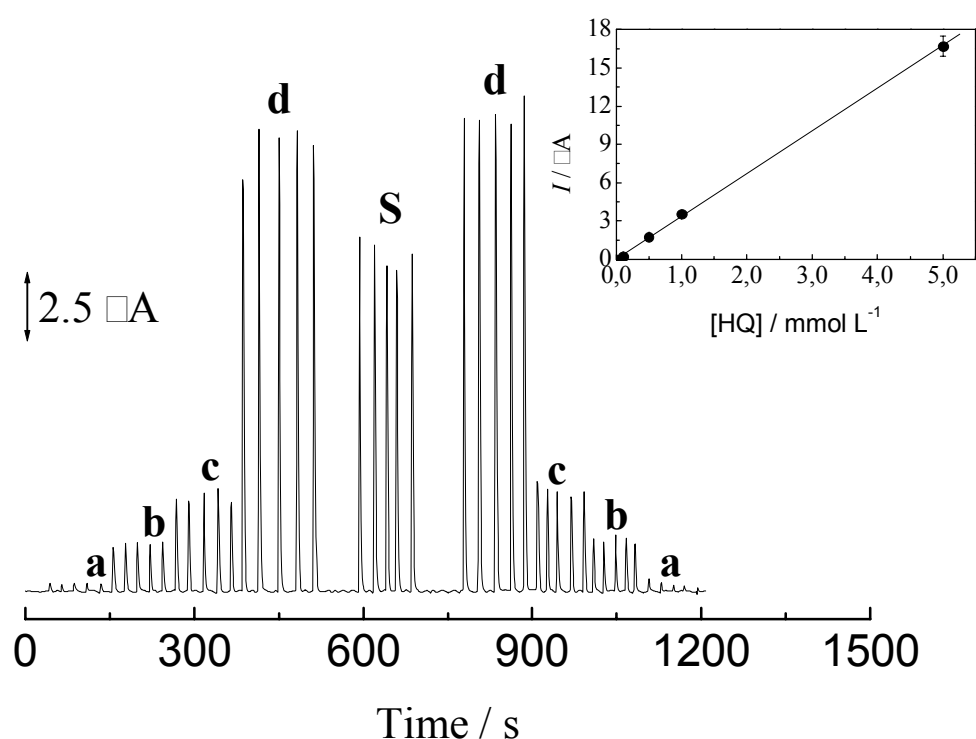
Figure 7: Transient signals for determination of HQ in photographic developer using 60% (graphite, *w/w*) composite electrode in 0.1 mol L^{-1} buffer acetate pH 4.5 as a carrier, flow rate of de 5.5 mL min^{-1}, detection potential of 450 mV and sample loop volume of 194.6 μL, at (a) 1.00.10^{-4}, (b) 5.00.10^{-4}, (c) 1.00.10^{-3}, (d) 5.00.10^{-3} and (S) 3.00.10^{-3}. In the detail the linear region of the analytical curve.

TABLE 1: Determination of HQ in the Kodak D-76 photographic developer using both the proposed flow procedure and HPLC

Sample	Hydroquinone (mol L^{-1})			E$_1$	E$_2$
	Labeled	FIA	HPLC		
1	50.0	50.3 ± 0.1	51.5 ± 0.1	0.6	2.3

E$_1$: FIA vs label (FIA - label/label) x 100%
E$_2$: FIA vs HPLC (FIA - HPLC/HPLC) x 100%

perimental section. Figure 7 shows the transient signals obtained for standard ans sample solutions, and the resulting analytical curve.

In TABLE 1 are presented the results obtained using the composite in FIA and the HPLC techniques. The results agreed within 95% of confidence level according to the t-Student test[25].

Recoveries between 98-110% were observed for the HQ injected in the photographic developer samples, as presented in TABLE 2.

The electrodes are mechanically resistant and presented a long useful life. Sulphite interference was observed in both HPLC and electroanalytical detec-

TABLE 2: Recovery results for HQ in the photographic developer in three different concentrations (n = 5)

Hydroquinone (mmol L^{-1})		
Added	Found	Recovery (%)
0.10	0.10	100
0.50	0.49	98
1.00	1.10	110
5.00	4.90	98
10.0	10.0	100

tion , but it could be removed by sample preparation as described.

CONCLUSIONS

The results showed that the new 60% (graphite, *w/w*) composite electrode presents a satisfactory performance when used as an amperometric detector under hydrodynamic conditions, as those in flow injection systems and are promising detectors in such systems.

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The electrodes showed repeatability, mechanical resistant, long useful life, precision and accuracy for use in flow conditions.

Capabilities of modification can be included in future studies improving selectivity, and may be sensitivity for determination of HQ and other analytes.

ACKNOWLEDGMENTS

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