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A square-wave voltammetric method for analysing the colour marker quinizarine in petrol and diesel fuels

Magno Aparecido Gonçalves Trindade [a], Valdir Souza Ferreira [b], Maria Valnice Boldrin Zanoni [a,*]

[a] *Department of Analytical Chemistry, Institute of Chemistry, Araraquara, UNESP, Rua Francisco Degni, s/no Bairro Quitandinha, 14800-900 Araraquara, SP, Brazil*

[b] *Department of Chemistry, CCET, Universidade Federal de Mato Grosso do Sul, Av. Filinto Muller, 1555, Caixa Postal 549, 79074-460 Campo Grande, MS, Brazil*

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Abstract

This work presents an electroanalytical method based on square-wave voltammetry (SWV) for the determination of quinizarine (QNZ) in a mixture of Britton–Robinson buffer 0.08 mol L^{-1} with 30% of acetonitrile. The QNZ was oxidized at glassy carbon electrode in and the well-defined peak at +0.45 V vs. Ag/AgCl can be used for its determination as colour marker in fuel samples. All parameters were optimized and analytical curves can be constructed for QNZ concentrations ranging from 2.0×10^{-6} mol L^{-1} to 1.4×10^{-5} mol L^{-1}, using $f = 60$ Hz and $E_{sw} = 25$ mV. The method offers a limit detection of 4.12×10^{-7} mol L^{-1} and a standard deviation of 4.5% when six measurements of 1.25×10^{-5} mol L^{-1} are compared. The method was successfully applied for determining QNZ in gasoline and diesel oil and the obtained results showed good agreement with those reported previously.

Keywords: Quinizarine; Marker; Fuels; Electroanalytical method

1. Introduction

Unlike the textile, cosmetic and pharmaceutical industries, which employ dyes as one of the number of fundamental factors pertinent to the commercial success of a particular product, the use of markers in the fuel industry is not usually related to aesthetic attraction or improvement in the performance of the fuel. Markers are particularly used in these products with the aim of controlling specific types of fuels, to guarantee the identity of a given product, to discourage robberies and adulterations, as well as to popularize the quality of the product. In many cases, fuel distributors use demarcation of oil, petrol and even aviation kerosene for the purpose of impeding the mixture of such fuels with those of inferior quality [1–3]. To this end, a marker system has been suggested as a means for identifying brands of fuel and monitoring the tax classification of petroleum products through their identification when used irregularly in motor vehicles [1–5].

Quinizarine (QNZ), 1,4-dihydroxyanthraquinone (Fig. 1), is a yellow dye not soluble in water that is widely used as a marker of fuels mainly in countries of the European Community. The amount added to the fuel will usually depend upon a variety of factors, but it is reported that a minimum of 5.0 ppm in the finally tagged liquid petroleum fuel is typical [5]. Thus, the development of analytical methods to determine the presence and quantification of these markers in petroleum products is important, since they could then be used to

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* Corresponding author. Tel.: +55 16 3301 6619; fax: +55 16 3322 7932.
E-mail address: boldrinv@iq.unesp.br (M.V.B. Zanoni).

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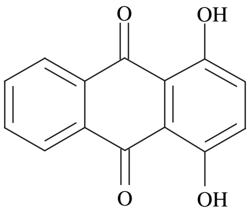

Fig. 1. Chemical structure of quinizarine.

distinguish between the large variety of fuel oils commercially available.

The analytical methods described in the literature for the determination of QNZ in fuel samples are based on high-performance liquid chromatography (HPLC) technique coupled to photometric detector [7–10] and derivative spectroscopy [11]. In most cases, best results are obtained after a cleaning-up and extraction of the markers from the matrix by means of solid phase extraction. Although, the electrochemistry of QNZ is well known [12–19], no electroanalytical method has been reported for the voltammetric determination of QNZ in a mixture of acetonitrile and aqueous solution.

Due to its lack of solubility in aqueous medium, the electrochemical behavior of QNZ in aqueous solution can be monitored only after an electrochemical pretreatment of the glassy carbon electrode, in which QNZ is strongly adsorbed onto the electrode surface. The adsorbed QNZ presents a two redox couple in aqueous solution at +0.8 V and −0.8 V, respectively, attributed to oxidation of the terminal hydroquinone and reduction of the central quinone [12,13]. According to the literature, QNZ is also strongly adsorbed onto mercury [14–19] and the reduction of quinone to the fully reduced state QNZ^{red} is responsible for a well-defined peak with reversible characteristics. Although the redox behavior of adsorbed QNZ in aqueous acidic solution and dimethyl sulphoxide has also been investigated by cyclic voltammetry, chronopotentiometry and chronoamperometry [20,21], there is no mention of its applicability for QNZ in fuel samples.

The present work describes an electroanalytical method for the determination of QNZ, based on its oxidation in Britton–Robinson (B–R) buffer with acetonitrile (7:3, v/v) on a glassy carbon electrode. The method is simple, fast, sensitive and provides a successful method of analysis of QNZ as a marker in samples of petrol and diesel oil by square-wave voltammetry.

2. Experimental

2.1. Instrumentation

The electrochemical analyses were performed using an Autolab PGSTAT-30 (Eco Chemie) interfaced to a microcomputer supplied by a general purpose electrochemical system (GPES) software (Eco Chemie). A conventional three-electrode system comprising a glassy carbon disc (2.5 mm diameter) set in a Teflon tube as working electrode, a saturated Ag/AgCl (inside a Luggin capillary containing 3.0 mol L^{-1} KCl) as reference electrode and a platinum wire as counter electrode was used.

All pH measurements were made using a combined glass electrode (Corning) connected to a digital pH-meter (Corning, model pH/ion analyzer 455). Deionized water was purified using a Milli-Q system (model Simplicity 185, Millipore).

2.2. Reagents and solutions

Stock solutions of 1.0×10^{-3} mol L^{-1} QNZ (Aldrich) were prepared by dissolving the solid product in acetonitrile (HPLC-grade). Dilute solutions of QNZ were freshly prepared by adding to the B–R buffer. The working solutions had sufficient stability throughout the duration of storage (up to four months of evaluation).

The solutions used as supporting electrolyte were prepared in the usual way: Britton–Robinson (B–R) buffer 0.08 mol L^{-1} in a mixture of 0.08 mol L^{-1} acetic acid (Merck), 0.08 mol L^{-1} boric acid (Merck) and 0.08 mol L^{-1} in orthophosphoric acid (Merck), with the appropriate amount of 1.0 mol L^{-1} sodium hydroxide (Merck) solution for the adjustment to the pH required. The phosphate buffer (0.08 mol L^{-1}) which was also used as a supporting electrolyte was prepared using di-sodium hydrogen phosphate di-hydrated (Merck) and sodium di-hydrogen phosphate monohydrated (Merck).

Samples of unmarked fuel (petrol and diesel oil) were fortified with QNZ at concentrations of 5.0 mg L^{-1}.

2.3. Procedure for voltammetric analysis

All electrochemical experiments were carried out by transference of an aliquot of 10 mL of the supporting electrolyte solution into the electrochemical cell; the solution was then submitted to 10 min of deaeration with nitrogen followed by a rest period for 5 s. The same procedure was repeated after the addition of an aliquot of QNZ by micropipette into the cell. Before each measurement, the glassy carbon electrode was polished with 1.0 μm alumina and then rinsed with deionized water and acetone.

2.4. Procedure for petrol pretreatment by solid phase extraction (SPE)

An aliquot of 10 mL of the petrol sample spiked with 5.0 mg L^{-1} of QNZ was evaporated to dryness under a nitrogen stream. After drying, the residue was reconstituted in approximately 5 mL of the mixture of B–R buffer solution (pH 6.5) and acetonitrile (9:1, v/v), assigned as B–R:ACN. In the sequence, the sample was extracted using reverse phase cartridge C_{18} (LC-18, Supelco, USA). Firstly, the cartridge was conditioned by means of 5 mL of methanol (HPLC-grade, J.T. Baker) followed by 5 mL of the mixture of B–R:ACN (9:1, v/v). The sample was then slowly loaded into the conditioned cartridge and the cartridge was then washed with 15 mL of the mixture of B–R:ACN (9:1, v/v) to remove the residue and the marker was eluted from the cartridge under gravity using approximately 15 mL of the mixture of B–R:ACN

(1:1, v/v). The eluent was collected in a volumetric flask (25 mL) and the volume was completed with B–R buffer solution (pH 6.5) and submitted to square-wave voltammetric analysis as previously described. The quantification of QNZ was performed using a standard addition method.

2.5. Procedure for diesel oil pretreatment by solid phase extraction (SPE)

For diesel oil, an aliquot containing 10 mL of the sample spiked with 5.0 mg L^{-1} of QNZ was mixed with 10 mL of ACN + B–R buffer (7:3, v/v) and shaken for approximately 30 s. The phase (ACN:B–R, 7:3, v/v) was collected in a glass flask and ACN was evaporated under a nitrogen stream. The residue was reconstituted in approximately 5 mL of the mixture (B–R:ACN, 9:1, v/v) and transferred to the solid phase extraction cartridge of C_{18} adopting the procedure described previously.

3. Results and discussion

3.1. Voltammetric behavior

Due to solubility reasons, the composition of the supporting electrolyte was used to follow the oxidation of 1.0×10^{-4} mol L^{-1} of QNZ by cyclic voltammetry. A mixture of B–R buffer or phosphate buffer and acetonitrile were employed at ratios of 9:1, 8:2, 7:3 and 6:4 (v/v) of buffer:acetonitrile, respectively; optimum results were obtained for the B–R buffer:ACN mixture of 7:3, v/v. As shown in Fig. 2, QNZ presents a well-defined oxidation peak at +0.45 V vs. Ag/AgCl (1a). In agreement with the literature [12,13] this peak can be attributed to the oxidation of the phenolic hydroxyl group present in the dye marker to its quinone derivative after two electrons' transfer. On the reverse scan, it is possible to detect the occurrence of two cathodic peaks at +0.17 and −0.53 V vs. Ag/AgCl, labeled as 2c and 3c, respectively, due to the reduction of species generated after secondary reaction involving the oxidized form [12]. For analytical purposes, the anodic peak at +0.45 V (1a) presents good performance and it was chosen for further studies.

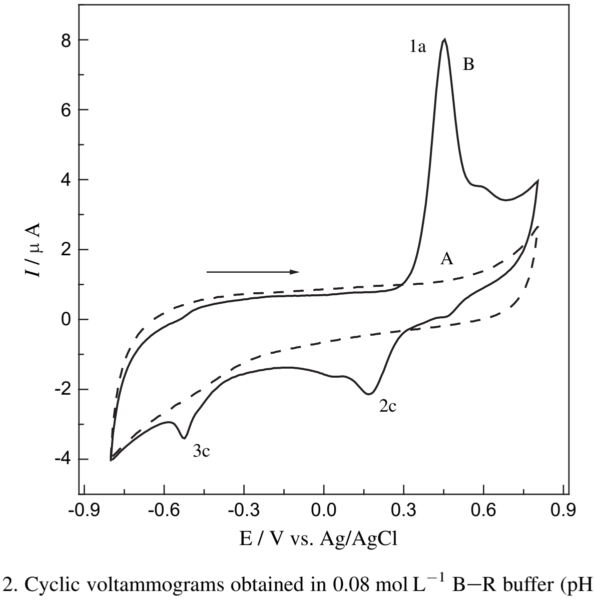

Fig. 2. Cyclic voltammograms obtained in 0.08 mol L^{-1} B–R buffer (pH 7.0) with 30% of acetonitrile for: (A) absence of QNZ and (B) presence of 1.0×10^{-4} mol L^{-1} of QNZ. Scan rate was 100 mV s^{-1}.

As verified in other experimental conditions [12,13], the strong adsorption of the product onto the electrode surface was also verified in B–R buffer (pH 7.0) containing 30% of acetonitrile. Successive cyclic voltammograms obtained from 1.0×10^{-4} mol L^{-1} QNZ in this condition at a scan rate of 100 mV s^{-1} exhibited a substantial decrease of the anodic peak after the first scan. This was confirmed by the linear relationship of peak current (I_p) and the variation of potential scans rate (v) from 20 to 200 mV s^{-1} [22]. Therefore, further experiments were carried out polishing the electrode between voltammetric curve recordings.

In order to increase the sensitivity of the voltammetric method for determining QNZ, other scan modes were used. The response of 5.0×10^{-6} mol L^{-1} of QNZ in B–R buffer:ACN (7:3, v/v) was compared using square-wave voltammetry (SWV) and differential pulse voltammetry (DPV) (Fig. 3). Both techniques gave well-defined peaks at +0.41 V vs. Ag/AgCl (SWV) and at +0.39 V vs. Ag/AgCl (DPV), respectively. Nevertheless, as shown in Fig. 3A, the analytical signal obtained for SWV is much higher than DPV; thus, this was chosen for further measurements and several parameters inherent of the system and SWV technique were optimized.

3.2. Analytical parameters

The effect of pH on the voltammetric behavior of 5.0×10^{-6} mol L^{-1} of QNZ was determined by mixing Britton–Robinson buffer at different pH values from 4.0 to 10.0 or

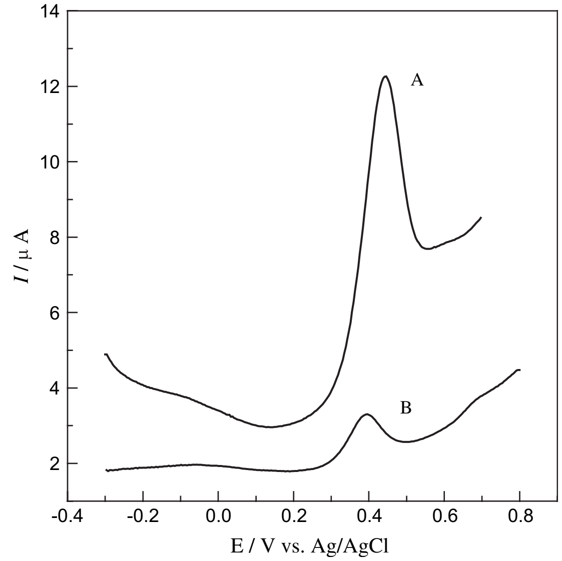

Fig. 3. Square-wave (A) and differential pulse (B) voltammograms registered in 0.08 mol L^{-1} B–R buffer (pH 7.0) with 30% of acetonitrile for 5.0×10^{-6} mol L^{-1} of QNZ. Parameters: SWV frequency (f) = 60 Hz, scan increment (ΔE_s) = 4 mV and pulse amplitude (E_{sw}) = 25 mV. DPV scan rate = 10 mV s^{-1} and pulse amplitude = 25 mV.

phosphate buffer from pH 4.0 to 9.0 with acetonitrile, keeping a constant ratio of 7:3 (v/v), respectively. It was possible to follow QNZ oxidation at all pH values investigated, but as a mixture of Britton–Robinson 0.08 mol L^{-1} with acetonitrile presented best voltammetric curves, this was adopted in further measurements.

The influence of pH variation on peak current and peak potential obtained from square-wave voltammograms recorded for 5.0×10^{-6} mol L^{-1} of QNZ in 0.08 mol L^{-1} Britton–Robinson buffer pH (4.0–10.0) is illustrated in Fig. 4. Plots of E_p vs. pH are shown in Fig. 4A. The peak potential of QNZ shifted to less positive values when the pH was increased, indicating that the electrode process is influenced by protonation reactions [13]. A linear relationship was observed from $4.0 \leq \text{pH} \leq 10.0$ following the equation: E_p (V) = 0.88–0.068 × pH ($r = 0.998$). By using the following relationship: $\Delta E_p/\Delta \text{pH} = 59 m_{H^+}/n$ (m_{H^+} = proton number and n = electron number [22], the slope of 68.0 mV pH^{-1} unit indicates that $m_{H^+} = 2.3$. This result can be indicative that the oxidation process of QNZ occurs by two-electron loses and two-protons, probably due to tautomerization reactions between quinone and hydroquinone as adjacent groups as verified previously on modified electrode [13].

The influence of pH variation on I_p is shown in Fig. 4B. Maximum current values were obtained at pH 7.0, but I_p decreased abruptly at pH values higher than 8.0 or lower than 6.0 and practically disappeared at pH < 4.0 and pH > 10.0. Therefore, for analytical purposes, by comparison of the yielding peak current values, shape and reproducibility of the recorded voltammograms, the best experimental condition to detect QNZ on glassy carbon electrode was obtained with Britton–Robinson buffer 0.08 mol L^{-1} at pH 7.0, and it was adopted in further measurements.

In order to develop a suitable analytical procedure for the determination of QNZ other experimental parameters were evaluated such as: influence of frequency (f) (of 10–120 Hz), scan increment (ΔE_s) (of 2–10 mV) and pulse amplitude (E_{sw}) (of 10–100 mV). Analysing the shape and intensity of the voltammetric curves, f = 60 Hz, ΔE_s = 4 mV and E_{sw} = 25 mV were chosen for analytical purposes.

Using the optimal conditions that are previously defined an analytical calibration graph was constructed from 1.0×10^{-6} mol L^{-1} to 1.6×10^{-5} mol L^{-1} QNZ using its oxidation peak in B–R buffer (pH 7.0) with 30% of acetonitrile by SWV. Fig. 5 illustrates the respective voltammograms obtained for QNZ at different concentrations, where the analytical curve is also shown (inset). A linear relationship is obtained from 2.0×10^{-6} mol L^{-1} to 14.0×10^{-6} mol L^{-1} following the equations I_p (μA) = $-0.194 + 7.20 \times 10^5 \times C$ (mol L^{-1}). The limits of detection (LOD) and quantitation (LOQ) were calculated using statistic treatment (3 × S.D.$_a$/b) and (10 × S.D.$_a$/b), respectively, where, (S.D.$_a$) is the standard deviation of the average arithmetic of 10 voltammograms of the blank obtained in the same potential oxidation of QNZ and (b) is the slope of the calibration curve. The values obtained for LOD and LOQ were 4.12×10^{-7} mol L^{-1} and 1.38×10^{-6} mol L^{-1}, respectively (Table 1). Both LOD and LOQ values indicated good sensitivity of the proposed method. The repeatability and accuracy of the method were evaluated by making successive six measurements for the solution of 1.25×10^{-5} mol L^{-1} of QNZ. The obtained relative standard deviation was 4.5%.

3.3. Analysis of QNZ in petrol and diesel oil

The proposed method was applied to the determination of QNZ in petrol and diesel oil samples using the standard addition method. The samples were spiked with 5.0 mg L^{-1} of

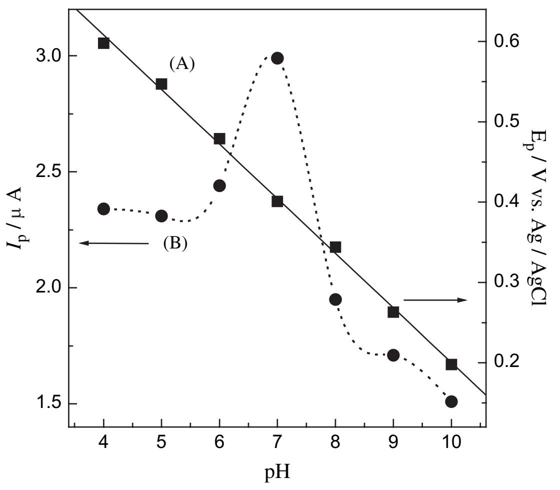

Fig. 4. Influence of pH on the peak potential (A) and peak current (B) response for 5.0×10^{-6} mol L^{-1} of QNZ registered in 0.08 mol L^{-1} B–R buffer with 30% of acetonitrile. Parameters: f = 60 Hz, ΔE_s = 4 mV and E_{sw} = 25 mV.

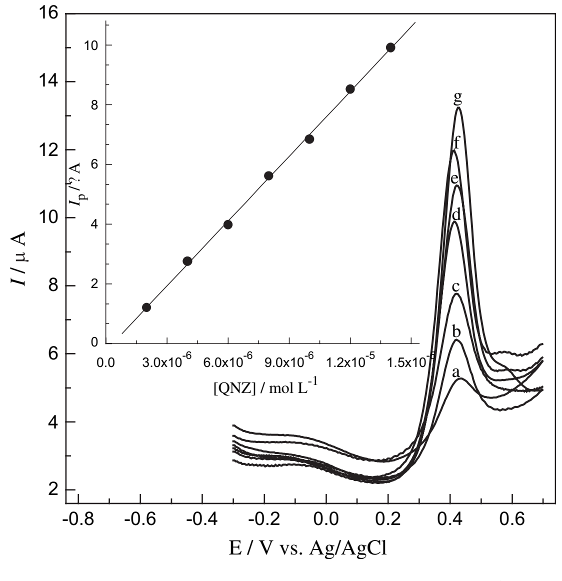

Fig. 5. Square-wave voltammograms registered in 0.08 mol L^{-1} B–R buffer (pH 7.0) with 30% of acetonitrile for the increasing concentrations of QNZ: (a) 2.0×10^{-6} mol L^{-1}; (b) 4.0×10^{-6} mol L^{-1}; (c) 6.0×10^{-6} mol L^{-1}; (d) 8.0×10^{-6} mol L^{-1}; (e) 10.0×10^{-6} mol L^{-1}; (f) 12.0×10^{-6} mol L^{-1} and (g) 14.0×10^{-6} mol L^{-1}, respectively. Inset: dependence of the peak current on QNZ concentration. Parameters: f = 60 Hz, ΔE_s = 4 mV and E_{sw} = 25 mV.

Table 1
Quantitative parameters for the assay of QNZ by the proposed method and reported method

Parameter	Proposed method	Reported method [7]
Studied conc. range (mol L^{-1})	$(2.0–20.0) \times 10^{-6}$	$(2.0–41.3) \times 10^{-6}$
Intercept	−0.194	nr
Slope	7.2×10^{5}	nr
Correlation of coef. (r)	0.999	nr
LOD (mol L^{-1})	4.12×10^{-7}	8.25×10^{-7}
LOQ (mol L^{-1})	1.38×10^{-6}	nr

nr: Not revealed value.

Table 2
Results of recovery assay to accuracy and precision of the proposed method for gasoline and diesel oil samples

Analysis method	Samples	Spiked (mg L^{-1})	Found (mg L^{-1})	Recovery (%)	R.S.D. (%)
Proposed method[a]	Diesel oil	5.00	4.71	94.20	0.60
	Gasoline	5.00	4.54	90.80	0.55
Reported method [6]	Diesel oil	1.99	1.89	94.97	nr

R.S.D.: relative standard deviation; nr: not revealed value.
[a] Average of the three determinations.

QNZ in petrol and diesel oil and submitted to square-wave voltammetric analysis. The direct determination of QNZ in diesel and petrol samples was not possible due to the interference of hydrocarbons and other components that suppress the voltammetric signal. Therefore, several procedures of cleaning-up of the samples were tested. The most successful one was described in Sections 2.4 and 2.5, respectively. Using an SPE procedure the voltammograms did not exhibit any modification due to endogenous material, as shown in Fig. 6 (line a). The typical square-wave voltammograms obtained for the petrol sample after the clean-up procedure as described in Section 2.4, as well its quantification after standard addition method are shown in Fig. 6 (lines b–e). It is possible to suggest that all hydrocarbons and other interferents present in the fuel samples were effectively removed in the clean-up stage and the analytical signal presents a well-defined peak for the used marker, which signal responds promptly for standard addition of QNZ.

The percentage recovery of QNZ in fuels samples, based on the average of three replicate measurements is listed in Table 2. The precision and accuracy of QNZ assay were obtained from three replicates (Table 2). The precision was expressed as the %R.S.D. and accuracy as a mean relative error (measured concentration − nominal concentration/nominal concentration × 100). The values obtained for recovery and %R.S.D. mean are acceptable and suggested that the proposed procedure should be applicable to the analysis of QNZ as marker dyes in samples of fuels; these results were also compared with those obtained by a published method [6]. It was found that the obtained values are in agreement with the reported method (Table 2). The obtained results are also in agreement with those obtained by May et al. [7], in which the obtained values for the recovery were between 65.0 and 80.0% to QNZ determination in diesel fuel.

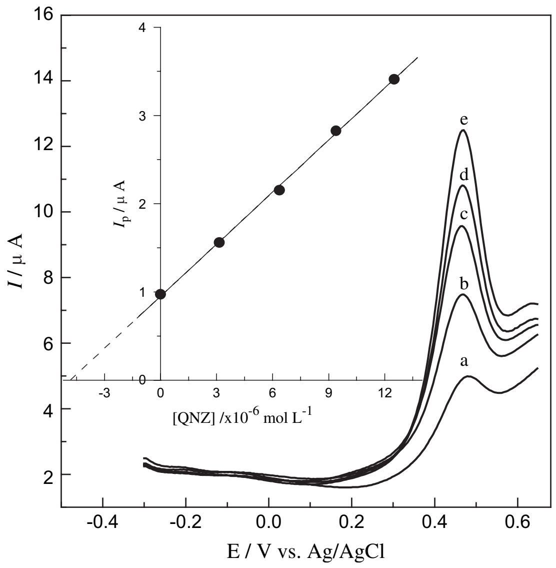

Fig. 6. Square-wave voltammograms obtained for the determination of QNZ. (a) Gasoline sample after extraction procedure as mentioned in Section 2.4, (b–e) successive standard additions of QNZ. Parameters: as in Fig. 5.

4. Conclusions

This study has shown that SWV is a suitable technique for the determination of QNZ in fuel. The Britton–Robinson buffer with 30% of acetonitrile was sufficient to maintain the solubility of the marker and to provide an adequate medium for QNZ analysis using square-wave voltammetry. The methodology was fast and simple, but with a sensitivity that was adequate for the determination of QNZ in spiked fuel, involving a simple step of sample pretreatment and resulting in short analysis times. Thus, the proposed method can be suggested as a good alternative for the routine quality control of this marker in fuel samples.

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References

[1] Nowak AV. Analysing marker dyes in liquid hydrocarbon fuels. United States: Atlantic Richfield Company; 1990. 4918020.

[2] Friswell MR, Orelup RB. Markers for petroleum, method of tagging, and method of detection. United States: Morton International Inc.; 1992. 5156653.

[3] Orelup RB. Colored petroleum markers. United States: Morton Thiokol Inc.; 1988. 4735631.

[4] Suwanprasop S, Nhujak T, Roengsumran S, Petsom A. Petroleum marker dyes synthesized from cardanol and aniline derivatives. Ind Eng Chem Res 2004;43:4973–8.

[5] The hydrocarbon oil (marking) regulations 2002. Statutory Instrument. 2002; no. 1773. <http://www.opsi.gov.uk/SI/si2002/20021773.htm>; [accessed in February 2006].

[6] Barwick VJ, Ellison SLR, Rafferty MJQ, Gill RS. The evaluation of measurement uncertainty from method validation studies. Part 2: the practical application of a laboratory protocol. Accred Qual Assur 2000;5:104−13.

[7] May EM, Hunt DC, Holcombe DG. Method for the determination of the marker and dye in heavy fuel oils. Analyst 1986;111:993−5.

[8] Sundberg LN, Andrasko J, Wistedt I, Kopp I. HPLC analysis of Solvent Yellow 124 − the marker in diesel oil. J Forensic Sci 1996;41:300−3.

[9] Henricsson S, Westerholm R. Liquid chromatographic method for analyzing the colour marker Solvent Yellow 124, *N*-ethyl-*N*-[2-(1-isobutoxyethoxy)ethyl](4-phenylazophenyl)amine, in diesel fuels. J Chromatogr A 1996;723:395−8.

[10] Timkovich R. Analysis of regulatory dye in diesel petroleum. Dyes Pigments 2000;46:69−79.

[11] Leung CP, Tam SYK. Quantitative determination of Solvent Red 24 in hydrocarbon oils by derivative spectroscopy. Analyst 1985;110: 883−4.

[12] Zinger B. Electrochemistry of quinizarine adsorbed on a glassy carbon electrode in aqueous solutions. J Electroanal Chem 1988;239:209−25.

[13] Bodini ME, Arancibia V. Redox chemistry of 1,4-dihydroxy-9,10-anthraquinone (quinizarine) and its manganese(II) complexes in dimethylsulphoxide. Polyhedron 1991;10:1929−37.

[14] Forster RJ. Kinetic separation of amperometric sensor responses. Analyst 1996;121:733−41.

[15] Forster RJ. Electron transfer dynamics and surface coverages of binary anthraquinone monolayers on mercury microelectrodes. Langmuir 1995;11:2247−55.

[16] He P, Crooks RM, Faulkner LR. Adsorption and electrode reactions of disulfonated anthraquinones at mercury electrodes. J Phys Chem 1990;94:1135−41.

[17] Soriaga MP, Hubard AT. Determination of the orientation of adsorbed molecules at solid−liquid interfaces by thin-layer electrochemistry: aromatic compounds at platinum electrodes. J Am Chem Soc 1982;104: 2735−42.

[18] Zhang J, Anson FC. Voltammetry and in-situ Fourier transform IR spectroscopy of two anthraquinone disulfonates adsorbed on graphite electrodes. J Electroanal Chem 1992;331:945−57.

[19] Finklea HO. In: Bard AJ, Rubinstein I, editors. Electroanalytical chemistry, vol. 19. New York: Marcel Dekker; 1996.

[20] Bodini ME, del Valle MA, Arancibia V. Redox chemistry and spectroscopy of the manganese−quinizarine−thiosalicylic acid mixed-ligand complex in aprotic medium. Polyhedron 1993;12:1733−8.

[21] Bodini ME, del Valle MA, Caceres S. Voltammetric and spectroscopic study of the manganese−quinizarine−quinaldic acid mixed-ligand complex in dimethylsulphoxide. Polyhedron 1997;16:2903−8.

[22] Bard AJ, Faulkner RL. Electrochemical methods − fundamentals and application. New York: John Wiley; 2001.