A simple electroanalytical method for the analysis of the dye solvent orange 7 in fuel ethanol

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ABSTRACT

The purpose of this paper is to develop a simple, rapid and accurate electroanalytical method for the determination of solvent orange 7 (SO-7), commercially used as a dye marker in fuel ethanol samples. SO-7 is oxidized in a mixture of Britton–Robinson buffer with N,N-dimethylformamide (1:1, v/v) at a glassy carbon electrode and presents a well-defined peak around +0.70 V vs. Ag/AgCl, which can be monitored by linear-scan voltammetry (LSV) and square-wave voltammetry (SWV). Using optimized parameters based on the SWV technique, it is possible to get a linear relationship between the peak current and the SO-7 dye concentration from 4.0×10^{-6} to 18.0×10^{-6} mol L^{-1} ($r = 0.995$). The proposed method was successfully applied to the direct quantification of the SO-7 dye in fuel ethanol samples, which gave good average recovery for commercial samples containing 5.0 mg L^{-1} and 10.0 mg L^{-1} of SO-7 dye, respectively.

1. Introduction

The fuel industry is one of the largest and most profitable in the world, such that fuel adulterations have been a common problem not only for Brazilian cities, but for practically every nation in the world. For example, Brazilian gasoline is a mixture of standard gasoline and dehydrated ethanol (produced from sugar cane), in which the concentration of dehydrated ethanol is varied between 20% and 26%. However, according to ANP (Brazilian National Petroleum Agency), Brazilian gasoline is being adulterated by adding a higher concentration of ethanol or by using ethanol with a higher concentration of water. For the purpose of distinguishing the hydrated ethanol from the dehydrated ethanol, a dye with orange coloration is prescribed by law (ANP) to be added to dehydrated ethanol [1]. Fuels are usually taxed according to government rates, which depend on the types of fuel as well as on their application purposes. Adulterated fuels may cause many problems to the car engine, may present health hazards and cause loss of tax revenues for the government [1–5]. In Brazil, it is considered that 38% of the total value of annual fuel-tax evasion originates from fuel alcohol adulteration [1]. Therefore, the ANP has prescribed the addition of the orange dye into dehydrated ethanol to discourage adulteration of gasoline and to guarantee the identity of the product.

Dyes are added to the fuels to distinguish liquids with chemical or physical similar properties. Thus, fuels marked with dyes can be visibly distinguished guarantying quality grade. They can also to

give distinction between lightly taxed products and to prevent fraudulent adulteration such as, blending kerosene, heating oil, diesel fuel or regular grade gasoline to that premium grade gasoline [3–6].

The solvent orange 7 (SO-7) dye, Fig. 1, azo dyes family, is a class of dyes widely employed in numerous coloring segments. Given the great variety of dyes commercially available with structure diversities and different physical-chemistry properties allied with the current concern of the addition of the water in fuel ethanol, the testing methods to evaluate the characteristic of fuels is becoming increasingly important. For this reason, it is essential to develop analytical methods able to identify and quantify these substances in this matrix to guarantee the quality of the product and distinguish between different varieties of fuel alcohols available on the market, as well as to differentiate between the different dyes available today.

High-performance liquid chromatography (HPLC) technique is the most common method for the quantification of some azo dyes in different fuel samples [7–12]. But, these methods sometimes require long analysis times and very expensive procedure. Therefore, methods economic, faster and simple are required for the fuel market control of its markers. No analytical methods have been reported in the literature for the identification and quantification of SO-7 or azo dyes in fuel ethanol.

The electrochemistry of some azo dyes is well known in literature [13–15], but no electroanalytical method has been reported for the voltammetric determination of SO-7 as an adulterant dye in fuel ethanol samples. In recent times, we reported that the electrochemical method could be a good alternative for the

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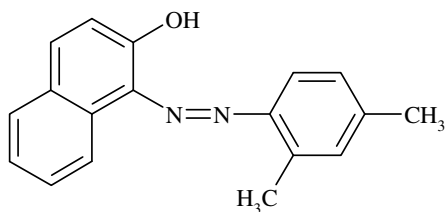E-mail address: boldrinv@iq.unesp.br (M.V.B. Zanoni).

Fig. 1. Structure of solvent orange (SO-7) dye.

quantification of quinizarin [16] and solvent blue 14 [17] as a dye marker in fuel samples. Hence, this work presents an electroanalytical method based on the oxidation of SO-7 dye on a glassy carbon electrode in a mixture of Britton–Robinson (B–R) buffer and *N,N*-dimethylformamide (1:1, v/v). The method offers a simple, fast and sensitive alternative for the analysis of the dye in fuel ethanol samples using the square-wave voltammetric technique.

2. Experimental

2.1. Instrumentation

An Autolab PGSTAT-30 (Eco Chemie) controlled by a General Purpose Electrochemical System (GPES) software (Eco Chemie) was used for the electrochemical measurements. A conventional three-electrode system was used, which was composed of a glassy carbon disc (2.5 mm diameter) set in a Teflon tube as the working electrode, plus a saturated Ag/AgCl (inside a Luggin capillary containing 3.0 mol L^{-1} KCl) used as the reference electrode and a platinum wire used as the counter electrode.

The spectrophotometric measurements were carried out using a spectrophotometer (HP model 8453) operating in the range of 200–800 nm using a quartz cell of 1.0 cm path length. All pH measurements were made using a combined glass electrode (Corning) connected to the digital pH-meter (Corning, model pH/ion analyzer 455) and are expressed as pH$_{apparent}$ (pH*). The deionized water was purified with a Milli-Q system (model Simplicity 185, Millipore).

2.2. Reagents and solutions

Stock solutions of SO-7 (Aldrich) (1.0×10^{-3} and 1.0×10^{-2} mol L^{-1}) were prepared by dissolving the solid product in acetonitrile (J.T. Baker). Dilute solutions of SO-7 were prepared immediately before use from a stock solution.

The solutions used as the supporting electrolyte were prepared in the usual way: Britton–Robinson (B–R) buffer 0.10 mol L^{-1} in a mixture of acetic acid (Merck), boric acid (Merck) and orthophosphoric acid (Merck) with the appropriate amount of sodium hydroxide (Merck) solution to adjust to the pH required.

2.3. Procedure for the voltammetric analysis

All the electrochemical experiments were carried out after transferring an aliquot of 10 mL of the supporting electrolyte solution into the electrochemical cell, 10 min of deaeration with nitrogen was done and then it was left for a rest period of 5 s. The same procedure was repeated after addition of an aliquot of SO-7 dye by micropipette into the cell. Before each series of measurements, the glassy carbon electrode was rinsed with acetone, polished with 1.0 μm alumina and washed with deionized water.

2.4. Analysis of SO-7 dye in an alcohol sample

Aliquots of 2.5 mL of the commercial fuel ethanol sample (collected from a gas station in Araraquara city, SP, Brazil) were spiked to 5.0 mg L^{-1} of SO-7 standard solution and diluted with 7.5 mL of supporting electrolyte. The resulting mixture was transferred directly to the electrochemical cell, submitted to deaeration with nitrogen for 10 min and analyzed via square-wave voltammetry. The quantification of the SO-7 dye was performed using the standard addition method.

Samples of fuel alcohol spiked to 10.0 mg L^{-1} of SO-7 dye was analyzed after transferring an aliquot of a solution prepared with 1.5 mL of the commercial fuel ethanol and 8.5 mL of B–R buffer and DMF (1:1, v/v) solution, to the electrochemical cell. The procedure for analysis via square-wave voltammetry was developed as described above.

2.5. Analysis of SO-7 dye in an alcohol sample using UV–vis spectrophotometry

Characteristics spectra of UV–vis obtained for SO-7 dye presents two maximum absorption bands at 272 and 493 nm. The adopted absorbance for measuring SO-7 dye was based on maximum signal at λ_{max} 493 nm against acetonitrile as blank reagent. The analytical curves for the SO-7 dye determination using the spectrophotometric method was carried out using aliquots between 50.0 and 500.0 μL of the dye stock solution (1.0×10^{-3} mol L^{-1}) previously prepared in acetonitrile. The dye quantification in the commercial ethanol fuel was performed using the following procedure: The sample spiked to 5.0 and 10.0 mg L^{-1} SO-7 dye was diluted in a 10.0 mL calibrated flask with acetonitrile. The resultant mixture was submitted to spectrophotometric analysis, recording the UV–vis spectrum and the quantification was performed using the standard addition method.

3. Results and discussion

3.1. Voltammetric behavior of the SO-7 dye

The SO-7 dye is not water soluble nor in a mixture containing DMF in a ratio lower than 40%. Nevertheless, optimal results concerning its solubility were obtained in a mixture of *N,N*-dimethylformamide (DMF) and Britton–Robinson buffer (1:1, v/v).

Fig. 2 shows typical cyclic voltammograms obtained for 2.0×10^{-5} mol L^{-1} of SO-7 dye in B–R buffer (pH* 7.0): DMF (1:1, v/v). Only one well-defined anodic peak is seen at around +0.70 V vs. Ag/AgCl, which could be attributed to the oxidation of the R–OH group. No peak is observed in the reverse scan, which indicates that the oxidation process is apparently irreversible.

The influence of scan rate on the cyclic voltammetric parameters was investigated from a scan rate of 10–500 mV s^{-1} for SO-7 dye in DMF: B–R buffer (pH* 5.0 and 9.0) following the ratio of 1:1 (v/v) in the mixture. A linear relationship between the peak current (I_p) and the scan rate variation (υ) was obtained and can be expressed as: I_{pa} (μA) = 0.17 + 0.0050υ; where υ = V s^{-1}; with a correlation coefficient of 0.9920, indicating that the oxidative process is controlled by the adsorption of the SO-7 dye onto the electrode surface [18].

In acidic medium (pH* 5.0), the media values obtained from $E_p - E_{1/2}$ = 34 mV of cyclic voltammograms indicate that the electron transfer number, *αn*, is equal to 1.4 [18]. The anodic potential (E_{pa}) shifts to a more positive value with an increase in the scan rate and the current function ($I_p \upsilon^{-1/2}$) is markedly decreased when the potential scan rate is increased. These results suggest that the oxidation step of the dye is complicated by adsorption effect [19].

In a mixture of DMF: B–R buffer at pH* 9.0, the cyclic voltammograms present media values of $E_p - E_{1/2}$ = 62 mV indicating that the electron transfer number, *αn*, is equal to 0.76 [18]. The height of the peak decreases strongly when the potential scan rate is in-