

Simultaneous determination of ethanol and methanol in fuel ethanol using cyclic voltammetry

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HIGHLIGHTS

- ▶ Simultaneous determination of ethanol and methanol in fuel ethanol.
- ▶ Fast cyclic voltammetric method identifies adulteration of fuel ethanol.
- ▶ The proposed method can be applied for on-site analysis.

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ABSTRACT

A new and simple strategy for the simultaneous determination of ethanol and methanol in fuel ethanol using cyclic voltammetry at a gold electrode is reported. A fuel ethanol aliquot was added into an electrochemical cell containing 0.5 mol L^{-1} NaOH and 0.1% (v/v) of methanol as the electrolyte and both analytes were determined using cyclic voltammetry. Ethanol was selectively detected at $+0.19 \text{ V}$ and both compounds were detected at $+1.20 \text{ V}$. Current subtraction (using a correction factor) could be used for the selective determination of methanol. The limits of detection were estimated to be 0.028% and 0.045% (v/v) for ethanol and methanol, respectively. The proposed method presented similar results to those obtained by gas chromatography at a 95% confidence level.

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1. Introduction

Fuel ethanol or bioethanol is one of the most important alternative energy sources and has been used widely in Brazil since 1975 [1,2]. Methanol, despite presenting similar physical–chemical properties, is not normally used as a fuel in Brazil due to its higher toxicity. However, the production of methanol is less expensive than ethanol and therefore it has been used as a common adulterant in Brazilian fuel ethanol. The addition of methanol to fuel ethanol does not cause visible effects (difficult detection during inspection) and does not generate mechanical engine problems, but can create serious health problems for users and especially for gas station attendants [3].

Few methods for the simultaneous determination of ethanol and methanol are reported in the literature, such as gas chromatography [4–7], flow injection analysis (FIA) with spectrophotometric detection [8], spectrophotometric method using artificial

neural network (ANN) methodologies for multivariate calibration [9], near infrared (NIR) spectroscopy with partial least squares (PLS) regression [10,11] and electrochemical methods employing modified electrodes with enzymes (biosensors) [12,13]. To our knowledge, there are no papers reporting the simultaneous determination of ethanol and methanol using electrochemical methods with unmodified electrodes.

As documented in the literature, ethanol [14–16] and methanol [17,18] can be oxidised at gold electrodes in alkaline solution. At 0.19 V , ethanol is oxidised to the corresponding aldehyde with its adsorption onto the gold surface, and at potentials higher than 1.00 V is oxidised to carbon dioxide, simultaneously with the formation of gold oxide. In turn, methanol is also initially oxidised to the corresponding aldehyde or formate ($E < 1.0 \text{ V}$) and at potentials higher than 1.0 V to carbon dioxide or carbonate [18]. However, as previously described [15], methanol is not electroactive in the potential region less positive than 1.0 V at concentrations lower than 0.5% (v/v) using gold as the working electrode in alkaline solution. Recently, our group developed a simple strategy for simultaneous determination employing FIA or BIA with multiple-pulse amperometric detection using a single working

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electrode [19–21]. In these studies, one compound is selectively detected at the first potential pulse, while both compounds are detected at the second potential pulse. Current subtraction (using a correction factor) was used for the selective determination of the analyte, which was only electroactive during the application of the second potential pulse. In the present work, a similar strategy is proposed for the simultaneous determination of ethanol and methanol in fuel ethanol using cyclic voltammetry.

2. Experimental

2.1. Reagents and samples

All solutions were prepared with deionised water (Millipore Direct-Q3) with a resistivity of no less than 18 MΩ-cm. All reagents were of analytical grade and were used without further purification. Sodium hydroxide was obtained from Dinâmica (Diadema, Brazil) and ethanol and methanol from Synth (Diadema, Brazil). Three fuel ethanol samples were purchased at different local fuel stations in the city of Uberlândia and were analysed after simple dilution in electrolyte solution containing 0.5 mol L⁻¹ NaOH/0.1% (v/v) methanol. External calibration procedure was used.

2.2. Instruments and apparatus

Cyclic voltammetric measurements were performed using a μ-Autolab Type III potentiostat (Metrohm Autolab B.V.). Miniaturised Ag/AgCl (KCl_{sat.}) [22], platinum and gold (∅ = 3 mm; Metrohm) were employed as the reference, auxiliary and working electrodes, respectively.

Results for the determination of ethanol and methanol in fuel ethanol were compared with those obtained by using gas chromatography (GC). A Shimadzu GC 2014 chromatograph with a flame ionisation detector (FID) and a carbowax column (30 m × 0.25 mm × 0.25 μm) was utilised. The GC method was adapted from the ASTM method (designation: D5501-04) [23]. The column temperature was kept constant at 40 °C during each experiment. The injector and detector temperatures were 180 and 210 °C, respectively. In all determinations, acetone was used as the internal standard and *n*-heptane as the solvent. The retention times were 2.787, 3.408, 4.484 and 5.369 min for *n*-heptane, acetone, methanol and ethanol, respectively.

3. Results and discussion

The electrochemistry of ethanol and methanol at bare gold electrodes was previously investigated in different pH solutions (acidic, neutral and alkaline) [18,24]. The highest oxidation currents are normally observed in alkaline solutions. Fig. 1 presents cyclic voltammograms obtained at the gold electrode in 0.5 mol L⁻¹ NaOH before (–) and after the addition of 0.5% (v/v) ethanol (– –) or 0.5% (v/v) methanol (....).

The results presented in Fig. 1 indicate that ethanol (0.5% v/v) is electroactive in two potential regions (between –0.25 and 1.20 V). As well-documented in the literature [16], at about +0.19 V, ethanol is oxidised to acetate or the corresponding aldehyde with the probable adsorption of these compounds onto the electrode surface. At potentials higher than +1.00 V, ethanol and/or the adsorbed compounds are oxidised to carbon dioxide [16] or carbonate [24] and the adsorbed material is oxidatively removed from the gold surface (cleaning procedure). Methanol is oxidised to formate or carbon dioxide [18] at potentials higher than +1.00 V and is electrochemically inactive at about +0.19 V in concentrations up to 0.5% (v/v) [15]. If higher concentrations are used, methanol is also oxidised in this potential region (+0.19 V).

Under these conditions (gold electrode, alkaline medium and cyclic voltammetry), ethanol can be quantified without methanol interference. However, selective and direct quantification of methanol is not possible, because ethanol is also electroactive in the same potential region (higher than +1.00 V). In the present paper, we propose a similar approach to that previously used for the simultaneous determination of paracetamol and caffeine using FIA with multiple pulse amperometric detection [20]. Thus, ethanol can be selectively detected around +0.19 V, while both ethanol and methanol can be detected at a more positive potential region (+1.20 V). The oxidation current of methanol can then be obtained by subtraction of the currents detected at the two potential regions. However, as can be observed in Fig. 1, the ethanol oxidation current detected at +0.19 V is much lower than the ethanol current detected at +1.20 V. Thus, simple subtraction between the currents detected at the two potential regions does not directly yield the methanol oxidation current. To bypass this problem, we applied a *correction factor* that corresponds to the exact difference between the current detected for ethanol at +0.19 V and +1.20 V. This *correction factor* is obtained by the analysis of a solution containing only ethanol by cyclic voltammetry and using the following equation:

$$\text{Correction factor} = i_{\text{ethanol}+1.20 \text{ V}} / i_{\text{ethanol}+0.19 \text{ V}}$$

Then, for the analysis of a solution simultaneously containing ethanol and methanol, the current originating from methanol oxidation (at +1.20 V) can be calculated using the following equation:

$$i_{\text{methanol}} = i_{+1.20 \text{ V}} - (\text{factor} \times i_{+0.19 \text{ V}})$$

The linear working range of the proposed system was determined by a series of experiments performed using standard solutions containing only ethanol or methanol. Ethanol displayed good linearity in a concentration range between 0.1% and 0.5% (v/v) at +0.19 V using 0.5 mol L⁻¹ NaOH as the electrolyte. However, under these conditions at +1.20 V, both compounds did not present good linearity. The oxidation current was always relatively higher for the first standard solution (methanol or ethanol) than the oxidation current for the remaining standard solution in the linear range of the proposed method. This probably took place because the oxidation of ethanol in alkaline solution occurs only when the gold surface is partially covered by gold oxides (potentials more positive than +1.0 V) [25]. Therefore, if the purpose is to obtain linear behaviour between the oxidation current and the ethanol or methanol concentration, gold oxide formation should be reproducible. However, gold oxide formation in alkaline solution varies considerably in the presence or absence of ethanol or methanol [18]. This problem was circumvented by the addition of 0.1% (v/v) methanol to the supporting electrolyte (0.5 mol L⁻¹ NaOH). Therefore, the formation of gold oxide only occurred in the presence of methanol or ethanol and improved reproducibility of the working electrode surface was obtained. Hence, a considerable improvement in the linearity of the calibration curves for both ethanol and methanol was also achieved. The choice of methanol (instead of ethanol) was made because it was not detected at +0.19 V. Therefore, a solution containing 0.5 mol L⁻¹ NaOH and 0.1% (v/v) methanol was used as the supporting electrolyte in subsequent studies.

Fig. 2 presents the calibration curves obtained at +0.19 V (■) and at +1.20 V (●) for standard solutions containing only ethanol.

Ethanol displayed good linearity in the studied concentration range (0.1–0.5%), with excellent correlation coefficients at +0.19 and +1.20 V (*R* = 0.999 and 0.998, respectively). The results presented in Fig. 2 were also used to check if the *correction factor* ($i_{\text{ethanol}+1.20 \text{ V}} / i_{\text{ethanol}+0.19 \text{ V}}$) was constant in the studied concentration range. These experiments demonstrated that the correction factor (2.37 ± 0.04) was constant in the studied concentration range with a relative standard deviation of 1.3%. The *correction*

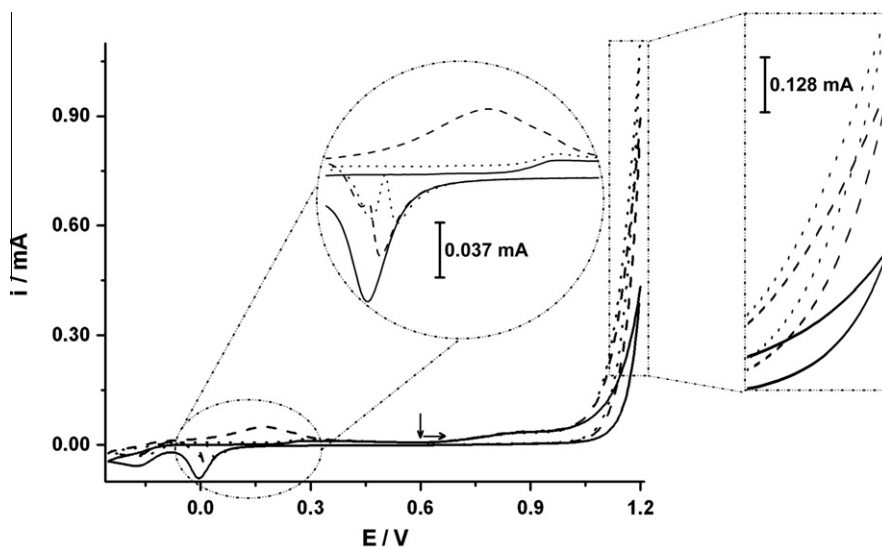


Fig. 1. Cyclic voltammograms obtained at a gold electrode in 0.5 mol L^{-1} NaOH before (—) and after the addition of 0.5% (v/v) ethanol (---) or methanol (.....). Scan rate = 50 mV s^{-1} . Step potential = 5 mV .

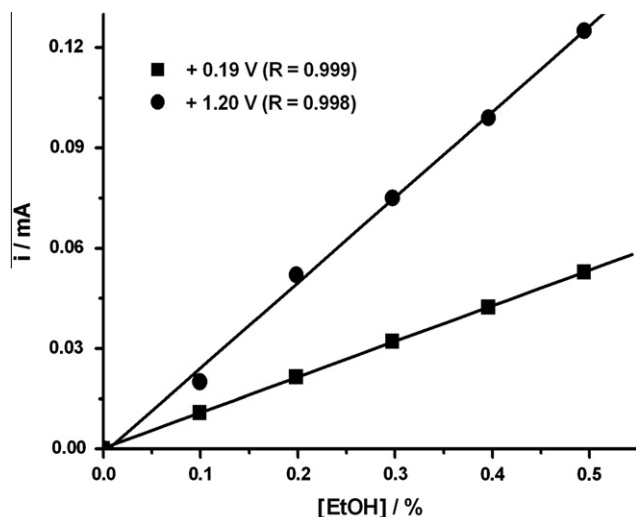


Fig. 2. Calibration curves obtained for ethanol at +0.19 V (■) and at +1.20 V (●).

factor should still be determined for each calibration procedure (by the analysis of a solution containing only ethanol), because small variations may occur between analyses conducted on different days.

The linear working range of the proposed method was also evaluated in a series of experiments using standard solutions containing only methanol. As methanol is considered an adulterant in fuel ethanol, these studies focused on identifying the lowest concentration range at which the relationship between concentration and the oxidation current was linear. This condition was obtained in a concentration range between 0.03% and 0.18% (v/v) methanol ($R = 0.998$).

The stability of the proposed method (Fig. 3) was assessed by successive analysis of a solution simultaneously containing ethanol and methanol (0.14% and 0.06% v/v, respectively).

The relative standard deviation ($n = 8$) was 0.9% and 1.3% for current responses at +0.19 V and +1.20 V, respectively. These results indicate that the proposed method presented good reproducibility despite the existence of an adsorption process on the gold electrode surface. It is probable that renovation of the electrode

surface occurs in the forward scan (1.20 to -0.25 V) of the cyclic voltammetry measurements (gold reduction) [15]. Square wave and differential pulse voltammetry techniques were also tested for this purpose. However, the results were not reproducible, possibly due to the absence of the reverse scan where gold oxide was removed. When cyclic voltammetry was used, the gold oxide that formed during the anodic scan was removed in the cathodic scan (electrochemical reduction) and the gold electrode surface was thus renewed at each experiment.

Fig. 4 presents cyclic voltammograms obtained from the analysis of five solutions simultaneously containing increasing concentrations of ethanol (0.00–0.35%, v/v) and methanol (0.00–0.15%, v/v).

The obtained analytical curves presented the following calibration equations:

$$I_{\text{ethanol}} = i_{+0.19 \text{ V}}; \quad i(\text{mA}) = 0.0014 + 0.1022C(\%, \text{v/v}); \quad R = 0.999$$

$$I_{\text{methanol}} = i_{+1.20 \text{ V}} - (\text{factor} \times i_{+0.19 \text{ V}}); \\ i(\text{mA}) = 0.0300 + 1.1094C(\%, \text{v/v}); \quad R = 0.993$$

The limits of detection (LOD; $3S/N$) were 0.028% and 0.045% (v/v) for ethanol and methanol, respectively. Table 1 presents the results obtained using the proposed method for the simultaneous determination of ethanol and methanol in three fuel ethanol samples. The samples were analysed before (1a, 2a and 3a) and after adulteration with methanol and water (1b), or only with methanol (2b and 3b). The results were compared to those obtained using gas chromatography.

As presented in Table 1, the results obtained using the proposed method were in good agreement with those obtained using gas chromatography. At a 95% confidence level, the calculated *t* values (paired Student's *t*-test) were smaller than the critical value (2.78; $n = 3$), demonstrating that there were no significant differences between the results obtained by these two methods. The results obtained for the ethanol concentration in sample "1b" can be considered an exception because the result obtained by cyclic voltammetry was not in agreement at the 95% confidence level with the result obtained by the GC method. However, the result obtained with the proposed method seems to be more accurate since the expected result would be close to 86% (v/v) (due to adulteration with 5% methanol + 8% H_2O).

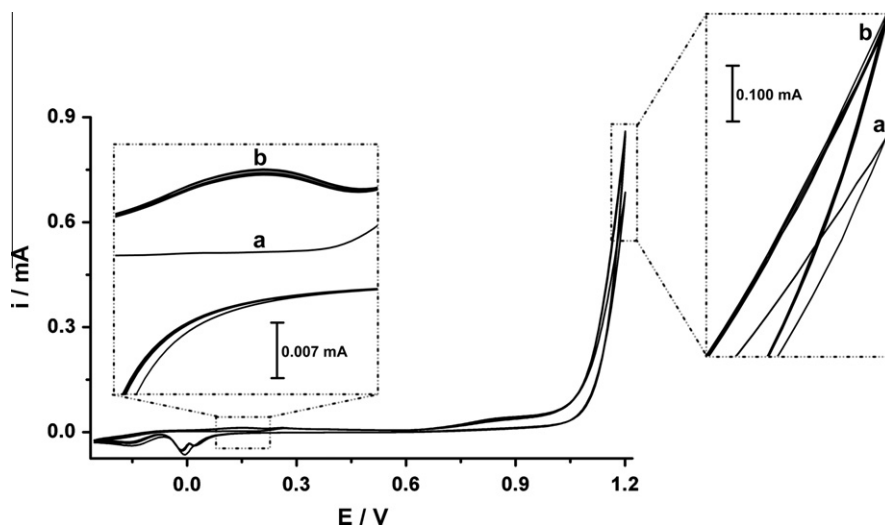


Fig. 3. Cyclic voltammograms obtained for the successive analysis ($n = 8$) of a solution simultaneously containing 0.14% ethanol and 0.06% methanol. (b). Blank experiment is indicated by (a). Scan rate = 50 mV s^{-1} . Step potential = 5 mV .

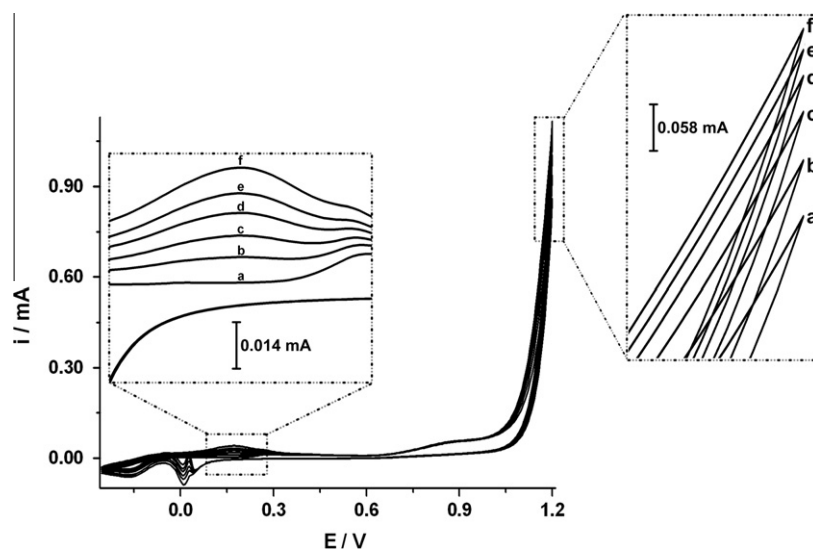


Fig. 4. Cyclic voltammograms obtained for solutions containing only the electrolyte (a: $0.5 \text{ mol L}^{-1} \text{ NaOH}/0.1\% \text{ v/v}$ methanol) and five solutions simultaneously containing increasing concentrations (b–f) of ethanol (0.07–0.35%; v/v) and methanol (0.03–0.15%; v/v). Scan rate = 50 mV s^{-1} . Step potential = 5 mV .

Table 1

Comparison of results ($n = 3$) obtained from the simultaneous determination of ethanol and methanol in fuel ethanol samples using cyclic voltammetry (CV) versus gas chromatography (GC).

Sample	Adulteration	[EtOH]/% (v/v)		[MetOH]/% (v/v)	
		GC	CV	GC	CV
1a	NA*	97 ± 3	100 ± 5	<LD	2 ± 2
1b	5% MetOH + 8% H ₂ O	63 ± 10	86 ± 8	3 ± 2	6 ± 1
2a	NA*	97 ± 4	100 ± 3	<LD	1 ± 2
2b	8% MetOH	86 ± 5	92 ± 6	8 ± 2	8 ± 2
3a	NA*	97 ± 3	96 ± 2	<LD	<LD
3b	14% MetOH	81 ± 6	84 ± 7	14 ± 2	14 ± 2

* NA corresponds to non-adulterated samples

4. Conclusions

An innovative, simple and low-cost method for the simultaneous determination of ethanol and methanol using cyclic voltammetry and a bare gold working electrode was developed. The proposed method is appropriate for use in inspections and for

the identification of adulterations in fuel ethanol with methanol because the assay is capable of detecting methanol in the presence of high concentrations of ethanol (around 10-fold higher). To our knowledge, this is the first study to demonstrate the possibility of simultaneous determination of ethanol and methanol using cyclic voltammetry in an alkaline solution with an unmodified gold electrode.

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