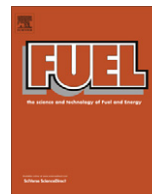




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Voltammetric determination of ethyl acetate in ethanol fuel using a Fe³⁺/Nafion[®]-coated glassy carbon electrode

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HIGHLIGHTS

- ▶ A new voltammetric method for the determination of ethyl acetate in ethanol fuel.
- ▶ A glassy carbon electrode was chemically modified with Fe³⁺/Nafion[®]-film.
- ▶ A well-defined voltammetric irreversible peak current at −0.02 V is obtained.
- ▶ SWV technique afforded the best response, bring linear from 9 to 100 μmol L^{−1}.

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ABSTRACT

A voltammetric method for the determination of ethyl acetate in ethanol fuel using a Fe³⁺/Nafion[®]-coated glassy carbon electrode (GCE) is proposed. The ethyl acetate present in the ethanol fuel was previously converted to acetoxyhydroxamic acid via pretreatment with hydroxylamine chloride. The acetoxyhydroxamic acid promptly reacted with the iron (III) present in the film, producing iron (III) acetoxyhydroxamate, which presents a well-defined voltammetric peak current at −0.02 V. Optimization of the voltammetric parameters for the cyclic, linear sweep, square wave, and differential pulse modalities was carried out for this chemically-modified electrode. Square wave voltammetry afforded the best response for acetoxyhydroxamic acid detection. The analytical curve for this species was linear from 9 to 100 μmol L^{−1} according to the following equation: $i_p (\mu\text{A}) = 0.27 + 2.55C_{\text{acetoxyhydroxamic acid}} (\mu\text{mol L}^{-1})$, with linear correlation coefficient equal to 0.993. The technique presented limit of detection equal to 5.3 μmol L^{−1} and quantification limit of 17.6 μmol L^{−1}. The proposed method was compared to the official method of ethyl acetate analysis (Gas Chromatography), and a satisfactory correlation was found between these techniques.

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1. Introduction

Petroleum-based fuels have been the main energy source for industries and vehicles since the industrial revolution. Several countries have become highly dependent on petroleum importation from mid eastern exporters. After the first petroleum crisis in the 1970s, which caused a sharp increase in oil prices, several countries embarked on an intensive search for an economically viable alternative to petroleum-based fuels [1,2].

In this sense, ethanol fuel can be cited as a successful option. Brazil, which has pioneered the technology of ethanol fuel production from sugarcane, created the National Alcohol Program (PRO-ALCOOL) in 1975, aiming to produce a substitute for gasoline and increase ethanol production for industrial applications [1]. Some

of the environmental advantages of ethanol in relation to fossil fuels, are the absence of lead-based additives, decreased SO₂ and CO emissions, and renewability, among others [3,4].

The popularization of ethanol fuel worldwide, associated with the development of flex fuel technology, has made it an important exportable alternative fuel, once its manufacture process is well developed today. In this context, ethanol quality control starting from its production until the final consumer is crucial. Several organic and inorganic contaminants must be analyzed by following official specifications, set by the producing country. In Brazil, for example, the official norms of quality control of organic contaminants in ethanol (established by the ANP – Brazilian Agency of Petroleum, Natural Gas, and Biofuels) concern acetal, acetaldehyde, ethyl acetate, acetone, methanol, higher alcohols [5], benzene [5,6], and formaldehyde [7] determination.

Among the organic contaminants of ethanol fuel, ethyl acetate deserves special attention. It is generated mainly by reaction of

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ethanol with the acetic acid present in this fuel. The official method of analysis of this compound employs the gas chromatography technique [5]. However, several other methods have been reported for the analysis of esters in the literature. To this end, a wide range of matrixes as well as chromatographic [8–12], spectrophotometric [13–15], electrophoretic [16,17], and voltammetric techniques [18–22] can be utilized.

Additionally, important information about the chemical reactivity of ethyl acetate and other esters has been described by Feigl [23], who has proposed a spot test for this substance. More specifically, ethyl acetate is added to a solution containing hydroxylamine in alkaline medium, with subsequent acidification, it is possible to obtain the corresponding hydroxamic acid, as in Scheme 1.

The resulting hydroxamic acid can easily form a complex Fe^{3+} ion in solution, giving rise to a chelate with a strong red color and octahedral configuration, as in Scheme 2.

The electrochemical behavior of Fe^{3+} hydroxamates generally presents a quasi-reversible, pH-dependent, one-electron wave process, with a peak separation of 70 mV (at a 100 mV/s scan rate). At pH 7 the observed formal potential E_f is -388 mV vs. SCE, decreasing by 60 mV/pH unit [24]. On the other hand, the electrochemical study of isolated hydroxamic acids only exhibits irreversible anodic reaction (two-electron process) in strongly alkaline conditions, under presence of oxidants [25,26].

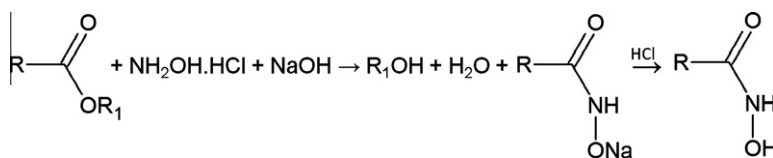
Nafion[®]-chemically modified electrodes constitute a very important class of transducers employed in voltammetric determination of a large number of organic and inorganic species in several matrixes [27–31], including ethanol fuel [29].

Despite the importance of voltammetric techniques for the analysis of several organic contaminants in ethanol fuel [20–22], the literature does not bring a specific voltammetric methodology for ethyl acetate determination. Hence, the aim of this work is to develop a chemically modified glassy carbon electrode coated with a Fe^{3+} /Nafion[®] film, in order to check the possibility of monitoring the ethyl acetate content in ethanol fuel through exploitation of the reactivity of this ester with hydroxylamine and the affinity of hydroxamic acid with Fe^{3+} ions.

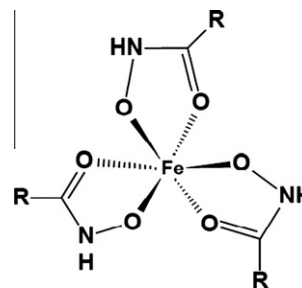
2. Experimental

2.1. Reagents

A commercial Nafion[®] solution from Sigma–Aldrich was used to prepare Nafion[®]-coated glassy carbon electrodes (Nafion[®]-GCE). The nominal content of Nafion[®] in this solution is 5% (w:w) dissolved in high purity methanol. Iron (III) aqueous solutions were prepared from nonhydrated ferric nitrate (Sigma–Aldrich). Ethanol (Quemis), ethyl acetate (Synth), nitric acid (Quemis), sodium hydroxide (Mallinckrodt), hydroxylamine (Synth), hexane (Tedia) and acetohydroxamic acid (ethanehydroxamic acid; Sigma–Aldrich) were analytical grade reagents and were used without further purification. All the employed aqueous solutions were prepared using ultrapure water (ASTM type I, resistivity $> 18 \text{ M}\Omega \text{ cm}$) produced from a Mili-Q[®] water purification system.



Scheme 1. Chemical reactions involved in the conversion of a generic ester to its corresponding hydroxamic acid.



Scheme 2. Chemical structure of iron (III) acetohydroxamate chelate.

2.2. Apparatus

All the voltammetric experiments were performed using an Autolab PGSTAT-30 potentiostat/galvanostat from Ecochemie coupled to a microcomputer and controlled by the GPES 4.9 software. The electrochemical experiments were conducted at room temperature, in a one-compartment electrochemical cell. A three-electrode system comprising a platinum wire as auxiliary electrode, a KCl saturated-Ag/AgCl (AgCl_{sat}) as reference electrode, and a 3.0 mm diameter glassy carbon disc as working electrode was used in all the experiments. Gas Chromatography (GC) with a Flame Ionization Detector (FID) was employed as comparative analytical method. GC experiments were accomplished on Agilent 6890 N instrument equipped with a $60 \text{ m} \times 0.25 \text{ mm}$ capillary column coated with a $0.5 \mu\text{m}$ DBWAX film. Helium, purity $> 99.999\%$, was utilized as carrier gas at a flow rate of 1.0 mL min^{-1} . The injector and detector temperatures were kept at 100°C . Sample injection was carried out in the 1:100 split mode.

2.3. Electrode preparation

Previously to Nafion[®] deposition onto the glassy carbon surface, the electrode was polished with alumina $0.5 \mu\text{m}$, followed by rinsing with ultrapure water. After that, $5 \mu\text{L}$ Nafion[®] solution were placed on the glassy carbon surface, and the electrode was then set aside and allowed to dry at room temperature (approximately 2 min). Finally, Nafion[®]-GCE was immersed in a Fe^{3+} aqueous solution at constant stirring, in order to promote Fe^{3+} incorporation into the Nafion[®] film.

2.4. Analytical procedure

The proposed method was based on the indirect determination of ethyl acetate after its chemical conversion to acetohydroxamic acid. At electrode surface, Fe^{3+} incorporated into the Nafion[®] film reacts with acetohydroxamic acid, forming iron (III) acetohydroxamate. The electrochemical reduction of the latter complex provides a voltammetric signal related to the ethyl acetate concentration. Therefore, the analytical procedure comprises four steps: (1) Nafion[®] deposition onto the glassy carbon surface; (2) Fe^{3+} incorporation into the Nafion[®] film by immersion of Nafion[®]-GCE in an Fe^{3+} aqueous solution; (3) iron (III) acetohydroxamate formation at

the electrode surface by Fe^{3+} /Nafion[®]-GCE exposure to acetoxyhydroxamic acid, and (4) electrode transfer to an electrochemical cell containing $0.1 \text{ mol L}^{-1} \text{ HNO}_3$ solution and square wave voltammetry recording.

In order to achieve the chemical conversion of ethyl acetate to acetoxyhydroxamic acid 2 mL of a saturated ethanolic hydroxylamine solution were added to 2 mL saturated ethanolic sodium hydroxide solution. After that, 1 mL ethanol fuel sample was added, and the mixture was heated to reflux. The mixture was kept refluxing for 1 min followed by the addition of 5 mL of $2.0 \text{ mol L}^{-1} \text{ HCl}$ aqueous solution. The resulting acetoxyhydroxamic acid was extracted with 10 mL hexane. The Fe^{3+} /Nafion[®]-coated glassy carbon electrode (Fe^{3+} /Nafion[®]-GCE) was then immersed in hexane containing extracted acetoxyhydroxamic acid, leading to iron (III) acetoxyhydroxamate formation at the electrode surface.

3. Results and discussion

3.1. Fe^{3+} incorporation into Nafion[®]-GCE

Fe^{3+} incorporation into Nafion[®]-GCE was studied by cyclic voltammetry. The cyclic voltammograms were recorded in $0.1 \text{ mol L}^{-1} \text{ HNO}_3$ aqueous solution after immersion of Nafion[®]-GCE in $10 \text{ mmol L}^{-1} \text{ Fe}^{3+}$ aqueous solution, under constant stirring. This procedure enabled spontaneous Fe^{3+} incorporation into the Nafion[®] film via electrostatic attraction between the Fe^{3+} ions and the Nafion[®] negatively-charged sulfonic groups. The cyclic voltammograms recorded in $0.1 \text{ mol L}^{-1} \text{ HNO}_3$ aqueous solution after 1 and 3 min of immersion in Fe^{3+} aqueous solution are presented in Fig. 1. At this figure the voltammetric response for a bare glassy carbon electrode is also presented for comparison purposes.

The pair of voltammetric peaks can be attributed to the Fe^{3+} /Nafion[®]- Fe^{2+} /Nafion[®] couple [24], confirming that Fe^{3+} was indeed incorporated into the Nafion[®] film. There is an increase in the intensity of these voltammetric peaks on going from 1 to 3 min of immersion time. Longer immersion times do not increase the intensity of these peaks, indicating that Fe^{3+} incorporation into the Nafion[®] film is very fast. In other words, only a few minutes are necessary for saturation of the Nafion[®] film with Fe^{3+} . Based on this result, 3 min of immersion was adopted for preparation of the Fe^{3+} /Nafion[®]-GCE used in all the subsequent experiments.

3.2. Voltammetric behavior of Fe^{3+} /Nafion[®]-GCE containing iron (III) acetoxyhydroxamate

The electrochemical behavior of Fe^{3+} /Nafion[®]-GCE after its exposure to acetoxyhydroxamic acid was evaluated by cyclic voltammetry. Cyclic voltammograms were recorded in $0.1 \text{ mol L}^{-1} \text{ HNO}_3$ aqueous solution after immersion of Fe^{3+} /Nafion[®]-GCE in a 1.0 mmol L^{-1} acetoxyhydroxamic acid solution prepared with hexane as solvent. Fig. 2 illustrates the cyclic voltammograms registered using Nafion[®]-GCE and Fe^{3+} /Nafion[®]-GCE before and after its exposure to acetoxyhydroxamic acid.

Nafion[®]-GCE does not display any voltammetric peak in this potential range, even after its exposure to acetoxyhydroxamic acid. This indicates that there is no interaction between Nafion[®] and acetoxyhydroxamic acid able leading to an electroactive species in this potential range. After immersion of Nafion[®]-GCE in an aqueous Fe^{3+} solution, voltammetric peaks attributed to the Fe^{3+} /Nafion[®]- Fe^{2+} /Nafion[®] couple can be detected, as previously discussed. A second cathodic peak is noted at -0.02 V when Fe^{3+} /Nafion[®]-GCE is previously immersed in a solution containing acetoxyhydroxamic acid. This is a clear demonstration that Fe^{3+} /Nafion[®] is reacting with acetoxyhydroxamic acid at the electrode surface, forming iron (III)

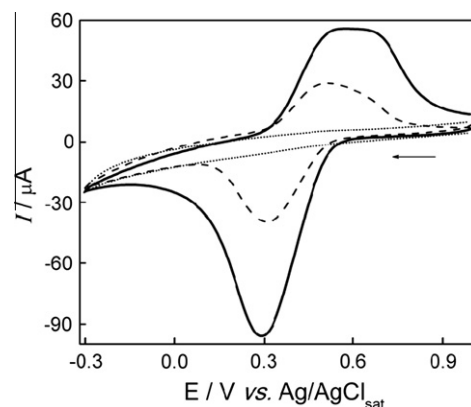


Fig. 1. Cyclic voltammograms recorded in $0.1 \text{ mol L}^{-1} \text{ HNO}_3$ aqueous solution at 100 mV s^{-1} after immersion of Nafion[®]-GCE in a $10 \text{ mmol L}^{-1} \text{ Fe}^{3+}$ solution. (---) 1 min immersion time. (—) 3 min immersion time. (···) Voltammetric response for a bare glassy carbon electrode.

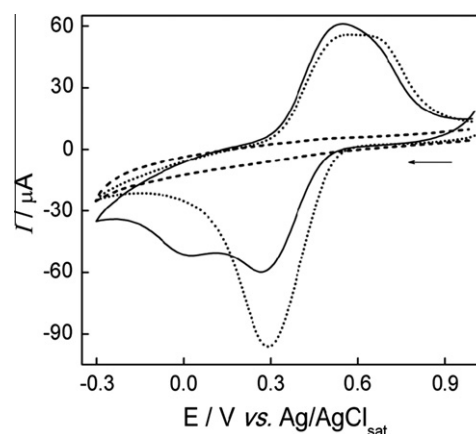


Fig. 2. Cyclic voltammograms recorded in $0.1 \text{ mol L}^{-1} \text{ HNO}_3$ aqueous solution at 100 mV s^{-1} . (---) Nafion[®]-GCE after immersion in 1.0 mmol L^{-1} acetoxyhydroxamic acid solution in hexane for 30 s. (···) Nafion[®]-GCE after immersion in a $10 \text{ mmol L}^{-1} \text{ Fe}^{3+}$ solution for 3 min. (—) Fe^{3+} /Nafion[®]-GCE after immersion in 1.0 mmol L^{-1} acetoxyhydroxamic acid solution in hexane for 30 s.

acetoxyhydroxamate. The latter is reduced to iron (II) acetoxyhydroxamate, giving rise to the cathodic peak observed at -0.02 V . The decrease in the peak associated with Fe^{3+} /Nafion[®] reduction that is observed when the electrode is exposed to acetoxyhydroxamic acid agrees with iron (III) acetoxyhydroxamate formation, which diminishes the amount of Fe^{3+} /Nafion[®] at the electrode surface and lowers the voltammetric peak corresponding to Fe^{3+} /Nafion[®] reduction to Fe^{2+} /Nafion[®].

The voltammetric peak at -0.02 V associated with iron (III) acetoxyhydroxamate reduction, provides a very interesting way of indirectly quantifying ethyl acetate after its chemical conversion to acetoxyhydroxamic acid. The absence of its corresponding anodic peak on the reverse scan suggests that iron (III) acetoxyhydroxamate reduction is an irreversible process, or that the electrochemical step is followed by a chemical reaction that consumes the reduced form. This last hypothesis seems to be more probable, since an anodic peak apparently related to the cathodic peak at -0.02 V could be observed at high scan rates (data not shown). This anodic peak is strongly overlapped with the anodic peak associated with the Fe^{2+} /Nafion[®]- Fe^{3+} /Nafion[®] process, which makes determination of its voltammetric parameters impossible and hampers additional studies on the nature of this peak as well as on its relationship with the cathodic peak at -0.02 V .

The effect of the immersion time of $\text{Fe}^{3+}/\text{Nafion}^{\text{®}}\text{-GCE}$ in a 1.0 mmol L^{-1} acetohydroxamic acid solution on the intensity of the voltammetric peak at -0.02 V was examined. The results showed that 1 min of immersion results in the largest voltammetric signal. Longer immersion times do not enhance the intensity of the voltammetric peak at -0.02 V . This demonstrates that the reaction between $\text{Fe}^{3+}/\text{Nafion}^{\text{®}}$ and acetohydroxamic acid is very fast, in agreement with previous reports on the kinetics of this reaction [23]. Therefore, 1 min of immersion time in acetohydroxamic acid solution was adopted in all the subsequent experiments.

After optimization of the procedures for electrode preparation and iron (III) acetohydroxamate formation, successive cyclic voltammograms using $\text{Fe}^{3+}/\text{Nafion}^{\text{®}}\text{-GCE}$ containing iron (III) acetohydroxamate were run. The voltammetric peak related to iron (III) acetohydroxamate reduction (at -0.02 V) is observed only in the first cyclic voltammogram, at the second scan, this peak is completely absent as shown in Fig. 3.

The behavior observed at Fig. 3, suggests that, after the electrochemical reduction of iron (III) acetohydroxamate, its oxidized form cannot be regenerated during the reverse scan. As a consequence, the cathodic peak at -0.02 V is absent in all the subsequent cyclic voltammograms. Based on this result, only the first cyclic voltammogram recorded with a freshly prepared $\text{Fe}^{3+}/\text{Nafion}^{\text{®}}\text{-GCE}$ was used for analytical applications.

3.3. Analytical applications

Analytical studies were performed by square wave voltammetry (SWV). In the initial stages of these studies it can be observed that in the previously optimized conditions SWV provides a very high and broad voltammetric peak, associated with $\text{Fe}^{3+}/\text{Nafion}^{\text{®}}$ reduction. The voltammetric peak attributed to iron (III) acetohydroxamate reduction is strongly overlapped with the $\text{Fe}^{3+}/\text{Nafion}^{\text{®}}$ reduction peak, making its use for analytical applications impossible. In order to overcome this limitation, the concentration of Fe^{3+} solution employed during incorporation of this metallic ion into the $\text{Nafion}^{\text{®}}$ film was lowered from 10 to 0.3 mmol L^{-1} . Thus, a smaller amount of Fe^{3+} was incorporated into the $\text{Nafion}^{\text{®}}$ film, leading to a less intense voltammetric peak associated with $\text{Fe}^{3+}/\text{Nafion}^{\text{®}}$ reduction. This strategy is very efficient for virtually complete separation of the voltammetric peaks associated with the $\text{Fe}^{3+}/\text{Nafion}^{\text{®}}$ and iron (III) acetohydroxamate reduction.

The SWV parameters were also optimized by keeping the Fe^{3+} and acetohydroxamic acid concentrations equal to 0.3 and 1.0 mmol L^{-1} , respectively. Immersion times in Fe^{3+} and in acetohydroxamic acid solutions were maintained at previously opti-

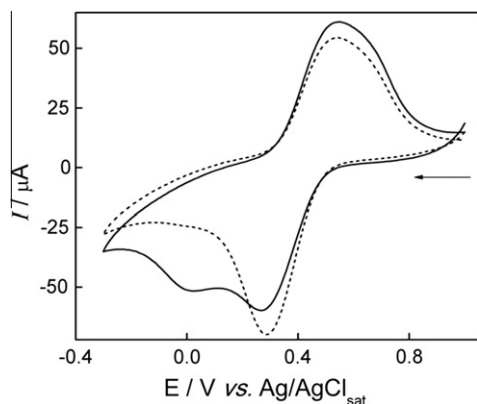


Fig. 3. Cyclic voltammograms recorded in $0.1 \text{ mol L}^{-1} \text{ HNO}_3$ aqueous solution at 100 mV s^{-1} using $\text{Fe}^{3+}/\text{Nafion}^{\text{®}}\text{-GCE}$ after its immersion in 1.0 mmol L^{-1} acetohydroxamic acid solution in hexane for 1 min. (—) First cycle. (---) Second cycle.

mized values; i.e., 3 and 1 min, respectively. The pulse amplitude (ΔE) effect was assessed from 25 to 125 mV. The potential value 75 mV provided the best voltammetric profile, since higher pulse amplitudes produced unacceptable broad and overlapped peaks. Therefore, a pulse amplitude of 75 mV was adopted in the subsequent experiments. Pulse frequency (f) was evaluated from 25 to 125 Hz, and the best voltammetric profile was obtained with 75 Hz, which was also adopted in this work. The optimized step potential value (ΔE_s) was 2.0 mV. Under these optimized conditions, square wave voltammograms were recorded with $\text{Fe}^{3+}/\text{Nafion}^{\text{®}}\text{-GCE}$ after its exposure to different acetohydroxamic acid concentrations. The plots of I_p for iron (III) acetohydroxamate reduction and I_p for $\text{Fe}^{3+}/\text{Nafion}^{\text{®}}$ reduction as a function of acetohydroxamic acid solution are presented in Fig. 4.

Fig. 4 shows a decrease of the voltammetric peak attributed to $\text{Fe}^{3+}/\text{Nafion}^{\text{®}}$ reduction by increasing acetohydroxamic acid concentration. This is consistent with the consumption of this metallic ion at surface electrode to give iron (III) acetohydroxamate, as previously discussed. Peak current (I_p) values for iron (III) acetohydroxamate reduction were utilized for construction of an analytical curve, which was linear from 9 to $100 \text{ } \mu\text{mol L}^{-1}$ according to the following equation: $i_p (\mu\text{A}) = 0.27 + 2.55C_{\text{acetohydroxamic acid}} (\mu\text{mol L}^{-1})$. The linear correlation coefficient was equal to 0.9968, and the limit of detection (LOD) was found to be $5.3 \text{ } \mu\text{mol L}^{-1}$. LOD was evaluated by the equation: $\text{LOD} = 3\text{SD}/(\text{analytical curve slope})$ [32], where SD is equivalent to the standard deviation of the blank signal at the peak potential of iron (III) acetohydroxamic reduction. The limit of quantification (LOQ), calculated by means of the equation $\text{LOQ} = 10\text{SD}/(\text{analytical curve slope})$ [32], was $17.6 \text{ } \mu\text{mol L}^{-1}$.

The efficiency of the procedure adopted for the chemical conversion of ethyl acetate to hydroxamic acid as well as the efficiency of the extraction procedure were assessed. To perform these evaluations, an ethyl acetate solution $67.0 \text{ } \mu\text{mol L}^{-1}$ in absolute ethanol was prepared. This solution was submitted to the whole conversion and extraction procedure described in the experimental section. The solution obtained after extraction with hexane was analyzed by SWV using the same conditions adopted for construction of the analytical curve. This procedure was carried out in triplicate, and the obtained peak current values were used for computation of the ethyl acetate concentration. The average ethyl acetate concentration was $65.3 \text{ } \mu\text{mol L}^{-1}$, and standard deviation was equal to $1.9 \text{ } \mu\text{mol L}^{-1}$ ($N = 3$). Statistical studies using t -test at 95% confidence level [32] provided a confidence interval of $\pm 4.7 \text{ } \mu\text{mol L}^{-1}$. Therefore, the known value of concentration ($67.0 \text{ } \mu\text{mol L}^{-1}$) is contained in the confidence interval, indicating that there are no statistical differences between known and exper-

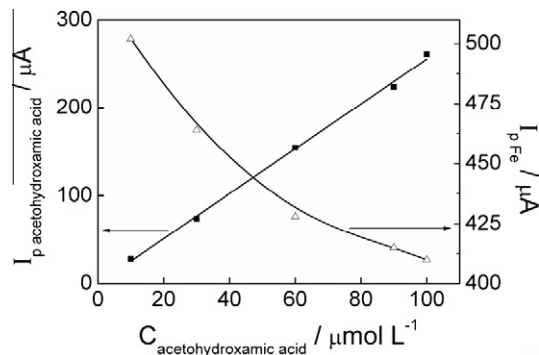


Fig. 4. Plots of I_p as a function of acetohydroxamic acid concentration. (Δ) Fe^{3+} reduction. (\blacksquare) iron (III) acetohydroxamate reduction. I_p values obtained from square wave voltammograms recorded in HNO_3 0.1 mol L^{-1} after immersing $\text{Fe}^{3+}/\text{Nafion}^{\text{®}}\text{-GCE}$ for 1 min in different acetohydroxamic acid concentrations. Voltammetric conditions: $\Delta E = 75 \text{ mV}$, $f = 75 \text{ Hz}$ and $\Delta E_s = 2.0 \text{ mV}$.

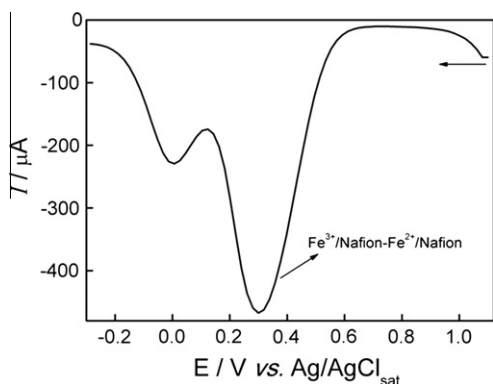


Fig. 5. Square wave voltammogram recorded in HNO_3 0.1 mol L^{-1} after immersing $\text{Fe}^{3+}/\text{Nafion}^{\text{®}}$ -GCE for 1 min in aceto-hydroxamic acid extracted from the commercial ethanol fuel sample. $\Delta E = 75 \text{ mV}$, $f = 75 \text{ Hz}$ and $\Delta E_s = 2.0 \text{ mV}$.

imental values at 95% confidence level. This result is a clear demonstration that ethyl acetate is quantitatively converted to aceto-hydroxamic acid, which in turn is quantitatively extracted with hexane. Thus, the proposed voltammetric method can be used for the reliable quantification of ethyl acetate in ethanol fuel samples.

3.4. Real samples analyses

The proposed method was utilized for ethyl acetate quantification in a commercial ethanol fuel sample acquired from a local gas station. The ethyl acetate contained in this sample was chemically converted to aceto-hydroxamic acid, followed by extraction with hexane, according to the previously described procedures. The resulting solution containing the extracted aceto-hydroxamic acid was analyzed by the proposed method and the corresponding square wave voltammogram is presented in Fig. 5.

The ethyl acetate content found in this commercial ethanol fuel sample was $49.9 \mu\text{mol L}^{-1}$ with standard deviation equal to $2.6 \mu\text{mol L}^{-1}$ ($N = 3$). Regarding the 10-fold dilution was submitted to the sample, the ethyl acetate concentration in the original sample was 43.97 mg L^{-1} with standard deviation equal 2.3 mg L^{-1} ($N = 3$). Using the t -test at 95% of confidence level [32] the confidence interval was determined as $44.0 \pm 5.7 \text{ mg L}^{-1}$. This same sample was also analyzed by GC, as described in the experimental section. The final ethyl acetate concentration in this sample obtained by GC was 48.5 mg L^{-1} . This value lies in the confidence interval of the voltammetric method, indicating that there are no statistical differences between the results provided by both analytical methods. This is a clear demonstration of the reliability and accuracy of the proposed voltammetric method, showing that it can be successfully employed for ethyl acetate quantification in commercial ethanol fuel samples.

4. Conclusions

The chemical conversion of ethyl acetate to aceto-hydroxamic acid followed by its complexation with $\text{Fe}^{3+}/\text{Nafion}^{\text{®}}$ is very attractive approach for the development of a voltammetric method that is able to indirectly quantify ethyl acetate in commercial ethanol fuel samples. Fe^{3+} incorporation into the Nafion[®] film is a very fast process that is easily achieved by immersion of Nafion[®]-coated GCE in an Fe^{3+} aqueous solution. The analytical procedure adopted in this work enables the rapid and quantitative chemical conversion of ethyl acetate to aceto-hydroxamic acid, which is quantitatively extracted with hexane. The electrochemical reduction of iron (III) aceto-hydroxamate formed at the $\text{Fe}^{3+}/\text{Nafion}^{\text{®}}$ -GCE surface furnishes a well-defined voltammetric peak, which can be

used as analytical signal for the indirect quantification of ethyl acetate. In conclusion, this work has demonstrated that $\text{Fe}^{3+}/\text{Nafion}^{\text{®}}$ -GCE can be successfully applied for the indirect quantification of ethyl acetate in commercial ethanol fuel samples using square wave voltammetric technique.

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