Voltammetric Determination of Total Iron in Fuel Ethanol Using a 1,10 Fenantroline/Nafion Carbon Paste-Modified Electrode

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This work presents a methodology for iron determination in fuel ethanol using a modified carbon paste electrode with 1.10 fenantroline/nafion. The electrochemical parameters were optimized for the proposed system and the voltammetric technique of square wave was employed for iron determination. An accumulation time of 5 minutes, such as a 100 mV of pulse magnitude (E_{sw}) and frequency (f) of 25 Hz were used as optimized experimental conditions. The modified carbon paste electrode presented linear dependence of amperometric signal with iron concentration in a work range from 6.0×10^{-6} until 2.0×10^{-5} mol L^{-1} of iron, exhibiting a linear correlation coefficient of 0.9884, a detection limit of 2.4 $\times 10^{-6}$ mol L^{-1} (n =3) and amperometric sensibility of 4.5×10^{5} μA/mol L^{-1}. Analytical curve method was used for iron determination at a commercial fuel sample. Flame atomic absorption spectroscopy was employed as comparative technique.

1. INTRODUCTION

The rising importance of fuel ethanol in economic Brazilian set as an alternative automotive fuel or raw material for alcoholchemical industry, requires the identification and control of its

contaminants, due to its potentiality for engine corrosion effects and passivation of industrial catalyzers [1].

Several organic [1,2] and inorganic [3-7] contaminants have been studied in fuel ethanol by different instrumental methods. These contaminants can be originated from micro-nutrients used on sugar cane production, during the fermentation process, such as transport and storage of final product.

Under the analytical point of view, the use of chemically modified electrodes (CME) coupled to electrochemical methods has presented a considerable increase in the last decade, specially for dosage of metallic species.

In this context, several works on literature have reported electrochemical detection of iron in aqueous medium using a broad spectrum of chemically modified electrodes with different organic and inorganic complexants such as: poly(p-vinilbenzoilacetone) [8], N-fenylcynamohidroxamic acid [9], $\alpha\alpha$-bipiridine, $[Os(bipy)_2(PS)_{7,5}(DMAP)_{2,5}Cl]Cl$, where bipy = 2,2'-bipiridile, PS = poliestirene and DMAP = poly[4-(N-Metil-N-p-vinilbenzilamino)] [10] ; 3-hydroxi-1-methilpiridine-4-one and 2-metyl-3-hydroxipiridine-2-one [11]; hidroxâmic acids [12]; Nafion and 2,2'-bipiridile [13], Nafion and 1,10-fenantroline [14]. Carbon paste electrodes have also been chemically modified with Chitin-EDTA [15], poly-vinilferrocene-4-vinil-4'-methil-2,2'-bipiridine [16], $NiFe(CN)_6$ [17], Tris[4,7-difenyl-1,10-fenantroline] [18] and with poly (4-vinilpiridine) containing cross-linked 4,7-difenil-1,10-fenantrolinedissulfonic acid [19] for iron determination.

However, there were not found citations on literature about iron determination in fuel ethanol by using CMEs. So, the aim of this work was to develop a 1,10 fenantroline/Nafion CME for iron determination in this fuel using the voltammetric technique of square wave.

2. EXPERIMENTAL PART

2.1. Reagents

Stock solution of aqueous acetate buffer (Merck) of pH 4.5 containing hidroxylamine chloride (Sigma) at 12% (w/w) was prepared. Standard solution of iron (II) (amoniacal ferrous sulfate, from Merck) was prepared by dissolution of proper mass in a solution containing ethanol (Merck) /acetate buffer of pH 4.5 at 20%/80% (w/w). A commercial sample of fuel a gas station of Araraquara city was also previously diluted with aqueous acetate buffer above described until the rate of 20%/80% (w/w). Synthetic samples of fuel ethanol were prepared at ethanol/acetate buffer 20%/80% (w/w). The maximum value of 20% for ethanol percentage in aqueous solution was employed according to optimized conditions reported on literature [7], in order to decrease matrix effects and also to prevent partial solubilization of the CME, once nafion is employed. Previous tests indicated good stability of the CME at these experimental conditions. Deionised water (resistivity of 18.2 MΩcm) obtained from Milli-Q system was employed at all hydroalcoholic solutions.

For iron determination by Flame Atomic Absorption Spectrometry (FAAS), stock solution of iron (20 mg L^{-1}) was prepared using standard solution for atomic absorption (Normex). Standard solutions of iron at different concentration values were prepared by successive dilution of stock solution mentioned previously in aqueous solution of HNO_3 (Suprapur from Aldrich) 1% (w/w).

2.2. Equipment

2.2.1. Electrochemical

A potentiostat from Auto Lab, model PGSTAT 30 was employed. Electrochemical system was composed by a platinum plate as counter electrode, a saturated calomel electrode (SCE) as reference and a CME-carbon paste as working electrode.

2.2.2. Flame atomic absorption spectrometry

A spectrometer from Perkin Elmer, model A Analyst 100 was employed. Hollow cathode lamp for iron, from Perkin Elmer was used, presenting a wavelength of 248.1nm, being used a lamp current of 30 mA, wit spectral slit of 0.20 nm. Air/acetilene mixture at 2:8 proportion was used as oxidant flame. All spectrometric measurements were carried out in triplicate.

2.2.3. CME formation

The body of working electrode consists on a 15 cm cylindrical glass tube of 0.3 cm of internal diameter, with internal electrical connection by copper wire. The CME was prepared by mixing 0.86g of carbon powder (Merck) with 0.07g of 1.10-fenantroline (Aldrich). Good homogenization was obtained when methanol is added to mixture. Afterwards, the liquid solvent is removed until a dried solid is obtained. Finally, 80 μL of Nafion (0.07 g) is added to solid solution cited above and a new homogenization is obtained.

2.3. Experimental

2.3.1. Voltammetric measurements

All voltammetric measurements were carried out by following this sequence: accumulation step (mechanical stirring, 100 rpm) – transfer of electrode to electrochemical cell – voltammetric determination – electrode renewing. In the accumulation step, the studied solutions were put to a 15 mL volume becker with magnetic stirring. Afterwards, the CME is transferred to the electrochemical cell containing 25mL of acetate buffer (pH 4.5), where voltammetric measurements were carried out. Electrode renewing was obtained by mechanical removal of carbon paste from surface and subsequent mechanical deposition of a new layer of the substrate and polishing at dried paper.

2.3.2. Electroanalytical determination

After optimization step of accumulation time and instrumental parameters, an analytical curve was obtained for iron species. Optimized accumulation time of 5 min was applied. Each 10 mL of

studied sample contained 2 mL of fuel ethanol and 8 mL of supporting-electrolite (acetate buffer solution of pH 4.5 containing hidroxilamine at 12% v/v).

2.4. Flame atomic absorption spectrometry

The spectrometric determination of iron in the fuel sample was carried out according to official method described [20], using an accumulation step of 10 times, where 50mL of sample was evaporated until dryness, being pyrolised at 550 ^{o}C for 2 hours. Afterwards, the residue obtained was diluted with 5.0mL of HNO_3 1% (v/v). In sequence, an analytical curve was obtained by using aqueous standard solutions from 5.0×10^{-2} until 6.0×10^{-3} g L^{-1} of iron in HNO_3 1% (v/v).

## 3. RESULTS AND DISCUSSION

3.1. Optimization of experimental conditions

Carbon paste-modified electrodes are commonly prepared using mineral oil (Nujol, for example) in order to obtain a mechanic resistance for the paste. In this work, it was employed nafion, a perfluorosulfonated derivative of Teflon [21] as mechanical resistance agent. This polymer, very inert and with high chemical resistance, presents cation exchange propriety. The sulfonate group, negatively charged, permits the permeability of positively charged species by electrostatic interaction but it forms a selective polymeric net to anionic species.

When the CME was applied directly at pure ethanol solutions, a solubilization of nafion and degradation of CME was observed. This problem can be resolved when hydroalcoholic medium is used. In this case, a maximum value of ethanol percentage in solution at 20% (w/w) can be employed without solubilization of polymeric nafion.

3.2. Electrochemical behavior of Fe^{2+}-CME system

The first voltammetric studies were carried out using the mode of cyclic voltammetry, in order to check the electrochemical behavior of the Fe^{+2}-CME system. A scan rate of 100mV s^{-1} was employed. The cyclic voltammograms obtained for the CME at solution of supporting-electrolite without previous exposure at Fe^{2+} ions did not present peak current at the entire potential work range, from 0.0 until 1.2V (vs. SCE). When the CME is previously exposed at solutions containing Fe^{+2} ions, a well defined pair of reversible peak current at 0.84V and 0.9V is observed (Figure 1-A). This reversible system represents the oxi-reduction of Fe^{2+} species at solution as it follows:

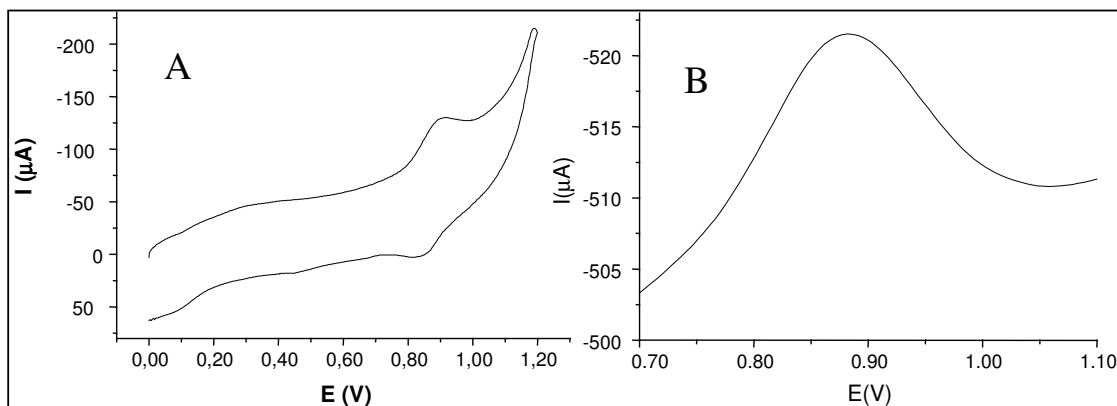$$Fe^{2+} \leftrightarrow Fe^{3+} + e^{-} \qquad\qquad (1)$$
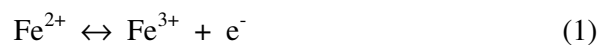
Figure 1. A) Cyclic voltammogram of hydroalcoholic solution in 20% (w/w) in acetate buffer (pH 4.5), previously immersed at iron (II) solution of $1.0x10^{-3}$molL^{-1} during 2 minutes. $v = 100$mVs^{-1}. B)Square wave voltammogram of hydroalcoholic solution in 20% (w/w) in acetate buffer (pH 4.5), previously immersed at iron (II) solution of $1.0x10^{-5}$molL^{-1} during 5 minutes. $E_{sw} = 100$mV; $f = 25.0$Hz.

3.3. Optimization of experimental parameters for square wave mode

The Figure 1-B illustrates a square wave voltammogram for CME electrode previously immersed at $1.0x10^{-5}$ mol L^{-1} Fe^{2+} solution using an E_{sw} value of 100mV and a frequency of 25.0Hz.

A decisive step on a electroanalytical methodology development employing carbon paste electrode consists on the optimization of voltammetric parameters. In this context, the accumulation time was optimized with the objective of increasing the analytical signal.
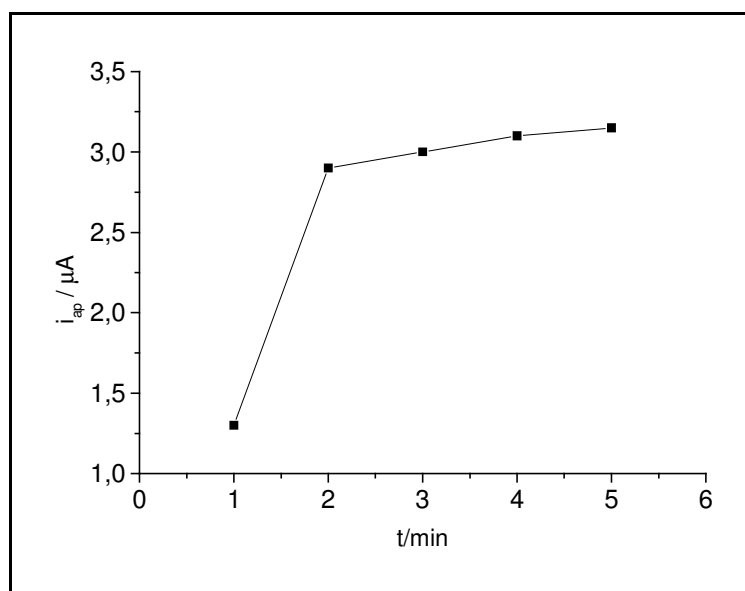

Figure 2. Influence of accumulation time (t_a) at anodic peak current for obtained voltammograms of fuel ethanol 20% (v/v) in acetate buffer (pH 4.5). $E_{sw} = 100$mV; $f = 8.0$ Hz.

As illustrated at Figure 2, a considerable increase of current signal is obtained until an accumulation time of 4 minutes, being obtained a landing of current after this value. So, an accumulation time of 5 minutes was established for subsequent determinations.

An increase of frequency has produced a proportional increase of current signal until the value of 25 Hz. At higher f values a decrease of amperometric signal is observed. So, for further measurements, a frequency value 0f 25Hz was chosen. The current signal for the CME showed a good linear dependence in relation of amplitude from 2 until 100 mV.

3.4. Analytical curve

The dependence of anodic current peak with iron concentration follows the relation bellow:

$$I_{ap} = 0.05 + 4.5 \times 10^5 \, C_{Fe} \qquad\qquad (2)$$

A linear correlation coefficient of 0.9984 is observed at range work from 6.0×10^{-6} mol L^{-1} until 2.0×10^{-5} mol L^{-1}. The amperometric sensibility of 4.5×10^5 μA mol^{-1} L was obtained for the relation cited above and a detection limit of 2.4×10^{-6} mol L^{-1} .

This methodology was used to determine iron concentration in a sample of fuel ethanol from a

3.5. Determination of Iron by flame atomic absorption spectrometry

The analytical curve obtained in the work range from 9.0×10^{-7} until 1.1×10^{-4} of iron in HNO_3 1% (v/v) presented a spectrometric sensitivity of 2.1×10^4 mol^{-1}L, with a linear correlation coefficient of 0.9974. The obtained detection limit for this curve was obtained as 5.4×10^{-7} mol L^{-1}.

After evaporation of 50 mL of fuel sample and subsequent redissolution in 5.0 mL of HNO_3 1% (v/v), the determination of iron concentration was determined by standard addition method, being obtained a corrected value of $1.6 \pm 0.1 \times 10^{-5}$ mol L^{-1} for the original sample.

Table 1. Comparison between the proposed electrochemical methodology and the official spectrometric method. (SWV = square wave voltammetry; FAAS = flame atomic absorption spectrometry).

	SWV	**FAAS**
Work range (10^{-6} mol L^{-1})	6 - 20	0.9 - 107
DL / 10^{-6} mol L^{-1}	2.4	0.54
RSD/%	4.7	3.8
[Fe^{2+}] (10^{-5} mol L^{-1})	1.7 ± 0.1	1.6 ± 0.1

A better comparison between the results obtained by the proposed electrochemical methodology and the spectrometric technique can be visualized at Table 1.

4. CONCLUSIONS

The development of the proposed carbon paste-CME for iron detection employing square wave voltammetry has presented good results for determination of total iron in hydroalcoholic medium, allowing this methodology for iron determination in commercial fuel ethanol samples. When the official FAAS method was used for comparison, a good correlation was obtained for iron dosage at fuel sample. The obtained results allow the proposed electrochemical methodology for iron determination in this kind of matrix.

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