Determination of Iron in Ethanol Fuel by UV-Visible Spectrophotometry

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Key Words

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Abstract

The application of Ultraviolet–Visible (UV-Visible) spectrophotometry was evaluated as a rapid method for the determination of Iron (Fe) in hydrated ethanol fuel. Ethanol fuel samples were purchased from local filling stations and direct analyses were performed using a simple and fast colorimetric reaction with 1,10-phenanthroline. The Limit of Detection (LOD) value of 0.012 mg/kg and Limit of Quantification (LOQ) value of 0.037 mg/kg were compliant with Brazilian legislation. The method accuracy was verified by addition-recovery experiments and the recoveries ranged from 93.3 to 101%.

Introduction

Since the 1970's, due to the petroleum crisis, ethanol fuel has been used as an alternative fuel in automobiles.[1] Ethanol fuel provides an option to reduce air pollution and greenhouse gas emissions. This, along with advances in the technology of modern automobile engines, has boosted hydrated ethanol consumption around the world. However, the presence of metallic contaminants in ethanol fuel may accelerate the corrosion of engines, deteriorating the quality of fuels and reducing their performance.[2]

Brazil is the second largest producer of ethanol in the world using sugar cane as feedstock.[1,3] According to Brazilian legislation (Brazilian National Agency of Petroleum, Natural Gas and Biofuels – ANP) the maximum concentration of Fe allowed in hydrated ethanol fuel is 5 mg/kg.[4]

Analytical methods for the determination and quantification of inorganic species in alcohol fuel can be found in the literature, including Flame Atomic Absorption Spectrometry (FAAS), which is recommended by the Brazilian Association for Technical Standards (ABNT NBR 11331).[2,5,6]

In this application note, we evaluated the feasibility of applying UV-Visible spectrophotometry to quantify Fe in ethanol fuel. This approach presents a rapid analytical procedure, using a simple and fast colorimetric reaction of Fe^{2+} with 1,10-phenanthroline ($Fe^{2+} + 3$ (1,10 phenanthroline) $\rightarrow [Fe(phenanthroline)_3]^{2+}$).[7]

Experimental Instrumentation

UV-Visible measurements were performed on a Thermo Scientific™ Evolution™ 220 UV-Visible spectrophotometer equipped with a xenon flash lamp in a double-beam configuration with dual silicon photodiode detectors. Ethanol fuel samples were measured at a wavelength of 510 nm using a 1 cm pathlength glass cell. Absorbance values at 510 nm (A_{510}), calibration curve slope (a) and intercept (b) parameters were obtained using Thermo Scientific™ INSIGHT™ software.

Reagents and Standard Solutions

A stock solution containing 1000 mg/L of Fe (Tec-Lab, Hexis, São Paulo, SP, Brazil) was used to prepare standard reference solutions, build the analytical calibration curves, and carry out addition and recovery experiments. Hydrochloric acid (HCl) (Synth, Diadema, SP, Brazil) previously purified by a sub-boiling distillation system (Milestone, Sorisole, Italy) and hydroxylamine hydrochloride (Sigma-Aldrich, Steinheim, Germany) were used to reduce Fe^{3+} to Fe^{2+}. Ammonium acetate (Synth) and acetic acid (Qhemis High Purity, Hexis, São Paulo, SP, Brazil) were used to prepare a buffer solution and 1,10-phenanthroline (Vetec, Rio de Janeiro, RJ, Brazil) was used to obtain the reddish-orange Fe complex.

Samples and Procedure

Six ethanol fuel samples (hydrated ethanol) were purchased from different local filling stations (São Carlos, SP, Brazil). Four drops of concentrated HCl and 120 µL of 100 g/L hydroxylamine hydrochloride were added to 6 mL of ethanol and incubated for 5 min to complete the reaction of Fe^{3+} reduction to Fe^{2+}. $[Fe(phenanthroline)_3]^{2+}$ complex was obtained by combining 600 µL of ammonium acetate buffer solution (pH 4.15) and 120 µL of 1.0 g/L 1,10-phenanthroline. Next, the solutions were mixed and incubated for 10 min to allow the development of the reddish-orange color. Standard reference solutions used in the external calibration method were prepared by diluting adequate volumes of inorganic standard solutions of Fe in ethanol 95% (v/v). The same procedure was then carried out using 6 mL of each solution, including the blank.

Results and Discussion

LOD and LOQ were calculated as 3 and 10 times the standard deviation of 10 consecutive measurements of the blank divided by the slope (a) of the calibration curve. LOD and LOQ values were 0.012 and 0.037 mg/kg, respectively, and the sensitivity, defined as the slope of the calibration curve, was 0.1942. A linear external calibration was built from 0.1 to 1.0 mg/L and a high linear correlation coefficient ($R^2 > 0.998$) was observed (Figures 1 and 2). An aqueous calibration curve was also built and the same linear behavior was observed. Molar absorptivity of the complex was 9.6×10^3 L/cm·mol in ethanol medium, which is similar to that established in aqueous media (1.1×10^4 L/cm·mol), indicating a minor influence of ethanol on complex formation.[8] Therefore, the data clearly demonstrate the sensitivity of the method and the high detection power of the Evolution 220 UV-Visible spectrophotometer.
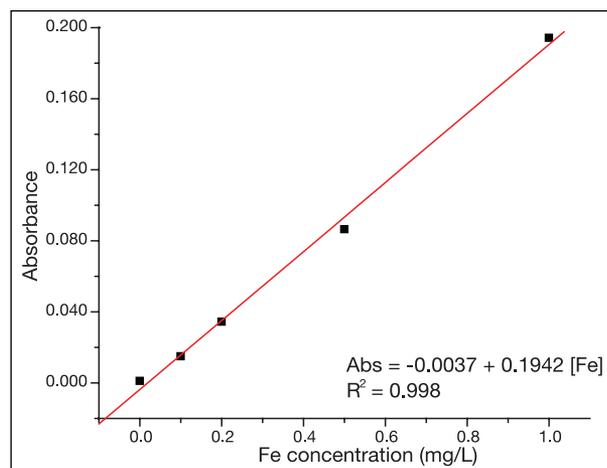

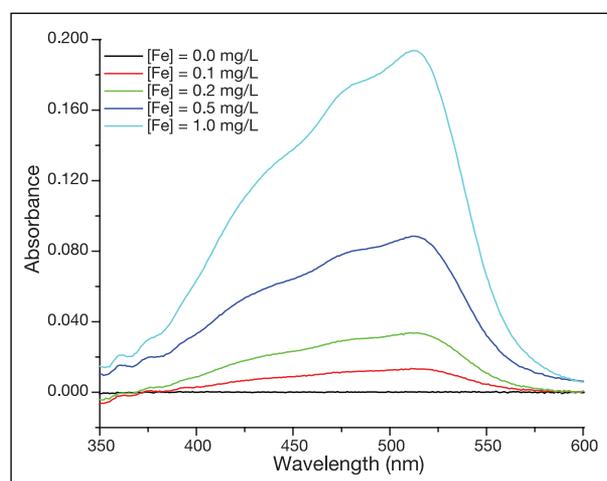Figure 1: External calibration curve from 0.1 to 1.0 mg/L

Figure 2: UV-Visible spectra obtained between 350 and 600 nm

The concentrations of Fe in all six different samples analyzed were below the limits of detection of the developed procedure (0.012 mg/kg). Thus, all analyzed samples comply with Brazilian legislation. The accuracy of the method was evaluated using spike experiments and the results are shown in Table 1. For all spiked samples, the recoveries varied from 93.3 to 101%, indicating proper accuracy of the developed procedure and the minimum effect of ethanol solvent on accuracy.

Sample	Added (mg/kg)	Found [a] (mg/kg)	Recovery (%)
A	0.610	0.569 ± 0.001	93.3
B	0.610	0.601 ± 0.002	98.5
C	0.610	0.614 ± 0.003	101.0
D	0.610	0.616 ± 0.002	101.0
E	0.610	0.595 ± 0.001	97.5
F	0.610	0.602 ± 0.003	98.7

[a] Results expressed as mean ± standard deviation (n = 3)

Table 1: Spike experiments for Fe determination in ethanol fuel samples

Conclusions

The method described in this application note is simple and effective for use in the direct analysis of iron in ethanol fuel samples with the Evolution 220 UV-Visible spectrophotometer. Six ethanol fuel samples were analyzed and Fe concentrations were below the LOQ in all of them. The spectrophotometer produced stable absorbance signal measurements and sensitivity in compliance with the legislation requirements. The Evolution 220 provides a low cost, low-maintenance solution for the determination of iron in ethanol fuels, allowing its implementation in routine analysis.

Acknowledgments

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