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Determination of ethanol in gasoline by high-performance liquid chromatography

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Lorena Morine Avila[a], Amanda Pereira Franco dos Santos[b,*],
Danielle Ignácio Mançano de Mattos[b], Cristiane Gimenes de Souza[b], Débora França de Andrade[c],
Luiz Antonio d'Avila[b]

[a] *Instituto de Química, Universidade Federal Fluminense, Niterói, Rio de Janeiro 24020-141, Rio de Janeiro, Brazil*
[b] *Engineering Program in Chemical and Biochemical Processes, Escola de Química, Universidade Federal do Rio de Janeiro, 21941-909 Rio de Janeiro, Brazil*
[c] *Instituto de Química, Universidade Federal do Rio de Janeiro, Cidade Universitária, 21941-909 Rio de Janeiro, Brazil*

ARTICLE INFO

ABSTRACT

This study employed non-aqueous reversed-phase high-performance liquid chromatography (HPLC) with refractive-index detection and methanol as a mobile phase to quantify the ethanol content in gasoline. The advantages of HPLC are its good separation versatility, high resolution, relatively short analysis time, and automation. Standard samples were prepared to obtain a standard curve and partial validation. Accuracy, precision, linearity, selectivity for methanol (adulterant), and measurement uncertainty were investigated. In the partial validation analysis, the accuracy of the proposed method was identified as its main advantage over the reference method.

1. Introduction

When fuel is adulterated, it is usually done by adding a lower cost product in order to obtain illicit financial gains from its retail. The illegal addition of excess ethanol to gasoline is arguably the easiest and most common form of adulteration, since ethanol is already a component of the gasoline/ethanol blend used in Brazil (27% ± 1% by volume) and is cheaper than gasoline. According to the national bulletin of the Fuel Quality Monitoring Program run by the Brazilian fuel regulatory agency (ANP), the ethanol content of gasoline is the biggest cause of noncompliance found in samples of gasoline [1,2].

The reference method for determining ethanol content, described in ANP resolution N°40 of October 25, 2013, is detailed in Brazilian standard NBR 13992/2015, issued by the Brazilian technical standards association (Associação Brasileira de Normas Técnicas, ABNT) [3,4]. It is a quick, simple, practical method that can be done in the field to check gasoline purity. However, because of these very features, its measurement uncertainty is 1 vol%, and it has the added limitation of quantifying other water-soluble alcohols like methanol, impairing its accuracy.

The adulteration of ethanol by methanol has been verified in Brazil by the ANP [5–8], and this has motivated the development of tests to determine methanol content in ethanol [9,10].

The American Society for Testing and Materials (ASTM) has its own standard, D5501, published in 2012 and reapproved in 2016, which describes a standard method using gas chromatography (GC) for the determination of the ethanol (20 mass% or over) and methanol (0.01 mass%–0.6 mass%) content of fuels [3,11]. This method is not so easy to implement, as it is done using long columns (100 m and 150 m), which, while they do exist, are harder to find on the market and very expensive. In the case of the 100 m column, the initial temperature of the column is supposed to be 15 °C, but this is unfeasible in much of Brazil as it is lower than ambient temperature, meaning that a cooling stage would first have to be employed. Further, the specific density of all the samples must be calculated to correct the results obtained [11]. In Brazil, ABNT set up a working group at its Ethanol Fuel Study Commission to create a reference method for quantifying ethanol and methanol in gasoline and ethanol fuel. The chosen method was GC, but after much research no reference method for quantifying ethanol in gasoline was produced, since the compounds in gasoline are eluted in the same time as ethanol [12].

There are different methods described in the literature for analyzing oxygenates in gasoline for quality control and regulatory purposes, like Fourier-transform near-infrared spectroscopy [13] with partial least square (PLS) calibration [14,15]; Raman spectroscopy [16]; synchronous fluorescence spectroscopy with principal component regression or

* Corresponding author at: Centro de Tecnologia, Bloco K02, LABCOM, Cidade Universitária, Rio de Janeiro 21941-909, Brazil.
E-mail addresses: morineavila@gmail.com (L.M. Avila), apfranco@eq.ufrj.br (A.P.F. dos Santos), danielleignacio@eq.ufrj.br (D.I.M. de Mattos),
cristianegimenes@yahoo.com.br (C.G. de Souza), debora.franca.andrade@gmail.com (D.F. de Andrade), davila@eq.ufrj.br (L.A. d'Avila).

PLS calibration models [17]; a combination of excitation-emission matrix fluorescence spectroscopy with multiway partial least square regression (N-PLS) and unfolded PLS [17]; batch injection analysis with detection by multiple-pulse amperometry [18]; Terahertz spectroscopy [19]; proton nuclear magnetic resonance spectroscopy (^{1}H NMR) [20]; cyclic voltammetry and multivariate calibration [21,22]; and customized mobile near-infrared spectrometry [23].

ASTM D5599/2010 describes a procedure for determining oxygenate content in gasoline by GC, but only for the 0.1–20% by mass range, which is not enough for the Brazilian fuel market [24].

ASTM D4815/2013 describes a GC method for determining methyl *tert*-butyl ether (MTBE), ethyl *tert*-butyl ether (ETBE), diisopropyl ether (DIPE), *tert*-amyl alcohol, and C_1–C_4 alcohols in gasoline. However, this method is employed to determine alcohol levels of 0.2 mass% to 12 mass%, ruling out its use for ethanol-based fuels and making it unfeasible for testing Brazilian gasolines [25].

In this context, this study proposes the use of high-performance liquid chromatography (HPLC) with refractive index detection to develop a quick method for quantifying the ethanol content in gasoline. It is hoped that this method may replace the existing reference test for laboratory analyses and the monitoring and inspection of gasoline sold in Brazil, whose drawbacks are its minimum uncertainty of ± 1% (by volume) and the fact that it is not accurate enough for determining ethanol levels in gasoline if it is adulterated with methanol.

2. Materials and methods

2.1. Preparation of standard samples of gasoline with ethanol

Eighteen standard samples of gasoline containing different quantities of anhydrous ethanol fuel, ranging from 19 to 40% (by volume), were prepared. The gasoline was supplied by Companhia Brasileira de Petróleo Ipiranga and the ANP inspection department, and support was provided by the Fuel and Petroleum Products Laboratory at the School of Chemistry, Federal University of Rio de Janeiro (LABCOM/EQ/UFRJ). All the glassware used in preparing the samples (1.00, 2.00, 5.00, and 10.00 mL volumetric pipettes; 10–100 µL variable volume automatic micropipette; and 50.00 mL volumetric flask) were calibrated in advance. Six of the 18 samples were used to plot an analytical curve and 12 were used to verify the analytical curve and to partially validate the proposed method, as shown in Table 1.

Aside from the 18 standard samples, a sample of gasoline containing 12.5 vol% ethanol and 12.5 vol% methanol was prepared to verify accuracy when ethanol was adulterated with methanol and to demonstrate its selectivity for ethanol.

Table 1
Standard samples of gasoline containing different proportions of anhydrous ethanol fuel.

Standard Samples for Analytical Curve		Standard Samples for Verification	
Sample Code	Nominal Ethanol Value (% volume)[*]	Sample Code	Nominal Ethanol Value (% volume)[*]
A1	20.00	V1	19.00
A2	22.00	V2	20.00
A3	24.00	V3	21.00
A4	26.00	V4	23.00
A5	28.00	V5	23.00
A6	30.00	V6	25.00
		V7	26.00
		V8	27.00
		V9	27.00
		V10	31.00
		V11	32.00
		V12	40.00

[*] The nominal values were corrected using the data from the glassware calibration certificates (see Table 2, in Results).

Calibrated glassware (10.00 mL volumetric flask, 1.00 mL volumetric pipette, and 10–100 µL variable volume automatic micropipette) was also used in the preparation of this sample.

2.2. Analysis of the samples by high-performance liquid chromatography (HPLC)

All the samples were analyzed using non-aqueous reversed-phase high-performance liquid chromatography (HPLC) with a Dionex UltiMate™ 3000 quaternary pump (Thermo Scientific, Massachusetts, USA), a Shodex RI-101 refractive index detector (ECOM, Czech Republic), and an UltiMate™ WPS-3000 autosampler (Thermo Scientific) with a 100 µL sample loop. An Acclaim™ column (Thermo Scientific) measuring 250 mm long and 4.6 mm internal diameter was used with an octadecylsilane phase with 5 µm particle size and 120 Å pore diameter. The mobile phase was 100% pre-filtered HPLC-grade methanol (Tedia Brazil, Rio de Janeiro, Brazil). Total analysis time was 15 min at 40 °C (temperature of column oven), with a constant flow rate of 1 mL/min and 10 µL injection volume. The samples were injected in quadruplicate to evaluate repeatability. The chromatograms were analyzed using Chromeleon 6.80 SR11 software (Thermo Scientific) with manual integration.

2.3. Partial validation of proposed method

In order to use objective evidence to ascertain whether the proposed method produces reliable results that are fit for purpose – i.e. whether it meets the requirements and standards for the specific proposed use – we assessed its linearity, selectivity for methanol (adulterant), accuracy, precision, and measurement uncertainty [26–30].

Linearity was checked by the coefficient of determination (R^2) of the straight line. Values over 0.99 indicated the linear working range, where the angular coefficient of the straight line could be considered constant [26].

The selectivity of the HPLC method for methanol was checked by injecting a sample of pure gasoline (matrix) and a standard sample containing 12.5 vol% ethanol, 12.5 vol% methanol, and 75 vol% gasoline, since no certified reference material exists for such a determination.

In order to assess the accuracy of the verification samples, we used Eq. (1) to ascertain relative error (E_{rel}) [26]:

$$E_{rel} = \left| \frac{x_{lab} - x_v}{x_v} \right| * 100 \tag{1}$$

where:

E_{rel} is relative error (%);
X_{lab} is the single value obtained experimentally or the mean of the laboratory results;
X_v is the value accepted as being true.

In this study, the relative error of the 12 verification samples (V1–V12) was calculated, assuming a 95% confidence interval for the statistical treatment of the results obtained. As such, the maximum admissible error was set at 5%.

The repeatability limit (r) calculated by Eq. (2) and the total amplitude of the measurements (difference between the highest and lowest value from a dataset) were used to evaluate the precision of the proposed method [27].

$$r = 2.8 * S_r \tag{2}$$

where:

r is the repeatability limit;
S_r is the standard deviation of repeatability, meaning the standard deviation of the results for each concentration.