Determination of saturates, aromatics and ethanol in Brazilian commercial gasoline with low olefin content using ^{1}H NMR spectroscopy

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Abstract – In this work, a Hydrogen Nuclear Magnetic Resonance (^{1}H NMR) method has been developed to determine aromatics and ethanol in Brazilian commercial gasoline with low olefin content. The proposed method involves subdividing an ^{1}H NMR spectrum into regions, each of which is assumed to be associated with a specific type of structural group (OH, CH, CH_2 and CH_3). The method is based on the assignment of overlapping regions of ^{1}H NMR spectra due to the signals of naphthene (N), iso and normal paraffins (P) and ethanol (E). Each ^{1}H NMR spectrum was divided into 8 regions and the integration was correlated to the percentage of the substances to be determined. The results of the analysis by ^{1}H NMR were compared with analysis of GC-FID obtained with the PONA system. The proposed technique of ^{1}H NMR was shown to be an appropriate method for this sample type.

Keywords: 1. Commercial Gasoline; 2. Ethanol; 3. ^{1}H NMR spectroscopy.

1. Introduction

Gasoline is a complex mixture of several hundreds hydrocarbon components (paraffins, naphthenes, olefins and aromatics). The relative proportions of these compounds depend on the petroleum and the refining process used. Gasoline is one of the most widely used fossil fuels in the world and there is great interest on the part of society concering to its quality. In order to guarantee gasoline quality and conformity to the specifications, specific components such as paraffins, iso-paraffins, olefins, naphthenes and aromatics (PIONA), must be measured accurately. Such analysis is carried out by separating the hydrocarbons compounds into single components or components groups, followed by subsequent identification and quantification. This is performed by chromatographic methods, e.g. gas chromatography (GC) [1-7], supercritical fluid chromatography (SFC) [8, 9], liquid chromatography (LC) with fluorescent indicator adsorption (FIA) [10], infrared spectroscopy (IR) [11-14] and mass spectroscopy (MS) [15]. In recent years, nuclear magnetic ressonance (NMR) [16-24] has become a powerful tool for the analysis of gasoline. ^{1}H NMR measurements have a short analysis time of only a few minutes per sample.

One of the main characteristics of gasoline which is related to the performance of the internal combustion engine is its octane rating, or its octane number. To improve the octane number, two oxygenated-type chemicals can be added to the gasoline: alcohols or aliphatic ethers.

Since 1977, different volumes of ethanol have been added to the gasoline sold in Brazil. The proportion of ethanol in automotive gasoline has varied from 20 to 25% v/v over the last five years. The ethanol concentration is established by the National Petroleum Agency (ANP). From an environmental point of view, the addition of ethanol is of fundamental importance because it reduces the emission of pollutants into the atmosphere and it also has the advantage of being a renewable fuel.

There are numerous standard test methods from the American Society for Testing and Materials (ASTM) being used in the petroleum industry all over the world for analyzing gasoline products. Each country has its own specifications, that is, EN-228 in Europe, ASTM D4814 in the USA, JIS K 2202 in Japan and IS 2796 in India. In Brazil, this specification is established by the National Petroleum Agency (ANP) [25], designated as Brazilian Regulation number 309, of 27 December of 2001. The properties included in the Brazilian specifications are: color, aspect, anhydrous ethanol content (AEAC-ethanol), density, distillation curves, MON, AKI, vapor pressure, current gum, sulfur content, benzene, aromatic hydrocarbon and olefins.

The National Petroleum Agency (ANP) classifies au-

tomotive gasoline as: Type A - gasoline without oxygenated compounds present; and, Type C - commercial gasoline, which is a blend of gasoline A and ethanol. Only gasoline C is available at the gas stations. Due to the high ethanol content in gasolines, there is a need to develop specific methodologies to analyze the gasoline consumed in Brazil.

In this paper, the relationships established by Sarpal et al. [21] are used as the starting point and a fast and simple method is developed to determine aromatic hydrocarbon content, as well as ethanol content, without the need of any chemical pretreatment of the sample or the addition of a reference compound.

2. Experimental
2.1. Gasoline Samples

Thirty-three commercial gasoline samples (regular and podium, which differ only by the octane number), having low olefin content, were provided by CEMPEQC - Center of Monitoring and Research of Fuel Quality, a laboratory responsible for monitoring the quality of automotive fuels, in particular, gasoline, ethanol and diesel oil. Gasoline samples, collected randomly from different gas stations in São Paulo state, Brazil, were stored in polyethylene terephthalate flasks and transported in refrigerated boxes, following ANP regulatory procedures. When arriving at the lab, 90 mL samples were immediately collected in 100 mL amber PET flasks with sealing caps and stored in a freezer to avoid volatilization and keep their integrity. Moreover, gasoline A, obtained from REPLAN refinery in Paulínia-SP, and ethanol p.a. from Merck were used as reference samples for the calibration curve.

All gasoline samples were previously analyzed by several properties as stated in ANP Regulation nº 309, namely, atmospheric distillation temperatures at 10%, 50% and 90% recovery volumes, final boiling point and distillation residue (ASTM D86), density (ASTM D4052), motor octane number – MON (ASTM D2699), research octane number – RON (ASTM D2700), antiknock index (MON + RON / 2), benzene content (% v/v) (ASTM D6277), ethanol content (NBR 13992) and hydrocarbons (saturates, olefins and aromatics – by Fluorescent Indicator Adsorption correlated to ASTM D1319).

Anhydrous ethanol content in gasoline samples was determined by the aqueous extraction method, by using 50 mL of sample and 50 mL of aqueous 10% NaCl solution (w/v). Distillation temperature profiles were performed in an automatic distiller unit, NDI440 v.1.70C (Normalab, Lintot, France) and density measurements was obtained by an automatic digital densimeter, Anton Paar v.4.600.b (Anton Paar, Graz, Austria). The other parameters were obtained by using a portable Grabner IROX2000 v.2.02 infrared analyzer

(Grabner Instruments, Vienna, Austria) via FTIR spectra in the range 3500–650 cm^{-1} at a nominal resolution of 4 cm^{-1}. To avoid cell manipulation and to increase the sample throughput, 7.5 mL of sample were introduced in the FTIR spectrophotometer by using the internal equipment pump. The samples were drawn in directly from the sample container through flexible tubing. To avoid out gassing, the samples were drawn carefully into an internal chamber and then pressurized through the absorption cell equipped with two Zn/Se windows, with a mean path length of 23 μm. After the measurement the samples were transferred into the connected disposal container.

2.2. NMR Spectrometry

All ^{1}H NMR spectroscopic spectra were acquired at room temperature on a Varian (Palo Alto, CA, USA) INOVA spectrometer, using a 5 mm single cell ^{1}H/^{13}C inverse detection flow probe. For each analysis, 30 μL of gasoline sample was dissolved in 600 μL of deuterated chloroform (CDCl$_3$). The ^{1}H NMR spectrum was obtained at 500 MHz for ^{1}H observation, using CDCl$_3$ as the solvent and tetramethylsilane (TMS) as the internal standard. The spectra were obtained using 45° rf pulse (4.1 μs), a spectral width of 4725 Hz, 64 transients with 64 000 data points, an acquisition time of 2 min and relaxation delays of 1 s. Thirty-two scans were accumulated for each spectra and processed with 32 000 data points using an exponential weighing factor corresponding to a line broadening of 0.1 Hz. ^{1}H NMR chemical shifts are reported in parts per million (ppm) relative to residual proton signals of CDCl$_3$ at 7.24 ppm. The FIDs were zero filled and Fourier transformed. The phase and baseline were manually corrected in all spectra.

2.3. GC-FID Analysis

General chromatographic PONA analysis was performed using a Shimadzu GC-17A with a flame ionization detector (FID), equipped with an automatic injector model AOC-20i and interfaced to a workstation using software from GCSolutions. The mass percent of each group (paraffins, olefins, naphthenes and aromatics) was calculated using the PONA Solution software from the chromatographic profile.

GC-FID system was equipped with a CBP1-PONA fused-silica capillary column (50 m x 0.15 mm x 0.42 μm; Shimadzu, Kyoto, Japan) with dimethylpolysiloxane as the stationary phase and helium as the carrier gas at a constant flow rate of 20 mL min^{-1}. Sample aliquots of 0.5 μL were injected in split mode (1:250) without solvent delay. Injector and detector temperature were maintained at 250 °C and the oven temperature was programmed as follows: the column was kept at 35 °C for 20 min and then heated to 155 °C at 3 °C min^{-1}.

Finally, the temperature was raised up to 215 °C at 6 °C min^{-1} and kept constant for 15 min.

2.4. GC-MS Analysis

A Shimadzu GC-17A-GCMS-QP5050A gas chromatograph coupled to the mass spectrometer was used to identify the gasoline components with the objective of calibrating the PONA solution in the GC-FID, to analyze the number of substituted α carbons in the aromatic ring and for the determination of the main iso-paraffins content in the gasoline samples. The mass spectra obtained were researched and correlated with NIST Library 98 Edition to identify and confirm the substances. GC-MS tests conditions were the same used for GC-FID.

3. Results and Discussion

The 500 MHz ^{1}H NMR spectra of a commercial gasoline sample with low olefin content is given in Figure 1. The proposed NMR method is based on the signal positions of the structural groups (OH, CH, CH_2 and CH_3) for each function (paraffins, naphthenes, aromatics and ethanol), elimination of signal overlap of the structural groups for each function and calculation of the total molar mass of the structural groups of the sample (T_M), aromatics (A_M) and ethanol (E_M), obtained from the intensity of the spectrum integrals. The software ACDLabs/Spec Manager v4.09 was used [26] to obtain the values of the integrals. The weight percentages of aromatic (A) and ethanol (E) are calculated using the relationships given by Sarpal et al. [21], adapting them to our system.

The ^{1}H NMR spectrum were divided into 08 spectral regions, namely A to J (Figure 1). The chemical shift region was assigned to one or more structural groups (OH, CH, CH_2 and CH_3). The attributions were based on research found in the Aldrich library of ^{1}H FT-NMR spectra Volume I and II [27] and in published papers [16-24].
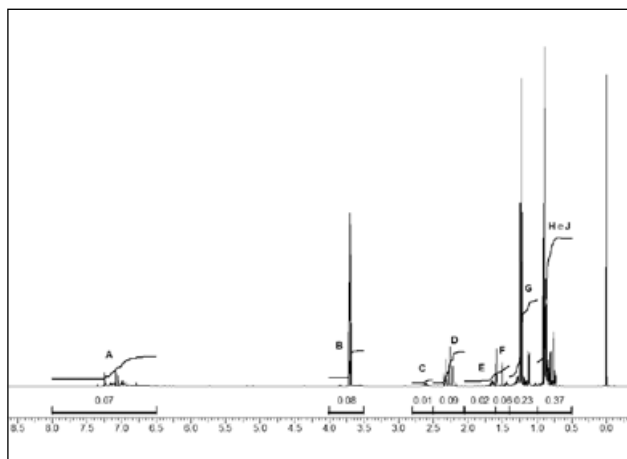
The region of 6.50 - 8.00 δ (A) is characteristic of aromatics. The signals due to α-substituent groups of the aromatics appear in the 2.50 - 2.80 δ (C) and 2.05 - 2.50 δ (D) regions and are due to CH_2 and CH_3 protons, respectively.

The signals due to ethanol generally appear in the 1.00-1.40 δ (G) region for CH_3 protons, the 3.50 - 4.00 δ (B) region for the CH_2 protons and the 1.40 - 1.60 δ (F) region for the OH proton.

The region between 0.50 - 2.05 δ (E, F, G, H and J) is highly overlapped and contains signals mainly due to naphthenes, ethanol and iso-paraffins. A broad assignment in terms of CH_n (n = 1, 2 and 3) is possible. For example, the region 0.50 - 1.00 δ (J) is due to CH_3 groups of saturated (naphthenes + paraffins) and the 1.00 - 1.40 δ (G) region is due to CH_2 groups of iso-paraffins and ethanol. The 1.40 - 2.05 δ (E, F and H) region is overlapped and consists of CH_2, and CH of naphthenes, iso-paraffins and OH protons of ethanol. The sharp signals appearing at 1.43 δ and 1.46 δ can be assigned to CH_2 protons of cyclohexane and cyclopentane respectively.

Although, the region of 1.40 - 2.05 δ seems to be characteristic for naphthenes, it cannot be used directly to estimate total naphthenic and ethanol content because of the following two factors:

a) considerable part of the signal intensity of naphthenes falls in the 0.50 - 1.40 δ region and severely overlaps with the signal intensity due to normal and iso-paraffins and CH_3 protons of the ethanol. For the quantitative estimation of ethanol content, the contribution of all the ethanol must be extracted from the other overlapped regions as well. This will lead to the resolution of signal intensity due to ethanol in the ^{1}H NMR spectrum of the gasoline sample.

b) 1.40 - 2.05 δ region also contain signals due to methine (CH) protons from iso-paraffins and hydroxy proton (OH) from the ethanol.

Therefore, to determine total saturated (naphthene + paraffin) content, it is necessary to determine the quantitative average extent of overlapping of the structural groups (OH, CH, CH_2 and CH_3) of standard ethanol and of the iso-paraffin mixture.

The contribution of the iso-paraffin CH_2 group was determined by subtracting the contribution of the ethanol CH_3 group with proton signals present in the same region of chemical shift. The extent of the CH_3 signals overlapping the ethanol with the CH_2 signals of the iso-paraffins was obtained by integrating the region between 1.00-1.40 δ and subtracting the value corresponding to the signals of the protons of the ethanol CH_3 region which has the same value as 3/2 of the integral (I) in the region between 3.50 - 4.00 δ. This corre-

sponds to the signal of the ethanol CH_2 protons where there is no overlapping. In this way, we obtained the following relationship:

$$I_{1.0-1.4} - \frac{3}{2} I_{3.5-4.0} \quad (1)$$

$$G = I_{1.0-1.4} - \frac{3}{2} B \quad (2)$$

the value "3/2" comes from the relationship of the ethanol protons (CH_3CH_2OH) which is given by:

$$I_{CH3} = \frac{3}{2}(I_{CH2}) = 3(I_{OH}) \quad (3)$$

The extent of the naphthene and iso-paraffin signal overlappings was determined using the relationship given by Sarpal et al. [21]. This relationship is obtained from the spectrum of a mixture of iso-parafin standards.

As shown previously, the contribution of iso-paraffins in the 1.40 - 2.05 δ region must be subtracted before this region is used for estimation of total saturated content in a mixture. The simple spectrum of the isoparafin mixture spreads in a narrow region of 1.60 - 0.50 δ and can be divided into three distinct bands: 0.50 to 1.00δ, 1.00 to 1.40δ and 1.40 to 1.60 δ. These regions are due to CH_3, CH_2 and CH protons, respectively, and are regions of interest due to CH protons.

Sarpal et al. [21] have observed that around 10% of the intensity of the 0.50 to 1.00 δ region signal is approximately equal to the intensity of the 1.40 to 1.60 δ region signal, i.e:

$$I_{1.4-1.6} = \frac{I_{0.5-1.0}}{10} \quad (4)$$

The above relationships were used to subtract the overlapping of CH_2 proton signals caused by naphthenes, from the CH proton signals caused by iso-paraffins in the 1.40 - 2.05 δ region of the ^{1}H NMR spectrum. The 0.50 - 1.00 δ region was named 'J', therefore, the intensity J/10 (named 'H') is subtracted from the intensity of region 1.40 - 1.60 δ to obtain the true contribution of saturates. The intensity $I_{1.4-1.6}$ minus 'H' and the value corresponding to the signal from the ethanol's OH proton, which has a value equal to 1/2 of the integral in the 3.50 - 4.00 δ region (Equation 3), was named 'F' and is given by cyclopentane and cyclohexane CH_2 protons. This way, we obtain the following relationships starting from Equation 4:

$$J = I_{0.5-1.0} \text{ and } H = \frac{J}{10} \quad (5)$$

$$F = I_{1.4-1.6} - H - \frac{1}{2} B \quad (6)$$

the 1/2 comes from the relationship of the ethanol protons, Equation 3.

After all the ^{1}H NMR spectrum assignments (Table I and Figure 1) are completed and the extent of average overlap has been taken into account, the hydrocarbon composition can be estimated in terms of total aromatic and ethanol content.

Table I. Attributions from different regions of the ^{1}H NMR spectrum and the integral region used to analyze gasolines (δ in relation to internal standard TMS).

Chemical shift (δ)	Attributions	Integral regions
6.50 – 8.00	CH of the aromatic rings	A
3.50 – 4.00	CH_2 of the ethanol	B
2.50 – 2.80	CH_2 of the α-substituints in the aromatic	C
2.05 – 2.50	CH_3 of the α-substituints in the aromatic	D
1.60 – 2.05	CH_2 of the naphthenes	E
1.40 – 1.60 - H - ½B	CH_2 of the cyclohexane and cyclopentane + CH of the iso-paraffins + OH of the ethanol	F
1.00 – 1.40 - 3/2B	CH_2 of the iso-paraffins + CH_3 of the ethanol	G
0.50 – 1.00 = J/10	CH of the iso-paraffins	H
0.50 – 1.00	CH_3 of the naphthenes and of the paraffins	J

The first step involves the estimation of the total relative number of carbons (T_C) and the sample's total molecular-group weight (T_W). T_C was calculated by dividing each individual region in the ^{1}H NMR spectrum by the number of protons causing the signal. T_W was calculated by multiplying the values of T_C with the respective molar mass of the groups (i.e. 12 for C, 13 for CH, 14 for CH_2, and 15 for CH_3). Therefore, T_C and T_W are computed as follows:

$$T_C + \frac{A}{1} + \frac{B}{2} + \frac{C}{2} + \frac{D}{3} + \frac{E}{2} + \frac{F}{2} + \frac{G}{2} + \frac{H}{1} + \frac{J}{3} + Arq \quad (7)$$

where A, B, C, etc. are the integral intensities of the various specified regions given in Table I, Arq are the substituted aromatic quartenary carbons and do not show up in the ^{1}H NMR spectrum as there are no protons attached to such carbons. However, their contribution is given by the following simple relationships:

$$Arq = \frac{C}{2} + \frac{D}{3} \quad (8)$$

$$T_W = 13\frac{A}{1} + 45\frac{B}{2} + 14\frac{C}{2} + 15\frac{D}{3} +$$
$$14\frac{E}{2} + 14\frac{F}{2} + 14\frac{G}{2} + 13\frac{H}{1} + 15\frac{J}{3} + 12.Arq \quad (9)$$

The value 45(B/2) comes from the relationship of the protons of the ethanol, Equation 3.

$$45\left(\frac{B}{2}\right) = 15\left(I_{CH3}\right) + 14\left(I_{CH2}\right) + 17\left(I_{OH}\right) = 22.5(B) \quad (10)$$

Substituting the value of Arq the equation is simplified as shown here:

$$T_W = 13\left(A + C + H\right) + 7\left(E + F + G\right) + 22.5(B) + 9(D) + 5(J) + 7(B) \quad (11)$$

3.1. Determination of Aromatics

To estimate the total aromatic content (A) in the sample, the group molar mass of the aromatic (A_M) was calculated. This is expressed by Equation 12,

$$A_W = 13\left(\frac{A}{1}\right) + n(14)\left(\frac{C}{2}\right) + 15\left(\frac{D}{3}\right) + 12\left(Arq\right) \quad (12)$$

where, 'n' is the average chain length of the groups linked to the aromatic ring. This value was determined as 2 (two), using gas chromatography coupled with mass spectrometry (GC-MS).

The aromatic content (A) in %w/w was estimated by Equation 13.

$$A = \left(\frac{A_W}{T_W}\right).100\% \quad (13)$$

3.2. Determination of Ethanol

To estimate the total ethanol content (E) in the sample, the group molar mass of the ethanol (A_M) was calculated. This is expressed by Equation 14.

$$E_W = 15\left(I_{CH3}\right) + 14\left(I_{CH2}\right) + 17\left(I_{OH}\right) \quad (14)$$

Substituting the relationship of Equation 3 in Equation 14, we obtain:

$$E_W = 22.5(B) \quad (15)$$

The ethanol content (E) in %w/w was estimated by Equation 16.

$$E = \left(\frac{E_W}{T_W}\right)100\% \quad (16)$$

3.3. Determination of Saturates

To estimate the total saturates content (S) in the sample, just substract the sum between aromatics (A) and ethanol (E) contents, which was estimated by Equation 17.

$$S = 100 - (A + E) \quad (17)$$

3.4. Analytical Curves for Ethanol Obtained using GC-FID

The calibration curve was obtained by carrying out triplicate analysis of mixtures of the gasoline A and ethanol pa reference samples. These samples were prepared from by blending both products in different percentages to have the following ethanol content in volume percent: 20%, 22%, 24%, 26%, 28% and 30%. The linear regression equation was: ethanol = 0.5893 + 8.8512 x 10^{-5} area of chromatographic peak (R^2 = 0.9989; n=6).

3.5. Comparison of the Results with the GC-FID Method

The gasoline samples compositions, determined by NMR, were compared with the GC-FID method. The ethanol content was obtained via the calibration curve. The results are presented in Table II and compared using the t-test paired showing a 95% inter-

	Olefin (%w/w)	Aromatics (%w/w)			Ethanol (%v/v)		
Sample	**GC**	**FTIR**	**GC**	**NMR**	**FTIR**	**GC**	**NMR**
1*	0.00	26.3	28.19	28.15	23.6	24.38	24.95
2*	0.00	27.3	28.48	28.59	24.7	23.95	24.99
3*	0.00	25.7	28.85	27.74	23.2	24.59	24.97
4*	0.00	26.9	28.20	28.09	23.3	24.22	24.96
5*	0.00	27.1	28.22	29.52	24.3	24.31	24.94
6*	0.00	28.7	27.90	28.95	24.9	24.34	25.26
7*	0.11	24.1	23.90	23.66	24.8	24.14	24.50
8*	0.11	23.0	23.70	23.40	24.5	24.29	24.59
9*	0.12	23.2	23.70	23.73	24.9	23.62	24.48
10	0.38	9.1	10.23	7.99	26.9	25.91	24.87
11	0.43	10.7	9.27	10.76	25.2	25.34	25.11
12	0.45	19.6	23.22	22.15	25.9	25.59	25.03
13	0.78	8.3	7.60	7.12	21.0	21.23	20.56
14	0.90	10.6	8.51	8.47	25.3	25.03	24.93
15	1.03	10.8	5.95	5.16	21.9	19.91	20.69
16	1.24	9.6	7.09	9.71	27.5	26.14	26.37
17	1.27	9.7	7.52	8.41	25.9	25.35	25.73
18	1.46	16.1	13.32	11.34	27.2	25.81	24.43
19	1.48	15.7	10.43	9.59	26.3	25.07	24.64
20	1.59	7.9	6.42	8.36	24.6	22.47	23.23
21	1.66	7.1	6.24	7.63	25.0	25.25	25.39
22	1.67	9.7	10.17	10.12	21.4	21.31	20.94
23	1.82	19.9	21.21	20.47	22.0	24.00	24.06
24	1.91	6.6	4.78	6.59	21.7	23.27	22.96
25	1.96	12.0	7.34	9.91	25.1	25.90	25.77
26	1.99	10.0	6.75	9.19	25.3	25.16	25.67
27	2.13	14.6	7.62	10.59	25.4	23.59	24.27
28	2.27	9.9	7.58	10.11	25.9	25.35	26.28
29	2.28	10.6	7.65	10.49	25.3	24.56	24.97
30	3.13	12.3	6.30	5.52	23.5	24.65	25.00
31	3.56	15.7	17.78	15.94	21.9	20.95	20.77
32	4.14	14.9	12.27	13.08	25.4	24.21	24.33
33	5.47	11.5	9.41	12.02	25.1	24.05	24.97

TABLE II. Results of the analyses using the FTIR, GC and NMR methods.

* Podium Gasoline.

val confidence (Table III and IV). It can be seen that there is no significant difference between the GC and NMR methods when analyzing aromatics and ethanol. However, a significant difference exists between the GC and FTIR methods when analyzing aromatics, mainly when the olefin content increases. This occurs because the area designated to aromatic hydrogen begins to have interference from olefinic hydrogens.

TABLE III. COMPARISON BETWEEN THE GC-NMR AND GC-FTIR METHODS FOR AROMATICS, USING *T*-TEST PAIRED.

	t $_{calculated}$	t $_{table}$	STANDARD DEVIATION (SD)
GC-NMR	-1.917	2.042	± 1.521
GC-FTIR	-2.625	2.042	± 2.613

TABLE IV. COMPARISON BETWEEN THE GC-NMR AND GC-FTIR METHODS FOR ETHANOL, USING *T*-TEST PAIRED.

	t $_{calculated}$	t $_{table}$	STANDARD DEVIATION (SD)
GC-NMR	-1.947	2.042	± 0.596
GC-FTIR	-1.848	2.042	± 1.033

4. CONCLUSION

A fast and simple ^{1}H NMR spectroscopy method was developed to measure the concentration of aromatics and ethanol in commercial Brazilian gasolines, having a low olefin content (<5.47% w/w). The main advantages are that the total analysis time per sample is short and all concentrations are determined in one ^{1}H NMR experiment. However, several disadvantages in this technique, like equipment price and cost analysis, must be considered. The method demands no chemical pretreatment of the sample and requires only a small volume of sample (50 μL). This method can be applied to podium and regular commercial gasoline. Further work is in progress to extend the methodology for complete PONA (Paraffins, Olefins, Naphthenes and Aromatic) analysis and such results will be used to calculate octane number (MON and RON) using chemometrics methods.

5. ACKNOWLEDGEMENTS

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