

Simultaneous determination of methanol and ethanol in gasoline using NIR spectroscopy: Effect of gasoline composition

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Abstract

Near infrared (NIR) spectroscopy was employed for simultaneous determination of methanol and ethanol contents in gasoline. Spectra were collected in the range from 714 to 2500 nm and were used to construct quantitative models based on partial least squares (PLS) regression. Samples were prepared in the laboratory and the PLS regression models were developed using the spectral range from 1105 to 1682 nm, showing a root mean square error of prediction (RMSEP) of 0.28% (v/v) for ethanol for both PLS-1 and PLS-2 models and of 0.31 and 0.32% (v/v) for methanol for the PLS-1 and PLS-2 models, respectively. A RMSEP of 0.83% (v/v) was obtained for commercial samples. The effect of the gasoline composition was investigated, it being verified that some solvents, such as toluene and *o*-xylene, interfere in ethanol content prediction, while isooctane, *o*-xylene, *m*-xylene and *p*-xylene interfere in the methanol content prediction. Other spectral ranges were investigated and the range 1449–1611 nm showed the best results.

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1. Introduction

Gasoline is a sub-product from the fractional distillation of petroleum, being a complex mixture of hydrocarbons containing from 4 to 12 carbon atoms [1,2]. The gasoline produced at the beginning of the 20th century was composed of hydrocarbons having 10–16 carbon atoms, which was a low octane number fuel. During the last century, new production processes were developed to obtain fuel with higher octane numbers that could be used in vehicles with high compression engines. Aiming to increase the octane number, additives are often added to the gasoline. Some additives, such as tetraethyl lead, contribute to increase atmospheric pollution, while methyl-*tert*-butyl-ether (MTBE) has caused contamination of underground waters [3,4].

In recent last decades, gasoline having the addition of methanol or ethanol has been produced, resulting in a less polluting fuel, while keeping the octane number at the appropriate level for the current necessities of engines of light vehicles. Moreover, another advantage of these additives is that they could be

obtained from renewable sources, such as sugarcane (ethanol) and cellulose (methanol) [5].

Methanol and ethanol, both anhydrous, are added to the gasoline in many countries around the world, generally in the ratio of 10% (v/v). In Brazil, the percentage of ethanol is officially established [6], usually varying between 20 and 25% (v/v), although lower concentrations are admitted, depending on the regional difficulties of obtaining this product from the national market.

During the ethanol crisis of 1989 in Brazil, alternative additives were investigated to be incorporated into the gasoline, such as, the oxygenated compounds from petroleum (MTBE, ethyl-*tert*-butyl-ether and TAME, *tert*-amyl-methyl-ether). At that time, in addition to a reduction of the amount of anhydrous ethanol added to the gasoline, a new fuel called MEG (33%, v/v of methanol + 60%, v/v of ethanol + 7%, v/v of gasoline) was proposed. Although its production had been authorized, its commercialization was considered dangerous due to methanol manipulation, finally being abandoned [7]. The addition of methanol to gasoline is currently forbidden in Brazil, however in some countries, such as the USA, it is still used [8].

Although methanol has not been the most used compound for gasoline adulteration, its addition is not detected if only the extraction test based on the volume increase of the aque-

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ous phase (ABNT-NBR 13992) is carried out [9]. Although simple and efficient for the determination of the ethanol content in the gasoline, the extraction test cannot distinguish between methanol and ethanol, making this type of adulteration practically undetected at the moment of the inspection, if part or all of ethanol content in gasoline is substituted by methanol.

Due to the high fuel consumption, it has become more and more necessary to develop fast analytical methods that allow determination of different quality parameters by means of a single analysis. Among several instrumental analytical techniques, near infrared (NIR) spectroscopy has been revealed as promising for the quantitative determination of a great variety of chemical species. This fact is associated with its main characteristics, such as speed of attaining of the results, minimum sample preparation, low residue generation, easy adaptation to a production line and direct application in the field. Moreover, a single spectrum can give simultaneous information about the sample properties and its constituents [10].

Various studies have demonstrated the possibility of applying NIR spectroscopy for quality control of fuels [11–26]. Physical parameters, such as motor octane number (MON) and research octane number (RON), density, distillation temperature and vapor pressure Reid (VPR) can be determined by NIR spectroscopy, in many cases with precision and accuracy comparable to the standard method [17]. Other studies show the possibility of simultaneous determination of aromatic, unsaturated and saturated hydrocarbons content [24], MTBE [25] and sulfur [17,26]. Methanol [14] and ethanol [25,27] have been determined separately in gasoline using NIR spectroscopy. However, there are no studies demonstrating the possibility of simultaneous determination of methanol and ethanol in gasoline or how the gasoline composition can affect the determination of these alcohols.

Thus, this work is aimed at applying NIR spectroscopy, together with multivariate calibration (partial least squares, PLS), for the simultaneous determination of methanol and ethanol, verifying the robustness of the calibration models when confronted with alterations in the gasoline composition.

2. Experimental

2.1. Instrumentation and procedure for spectra acquisition

A FT-NIR spectrometer (Bomem, model MD-160) provided with a flow cuvette of 10 mm pathlength and 80 μL internal volume (Hellma, model 178.710-QS) was used for spectra acquisition between 14000 and 4000 cm^{-1} (714 and 2500 nm), with resolution of 8 cm^{-1} . The sample was pumped into the interior of the cuvette by a peristaltic-pump (Ismatec, model 7331-00) using Viton[®] tubing and Teflon[®] conduction tubing (0.8 mm i.d.). To prevent contamination between samples, before acquisition of each spectrum the cuvette was cleaned by initially pumping air and then 5 mL of gasoline sample. The pumping was interrupted during spectra acquisition. The spectrum of the empty cuvette was used as reference for absorbance measurements.

2.2. Sample set

A set formed by 120 samples containing methanol and ethanol, both in the concentration range from 0 to 30% (v/v), was prepared by the addition of known aliquots of methanol (Vetec 99.8%, v/v) and ethanol (Santa Cruz 99.5%, v/v) in to alcohol-free gasoline (gasoline type A, Petrobras). A multivariate calibration model was constructed with 80 samples, while 40 samples were used to verify the prediction capacity of the model (external validation set). To evaluate the precision of the proposed method, four replicates of type A gasoline samples were prepared containing methanol and ethanol mixtures in concentration of 2.5:2.5; 2.5:20.0; 15.0:12.5; 25.0:25.0 and 30.0:2.5% (v/v), respectively.

The proposed method was evaluated for the determination of the alcohol contents in 15 commercial gasoline samples containing ethanol (type C gasoline), commercialized in the Campinas Metropolitan Region, SP. The results were compared with the values of alcohol content determined by the standard method ABNT-NBR 13992 [9]. The procedure for NIR spectra acquisition of these samples was identical to those described above.

2.3. Gasoline composition alteration

The composition of type A gasoline was modified by addition of different hydrocarbons normally present in this fuel. Thus, *n*-hexane (Acros, 95.0%, HPLC grade), isooctane (Aldrich, 99.0%, HPLC grade), *o*-xylene (Acros, 98.0%, HPLC grade), *m*-xylene (Acros, 99.0%, HPLC grade), *p*-xylene (Acros, 99.0%, HPLC grade) and toluene (Acros, 99.0%, HPLC grade) in the concentration range from 1.0 to 8.0% (v/v) were added to type A gasoline. Later, methanol and ethanol were added to these mixtures in the concentrations of 10.0 and 25.0% (v/v), respectively.

2.4. Pre-processing and construction of calibration models

For the construction of the multivariate calibration model, using partial least squares (PLS-1 and PLS-2), initially all sample spectra were evaluated by Principal Component Analysis (PCA) with the purpose of observing their distribution and the existence of clusters and outliers. Pre-processing procedures based on baseline correction and first derivative were evaluated. Calculations were performed with Unscrambler[®] 9.2 (CAMO, Oslo, Norway).

3. Results and discussion

3.1. Construction of the calibration model and external validation

Fig. 1 shows the spectra of samples of gasoline containing methanol and ethanol, both in the concentration range of 0–30% (v/v), for the spectral range between 1105 and 1682 nm. In the inset of Fig. 1, it is possible to observe the full spectral range from 714 to 2500 nm. Under the experimental conditions employed, below 1105 nm absorption signals are practically inexistent, whereas above 1682 nm high absorption values are observed.

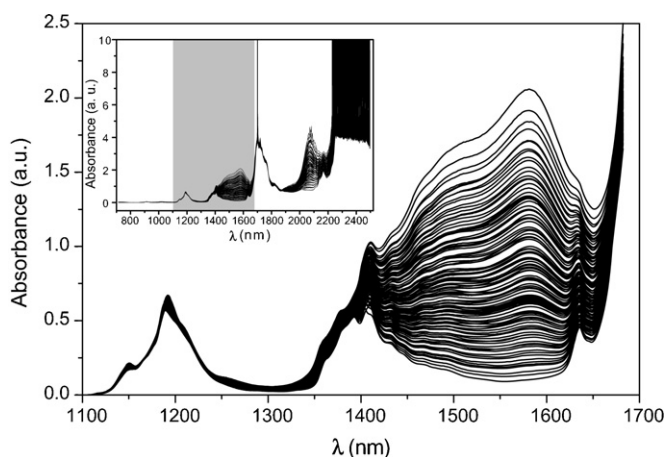


Fig. 1. Spectra of 120 gasoline samples with different methanol and ethanol contents in the spectral range from 1105 to 1682 nm. In the inset, the spectra in the range from 714 to 2500 nm are represented, and the range used is shaded. The range above 2200 nm presents high absorption, due to the use of a 10 mm pathlength cell.

Thus, the spectral range between 1105 and 1682 nm was selected for the construction of the calibration models. In this range, an intense absorption band between 1120 and 1270 nm is observed, referring to the 2nd overtone of the C–H bond stretching from the diverse hydrocarbons and the alcohols that compose the samples. Another band, also wide, between 1350 and 1670 nm, results from the overlapping of two absorption bands. The first, located between 1350 and 1550 nm, is related to first overtone of the combination band from C–H + C–H and C–H + C–C stretching and, the second, between 1400 and 1670 nm, is related to the first overtone of O–H stretching from the alcohols (methanol and ethanol). It is also possible to observe, above of 1650 nm, the beginning of the first overtone from aromatic C–H stretching.

Before initiating the construction of the calibration models, the presence of anomalous samples was verified by means of Principal Component Analysis (PCA). The results showed the existence of two samples, which presented distinct spectral behavior after baseline correction and, therefore, they were removed from the sample set. Several possible causes may contribute for the appearance of an anomalous sample, the most common coming from errors in sample preparation or problems that occurred at the moment of spectra acquisition, such as the presence of air bubbles in the optical path.

After outlier elimination, the 118 remaining samples were used, initially, to evaluate the best spectral data pre-processing

technique for the construction of the calibration model. Table 1 shows the results found for methanol and ethanol calibration models. The constructed models involved the use of spectra without any type of pre-processing and spectra whose baseline was corrected and/or to which first derivative was applied. In all procedures of construction of the calibration models, data were mean centered and full cross validation was employed for internal validation.

It was observed that calibration models for methanol and ethanol presented the lowest values of the root mean square error of cross validation (RMSECV) for the spectra set when the first derivative was applied with or without baseline correction. For these models, a maximum number of 4 latent variables (LV) was necessary to explain at least 99% of the spectral. Thus, these results demonstrate that optimum pre-processing is obtained by the application of first derivative in the original spectral signals, and that the prior correction of the baseline before the application of the derivative does not improve the quality of the models.

Then, the 118 samples were divided into two sets, where 2/3 (78 samples) were used for the construction of the calibration models for methanol and ethanol and 1/3 (40 samples) were used in the external validation set. In this last set, samples were selected carefully to represent all the concentration range without, however, including samples whose concentration of either alcohol was at the minimum or at the maximum. Moreover, they also included the samples prepared in replicates ($n=4$) aiming to evaluate the precision of the model.

Calibration models using PLS-1 (individual calibrations for methanol and ethanol) and PLS-2 (simultaneous calibration for both alcohols) were constructed. The models employed the first derivative of the original spectra, mean centering and full cross-validation. Table 2 shows the results for predictions of the methanol and ethanol contents of 40 samples of the external validation set. The values of root mean square error of prediction (RMSEP) obtained for ethanol for PLS-1 and PLS-2 were equal 0.28% (v/v), whereas for methanol this value was 0.31% (v/v) for PLS-1 and 0.32% (v/v) for PLS-2. These results indicate that both procedures can be used for methanol and ethanol determination when both or only one alcohol is present in gasoline. For the constructed models, a maximum of four latent variables was used.

The accepted absolute error for the determination of alcohol content in gasoline is $\pm 1\%$ (v/v) (relative error of $\pm 4\%$, considering the concentration of 25% (v/v) of alcohol in the gasoline). In this way, it can be observed that the accuracy in

Table 1
Results obtained by calibration models (PLS-1) for methanol (0–30%, v/v) and ethanol (0–30%, v/v) in gasoline, employing different types of pre-processed NIR spectra (gasoline C samples prepared in the laboratory; spectral range from 1105 to 1682 nm; RMSEC, root mean square error of calibration; R, correlation between the predicted and expected values; LV, number of latent variables)

Type of pre-processing	Methanol			Ethanol		
	RMSECV (% v/v)	R	LV	RMSECV (% v/v)	R	LV
No pre-processing	0.650	0.998	4	0.787	0.993	3
Base line correction	0.573	0.998	3	0.814	0.993	2
First derivative	0.297	0.999	3	0.459	0.998	3
Base line correction and first derivative	0.297	0.999	3	0.459	0.998	3

Table 2

Results obtained for determination of methanol and ethanol in samples of the external validation set using the calibration models constructed with PLS-1 and PLS-2 (spectral range from 1105 to 1682 nm and first derivative spectra; RMSEP, root mean square error of prediction, *R*, correlation between predicted and expected values)

Alcohol	Model	RMSEP	Slope	Intercept	<i>R</i>
Methanol	PLS-1	0.31	0.9988	0.1740	0.9996
	PLS-2	0.32	0.9989	0.1769	0.9996
Ethanol	PLS-1	0.28	0.9935	0.0044	0.9996
	PLS-2	0.28	0.9933	0.0111	0.9996

the alcohol content determination in gasoline, when NIR spectroscopy is used, is at least three times better than the standard method. The average repeatability expressed by the estimated standard deviation for the proposed method ($n=4$) was 0.29% for methanol and 0.19% for ethanol, evaluated for gasoline samples containing ratios of 2.5:2.5; 2.5:20.0; 15.0:12.5; 25.0:25.0 and 30.0:2.5% (v/v) of methanol and ethanol, respectively. These results demonstrate that the method presents superior repeatability compared to the standard method, being capable to differentiate methanol and ethanol when the concentration ratio between these alcohols is higher than 10 times (30.0:2.5%, v/v methanol:ethanol).

3.2. Effect of gasoline composition on the determination of alcohol

Gasoline compositions may vary depending on the origin of the oil used in its production and on the processing characteristics of a given refinery. This fact can affect the determination of different species using NIR spectroscopy, if the total variability of the sample matrix is not considered in the construction of the calibration model. Thus, this work also evaluated the effect of gasoline composition on the determination of methanol and ethanol. Changes in the sample matrix were simulated by the addition of linear, branched and aromatic hydrocarbons, commonly found in some gasolines A, before preparing the solutions containing the alcohols. Hydrocarbons such as *n*-hexane, isooctane, toluene, *o*-xylene, *m*-xylene and *p*-xylene were added to gasoline in the concentration range from 1.0 to 8.0% (v/v), followed by the addition of appropriate volumes of methanol and ethanol in order to make their final concentrations equal to 10.0% (v/v) and to 25.0% (v/v), respectively. These samples had their contents of methanol and ethanol predicted by the PLS model constructed with the original gasoline composition, whose results are shown in Fig. 2. The interrupted horizontal lines in each figure indicate the interval of concentrations delimited by the value of the RMSEP obtained from the models shown in Table 2, around the expected reference values for the alcohol concentrations in the samples.

It is possible to observe in Fig. 2A that the addition of *n*-hexane and toluene in gasoline in the 1.0–8.0% (v/v) range does not affect the prediction of methanol contents in gasoline, as the results are inside of the accepted interval (RMSEP) of the proposed method. On the other hand, the presence of others hydrocarbons (isooctane, *o*-xylene, *m*-xylene and *p*-xylene) at

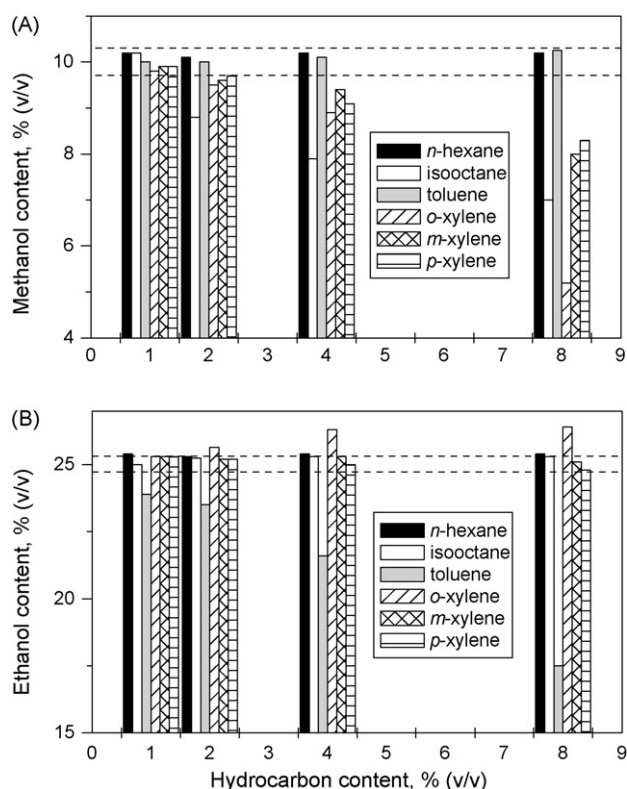


Fig. 2. Results obtained for determination of methanol (A) and ethanol (B) in gasoline samples whose composition was modified by addition of different hydrocarbons. The horizontal lines indicated in each figure were traced based on expected concentration values for methanol (10.0%, v/v) and ethanol (25.0%, v/v) and the root mean square error of prediction (RMSEP) from models (Table 2). The model was constructed using PLS-2 and the spectral range from 1105 to 1682 nm. Results represent averages of two determinations.

concentrations levels higher than 2.0% (v/v) significantly affect the determination of methanol content, with prediction values lower than the expected values. For instance, the addition of *o*-xylene at 8.0% causes a relative error of -48% in prediction of methanol content.

For the determination of ethanol (Fig. 2B), it is observed that the presence of 8.0% (v/v) of toluene as well as *o*-xylene in the fuel causes relative errors of -30% and $+6\%$, respectively. The addition of other hydrocarbons did not produce interferences in ethanol content prediction in gasoline, as the results are inside of the expected interval, considering the root mean square error of prediction (RMSEP) of the model.

These results indicate that the variation of gasoline composition significantly affects methanol and ethanol determination when multivariate calibration models are constructed from NIR spectra. This type of interference can be totally prevented if the sample set used in the construction of the calibration model represents the total variability of gasoline composition. However, the construction of a global model would be very difficult because it will require the inclusion of samples from different regions according with the variation of the gasoline composition, which, by its time, is dependent on the crude oil source. Local models are easily constructed, because the gasoline composition variability can be accomplished with the use of relatively few samples. Furthermore, in cases in which it is not possible to

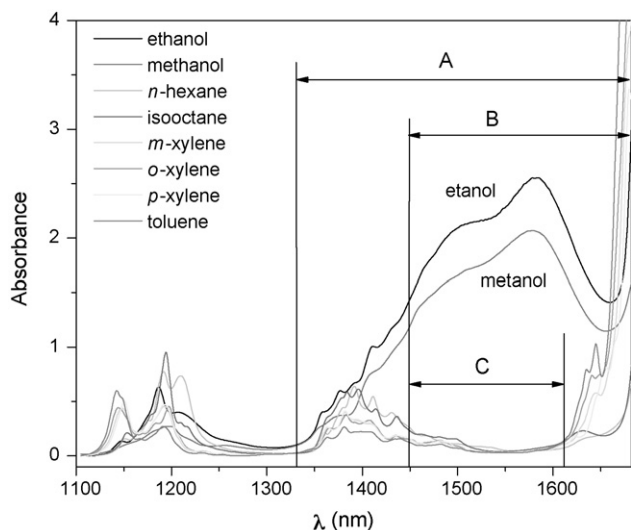


Fig. 3. Spectra of the hydrocarbons used for alteration of the gasoline matrix and of the alcohols studied. A–C are defined in the text.

prepare samples that represent matrix variations, the selection of variables or spectral ranges can lead to the construction of more robust models.

3.3. Selection of the spectral regions

Fig. 3 shows NIR spectra of methanol, ethanol and hydrocarbons used in the study of modification of the gasoline composition. It is observed that in the spectral range used for the calibration model construction there are some overlapping absorption bands, mainly those occurring between 1120 and 1270 nm, attributed to the 2nd overtone of C–H bond stretching. On the other hand, the range between 1400 and 1700 nm, related to first overtone of alcohol O–H bond (methanol and ethanol), presents lower overlap with the bands produced by the first overtone of combination bands (1350–1500 nm) due to C–H + C–H and C–H + C–C stretching. Thus, it is reasonable to suppose that calibration models made by using this range, or part of it, can provide more robust models, whose results are less dependent on the gasoline composition. In such a way, three spectral ranges were evaluated for determination of methanol and ethanol (indicated in Fig. 3): region “A” (1331–1682 nm), region “B” (1449–1682 nm) and region “C” (1449–1611 nm). The RMSEP values for methanol and ethanol determinations obtained for the external validation set by using the calibration models constructed using these three regions, are shown in Table 3.

For regions “A” (1331–1682 nm) and “B” (1449–1682 nm), the RMSEP values are similar those found when the wider spectral range is used for model construction (Table 2). For region “C” (1449–1611 nm) an increase in the RMSEP value is observed, indicating a decrease in the prediction capability of the regression model based on that spectral region. This is more evident for ethanol when PLS-2 is used. This result indicates that the use of only the region of first overtone of O–H bond makes the discrimination between methanol and ethanol, difficult since the region presenting absorption of the methyl (–CH₃)

Table 3

Results obtained for determination of methanol and ethanol in samples of the external validation set using the calibration models constructed PLS-1 and PLS-2 with the three regions shown in Fig. 3 after first derivative spectra (RMSEP, root mean square error of prediction)

Spectral range (nm)	RMSEP (% v/v)			
	Methanol		Ethanol	
	PLS-1	PLS-2	PLS-1	PLS-2
A (1331–1682)	0.33	0.34	0.30	0.30
B (1449–1682)	0.32	0.32	0.28	0.28
C (1449–1611)	0.47	0.47	0.39	1.04

and methylene (–CH₂–) groups is not included in the calibration model.

By using the constructed models for the spectral data from these three regions, the determination of methanol and ethanol in the same gasoline samples used for Fig. 2 construction was carried out. For the regions “A” and “B”, the results show that there is interference from isooctane and the three xylenes for the methanol determination and that toluene also begins to interfere when the calibration model using region “B” is employed. For ethanol determination, the interference of toluene and *o*-xylene continues being observed. On the other hand, the models constructed with region “C” show lower dependence on gasoline composition, as it can be seen through the data shown in Table 4. Considering that a relative error of 4% is acceptable for alcohol determination in gasoline, it can be concluded that only isooctane continues causing interference in methanol determination while for ethanol no interference from the studied hydrocarbons is observed.

A detailed analysis of region “C” (Fig. 3) shows that above 1611 nm there are absorptions referring to aromatic hydrocarbons (first overtone of C–H + C–H and C–H + C–C stretching), which is overlapped by absorptions of O–H stretching of alcohols. Thus, removing this spectral region for the construction of the calibration model minimizes the interference of aromatic hydrocarbons. In the region below 1449 nm, methyl (–CH₃) and methylene (–CH₂–) group absorptions coming from the different added hydrocarbons, are observed. Elimination of part of this region prevents interference of linear and aromatic hydrocarbons. However, if the lower limit selected for region “C” (1449–1611 nm) is increased to somewhat wavelengths, larger errors are observed due to the loss of information related to the methyl and methylene groups present in the alcohols. In the case of the isooctane interference, it was not possible to establish, in a definitive way, how much of its interference remains, even after carrying out the study of the different spectral regions. The most acceptable hypothesis is that isooctane has five methyl groups per molecule, which overlap with the absorption band from the only methyl group of methanol. On the other hand, ethanol has, besides the methyl group, a methylene group whose information must be used to differentiate ethanol and methanol, which would justify the reduced interference of isooctane in ethanol determination. The only way to deal with the interference of hydrocarbons such as isooctane is to ensure that the average composition

Table 4

Results obtained for determination of methanol and ethanol in gasoline samples whose matrix compositions were modified by the addition of different hydrocarbons, using the calibration model constructed in the spectral range from 1449 to 1611 nm

Hydrocarbons ^a	Methanol		Ethanol	
	Predicted (% v/v)	Relative error ^b (%)	Predicted (% v/v)	Relative error ^b (%)
<i>n</i> -Hexane	9.8	2.2	25.1	0.4
Isooctane	7.8	−21.7	25.9	3.6
Toluene	9.7	3.3	24.1	−3.6
<i>m</i> -Xilene	9.7	3.3	24.1	−3.6
<i>o</i> -Xilene	9.7	3.3	24.8	−0.8
<i>p</i> -Xilene	9.9	1.1	24.0	−4.0

^a Hydrocarbons content equal to 8.0% (v/v).

^b Calculated value in relation to predicted value for the sample without hydrocarbon addition (25.0%, v/v for ethanol and 10.0%, v/v for methanol). Results represent averages of two determinations.

Table 5

Results obtained by PLS-1 for ethanol determination in type C gasoline samples collected from gas stations

Sample	Standard method (% v/v)	1105–1682 nm		1449–1611 nm	
		Proposed method (% v/v)	Relative error (%)	Proposed method (% v/v)	Relative error (%)
1	26.0	25.2	−3.2	26.0	0.0
2	24.0	24.6	2.3	24.7	2.9
3	26.0	25.2	−3.3	25.4	−2.3
4	25.0	24.8	−0.8	25.5	2.0
5	26.0	25.3	−2.5	25.6	−1.5
6	25.0	25.4	1.6	25.9	3.6
7	25.0	25.5	1.9	26.0	4.0
8	25.0	25.2	0.6	25.6	2.4
9	25.0	25.4	1.5	25.8	3.2
10	25.0	25.5	2.0	25.9	3.6
11	61.0	61.3	0.5	63.9	4.8
12	25.0	22.4	−10.3	24.6	−1.6
13	25.0	25.4	1.6	25.8	3.2
14	26.0	26.5	2.0	26.4	1.5
15	25.0	24.6	−1.8	25.0	0.0

Calibration models were constructed using first derivative NIR spectra in the ranges 1105–1682 nm and 1449–1611 nm

of the gasoline does not change very much from batch-to-batch.

To validate the proposed method, the ethanol contents were determined in 15 commercial gasoline (type C) samples collected from gas stations in the Campinas region (SP, Brazil). Table 5 shows the results obtained with the PLS-1 model using all the spectral range and the PLS-1 model using only region “C” (1449–1611 nm). The results obtained were compared to the alcohol content determined by the standard method (ABNT-NBR 13992) [9]. Except for samples 11 and 12, all the results obtained are within the relative error range of $\pm 4\%$, accepted for ethanol determination in gasoline, in agreement with the standards of the ANP (National petroleum Agency, Brazil). Principal Component Analysis (PCA) reveals that samples 11 and 12 show different spectral behaviors from the other samples. In the case of sample 11, this behavior is justified by its high ethanol content (61%, v/v), being, therefore, classified as an adulterated gasoline. It is also interesting to note that the relative error of 4.8% found for this sample demonstrates perhaps that the method can produce good results even when the alcohol content is higher than the upper limit of 30.0% (v/v) used in the PLS-1 calibration model. The confidence limit found for the prediction of this sample also demonstrates this fact. However, this

result must be seen with caution as the majority of chemometric algorithms would give a very large confidence interval for this result.

In the case of sample 12, the results found using both models reveal that probably the composition of this sample is quite different from those used in calibration set and also from the other samples collected from the gas stations. This fact is justified on the basis of interference studies carried out, which demonstrate that only toluene causes negative errors on ethanol predictions when spectral region “C” is used for model construction. The results of ethanol prediction agree with the standard method.

4. Conclusions

The results obtained in this work show that NIR spectroscopy together with multivariate calibration (PLS-2) can be used for simultaneous determination of methanol and ethanol in gasoline. The main advantages are the non-destructive and non-polluting characteristics of the NIR method. Moreover, the method can determine methanol and ethanol in presence of each other, being appropriate for use in inspections and identification of adulterations made by the addition of methanol to gasoline. It is important to emphasize that the standard method does not

have this capability. The selection of the spectral region to be employed in the construction of the calibration model minimizes interference from linear and aromatic hydrocarbons on the determination of both alcohols. In the case of branched hydrocarbons, it was observed that the selection does not eliminate the interference of these types of compounds in methanol determination. Therefore, it is necessary to employ samples that represent the variability of these compounds or ensure that the variability is within an acceptable range.

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