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Carbon nuclear magnetic resonance spectroscopic fingerprinting of commercial gasoline: Pattern-recognition analyses for screening quality control purposes

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ABSTRACT

In this work, the combination of carbon nuclear magnetic resonance (^{13}C NMR) fingerprinting with pattern-recognition analyses provides an original and alternative approach to screening commercial gasoline quality. Soft Independent Modelling of Class Analogy (SIMCA) was performed on spectroscopic fingerprints to classify representative commercial gasoline samples, which were selected by Hierarchical Cluster Analyses (HCA) over several months in retails services of gas stations, into previously quality-defined classes. Following optimized ^{13}C NMR-SIMCA algorithm, sensitivity values were obtained in the training set (99.0%), with leave-one-out cross-validation, and external prediction set (92.0%). Governmental laboratories could employ this method as a rapid screening analysis to discourage adulteration practices.

1. Introduction

Brazilian commercial gasoline is a petroleum-derived product constituted by a complex mixture of liquid aliphatic and aromatic hydrocarbons, ranging from C_4 to C_{12} carbon atoms, of which boiling point ranges up to 225 °C. A typical gasoline is predominantly a mixture of paraffins (alkanes), olefins (alkenes), naphthenes (cycloalkanes), and aromatics, which can also contain some additives (aliphatic alcohols and/or methylethers) to improve its octane number. Oil feedstock, refining processes and aging are some of the factors that affect the detailed chemical composition of gasoline [1,2]. In Brazil, the commercial gasoline used as fuel in internal combustion engines may have an amount of anhydrous ethanol between 20 and 25%, a quantity not found in any other country [3].

The gasoline quality control is performed all around the world by refineries, distribution companies and government inspection departments. It is a crucial procedure, as gasoline must follow the quality standards set for local markets, meeting the requirements of car engines and with minimum possible damage to the environment [4]. Generally, quality control of fuels is ensured by the establishment of technical specifications, which vary according to the different areas of the world, i.e., EN 228 in Europe, ASTM D4814 in the USA, JIS K2202 in Japan and IS 2796 in India [5]. Unfortunately, the automotive gasoline adulteration is becoming a common practice because of economic issues. In fact, fuel adulteration has been worrying the Brazilian Government of Petroleum, Natural Gas and Biofuels Agency (Agência Nacional do Petróleo, Gás Natural e Biocombustíveis, ANP) not only for quality control reasons, but also for tax evasion. Adulteration involving the addition of anhydrous ethanol and of petrochemical organic solvents, such as light aliphatic (C_4–C_8), heavy aliphatic (C_{13}–C_{15}) and aromatic hydrocarbons, is one of the possibilities that can be observed. In addition, low cost, lower tax rates and similar chemical composition are factors that also contribute to their use in cases of adulteration [6].

Currently, in Brazil, commercial gasoline quality is controlled by several technical specifications (namely physicochemical parameters) established by the ANP Regulation 309 [7]. All these specifications are obtained by analytical protocols covered by international guides, mainly from the American Society for Testing and Materials (ASTM International) [8]. However, several of these specifications need large amounts of sample and involve manual operations, which are rather subjective, tedious and prone to operational errors. Moreover, it is not always possible to identify gasoline adulteration using these specifications because many solvents are very similar to gasoline, and consequently, physicochemical parameters are usually not efficient for detecting adulteration [2,4,6,9]. Previous studies have shown that

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physicochemical parameters are not enough to identify adulterations unless chemometric techniques had been employed. Only adulterations using high levels of anhydrous ethanol, aromatic solvents or heavy aliphatic hydrocarbons can be identified by physicochemical parameters [4,10,11–15]. Therefore, new alternative analytical methods must be developed to monitor such adulterations, as well as simple, fast and efficient methods to certify the quality and authenticity of the commercial fuels are desirable and, thus, recommended for routine applications in quality control monitoring programs.

Besides that, nuclear magnetic resonance (NMR) spectroscopy has especially become a powerful tool for gasoline analysis without pre-treatment, mainly due to the fact that measurements are fast and can be easily automated, allowing the analysis of a large number of samples in a short period of time. Therefore, it is recommended for routine applications in quality control monitoring programs. In general, the typical chemical shifts in the spectrum are subdivided into regions and each one is associated with a specific molecular substructure, for example, aromatic, olefinic, and aliphatic compounds. Thus, with the objective of inserting new insights into this research field, we present here an application based on carbon nuclear magnetic resonance spectroscopy (^{13}C NMR). Some interesting studies using ^{1}H NMR and NIR in gasoline composition analysis showed promising results when compared with other techniques and also with physicochemical parameters [4,6,16–22]. However, effective quality control and adulteration detection involving ^{13}C NMR analysis have not actually been undertaken before. As far as we know, this is the first application of pattern-recognition multivariate SIMCA chemometric coupled to ^{13}C NMR fingerprintings for commercial automotive gasoline quality control.

2. Experimental

2.1. Physicochemical parameters

The gasoline samples were provided by a laboratory responsible for monitoring the quality of automotive fuels, particularly, gasoline, ethanol and diesel oil. 2400 gasoline samples, collected randomly from different gas stations in São Paulo state, Brazil, over six months, were stored in polyethylene terephthalate flasks and transported in refrigerated boxes, following official ANP procedures. When arriving at the lab, 90 mL samples were immediately collected in 100 mL amber PET flasks with sealing caps and then, stored in a freezer to avoid volatilization and to keep their integrity. All gasoline samples were previously analyzed by several physicochemical parameters established in ANP Regulation 309, namely, atmospheric distillation temperatures – required to reduce the original volume of the sample to 10%, 50% and 90%, final boiling point and distillation residue (ASTM D86) [23]; relative density (ASTM D4052) [24]; motor octane number, research octane number and anti-knock index (correlation to ASTM D2699/D2700) [25,26]; percentage (v/v) of benzene (ASTM D6277) [27], anhydrous ethanol (NBR 13992) [28] and hydrocarbons (saturates, olefins and aromatics–correlated to ASTM D1319) [29]. The instruments employed in the analyses were an automatic distiller (Normalab NDI440 v.1.70C), a densimeter (Anton Paar DMA4500 v.4.600.b) and a portable IR analyzer (Grabner IROX2000 v.2.02). According to these results, the samples were classified in two groups: conform (meeting Brazilian specification) and nonconform (failing Brazilian specification). Based on the physicochemical parameters it was possible to select representative gasoline samples by exploratory analysis (Hierarchical Cluster Analysis, HCA) for further ^{13}C NMR analyses.

2.2. Carbon nuclear magnetic resonance (^{13}C NMR) analyses

All ^{13}C NMR spectroscopic fingerprintings were acquired at room temperature on a Varian (Palo Alto, CA, USA) INOVA Unit 500 MHz Spectrometer, using a 5 mm single cell 1H/13C inverse detection flow probe. For each analysis, 200 μL of gasoline sample was dissolved in 600 μL of deuterated chloroform ($CDCl_3$). ^{13}C NMR fingerprinting was obtained at 125 MHz frequency, using $CDCl_3$ as the solvent and internal standard. The spectral profiles of gasoline were acquired in 10 min under the experimental conditions. Acquisition parameters were optimized to 6.5 μs 45° pulse and 0.957 ms recycle delay. Acceptable spectra were obtained from 296 scans (transients) with spectral width set at 230 ppm (31 446.5 Hz) and using an exponential weighing factor corresponding to a line broadening of 1 Hz.

^{13}C NMR spectral profiles, taken into pattern-recognition chemometrics analysis, are reported in parts per million (ppm) relative to $CHCl_3$ residual signals at 77.0 ppm. The FIDs, acquired with 65 536 data points, were zero filled and Fourier transformed. The phase and baseline were automatically corrected in all spectra. Additionally, fingerprinting spectra were normalized to 1-norm (the area under the sample profile is set equal to one) for compensation of baseline distortions and bucket-width integrated (0.02 ppm) for more effective compensation of peak-shifts. At last, such spectra profile was exported as ASCII files and transferred to a PC for data analysis.

2.3. Pattern-recognition multivariate chemometric analysis

In this field, the pattern-recognition methods were divided in Hierarchical Cluster Analysis (HCA) and Soft Independent Modeling of Class Analogy (SIMCA). The first ones are unsupervised statistical methods that give complementary information about the similarities and groupings of the samples considered. If a trend exists, it is worthwhile evaluating the possibility of classifying the samples. In conjunction with these, SIMCA is a well-known multivariate supervised pattern-recognition method that constructs models using samples that were preassigned to a category, i.e., in this case, conform (meeting Brazilian specification) and nonconform (failing Brazilian specification).

HCA is used to emphasize and identify natural groups of samples based on their physicochemical parameters. Dendrograms, a visual representation of HCA results, illustrate the categories as clustering of samples and reveals similarities between them. Two criteria must be chosen to perform HCA: firstly, the distance between samples or groups and secondly, the criteria to link samples and groups. The usual way to calculate the distance is by using the Euclidean distance, where the distance between objects k and l is evaluated in J dimensions. Euclidean distance is an “ordinary” distance between two points that one would measure with a ruler. On the other hand, the most appropriate linkage criterion is incremental, by which the groups are linked causing a minimum “loss of information” and where two groups of samples differ only slightly. HCA, performed using Pirouette software (version 3.11, Infometrix Co., Woodinville, WA, USA) [30] and codified data, was applied to each monthly spreadsheet of physicochemical parameters results, used as variables. Firstly, the variables were autoscaled and then logarithmic transformed in order to select those representative samples that presented minimal similarity. The similarity line, which establishes clusters, presented values between 0.5 and 0.6. From the monthly dendrograms, each one constituted of 400 samples, 25 representative gasoline samples were monthly selected for further ^{13}C NMR analysis.

SIMCA chemometric method was applied in order to build a screening model of multivariate pattern-recognition technique.

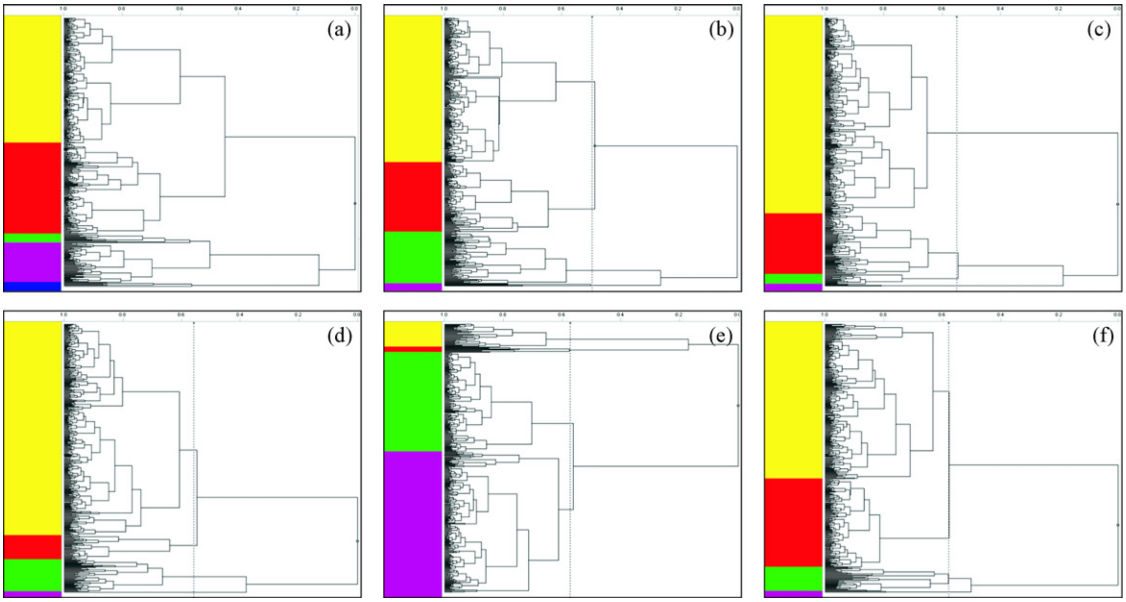

Fig. 1. Dendrograms for selection of the 25 representative monthly gasoline samples that exhibited least similarity: (a) April, (b) May, (c) June, (d) July, (e) August and (f) September.

This technique describes different classes of samples based on classification rules which are defined by the values of distinct measurements provided for a set of known samples (the training set). These rules are then used to classify external samples (the prediction set) on the basis of the same measurements. The number of samples correctly classified by the model is a measure of the quality of the criteria employed. If appropriate, the model can then, be used to classify unknown samples according to the same rules. In order to apply SIMCA modelling, ^{13}C NMR spectroscopic fingerprints of 150 representative gasoline samples were shifted to right or left as needed, with the TMS signal as the reference. ^{13}C NMR spectroscopic fingerprint of 100 gasoline samples were employed in the training set, and the remaining 50 samples formed the prediction set. These samples were selected from exploratory analysis HCA of its spectroscopic profiles. These spectra profile were saved as ASCII files and transferred to a PC for data analysis. The data matrix (26,713 × 150 × 2; chemical shifts × representative gasoline samples × preassigned categories: conform and nonconform) were constructed and imported into Pirouette software (version 3.11, InfoMetrix Co., Woodinville, WA) [30] for SIMCA algorithm. Each line in the matrix corresponds to a sample, and the columns represent the number values obtained from the chemical shifts and intensities of the peaks. ^{13}C NMR spectra were normalized to 1-norm (the area under the sample profile is set equal to one), and the logarithmic transformation was taken. Autoscaling – in which each variable is mean-centered and scaled to unity variance – was applied to give each variable equal weight and, therefore, large and small peaks were treated with equal emphasis. ^{13}C NMR-SIMCA algorithm was applied to whole data set, excluding $CDCl_3$ and TMS signals.

3. Results and discussion

Significant changes in the physicochemical parameters of Brazilian automotive gasoline may be caused by the addition of excess CAE and/or adulterating solvents, especially benzene, toluene, xylenes, hexane, complex hydrocarbon mixtures, mineral spirits, kerosene, rubber solvent, petrochemical naphtha, diesel and thinner. These solvents can give rise to variations in relative density, octane number, hydrocarbon composition and distillation curve profile. 2400 samples of commercial gasoline were collected in the State of São Paulo, Brazil, over a 6-month period and 150 representative samples (79 meeting Brazilian specification and 71 failing Brazilian specification) were selected using HCA analysis. Six dendrograms (Fig. 1) – each one constituted of 400 samples and obtained taking into account the Euclidean distance, incremental linkage and similarity line criteria – resulted in 25 clusters (represented by different colors). The color bar sequence, automatically assigned by the Pirouette chart preference, is also used to assign colors to sample and variable clusters in the dendrogram, based on the location of the similarity line. For each monthly dendrogram, 25 representative gasoline samples, that exhibited least similarity, were selected for ^{13}C NMR analysis, maintaining the representatively of the dataset. Summary of physicochemical parameters values of representative commercial gasoline samples is presented in Table 1.

^{13}C NMR spectrum fingerprinting of gasoline is very complex, showing peaks almost in all spectral regions. Based on these peaks, typical spectrum of Brazilian gasoline is shown in Fig. 2, but it is not possible to see that many compounds present in adulterating solvents are also present in gasoline. Also, all spectrum overlapping (Fig. 2) shows very similar spectroscopic fingerprinting from

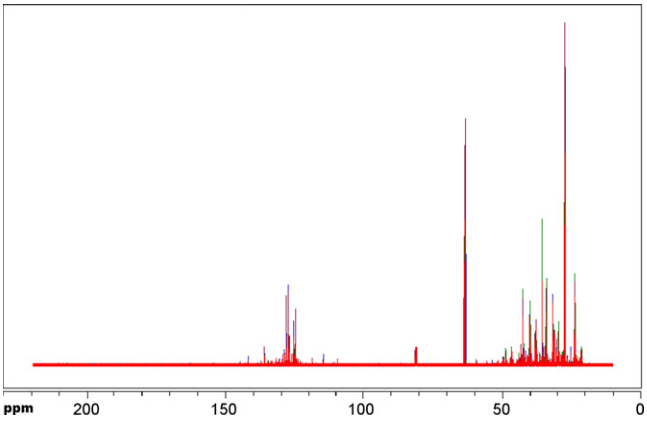

Fig. 2. Typical ^{13}C NMR overlapped spectroscopic fingerprints of all representative commercial gasoline samples ($CDCl_3$, 500 MHz).

Table 1
Summary of representative gasoline physicochemical parameters and its specification according to ANP Regulation 309.

Guide	Physicochemical parameters	ANP specification	Representative gasoline set			
			Minimum	Maximum	Range	Mean
ASTM D4052	Relative density (g cm^{-3})	Not specified	0.7298	0.7931	0.0633	0.7520
ASTM D6277	Benzene (% v/v)	1.0, max	0.0	0.62	0.62	0.33
NBR 13992	Anhydrous ethanol (% v/v)	25 ± 1	23.0	66.0	43.0	27.2
	Distillation curve					
ASTM D86	10% Evaporated (°C)	65.0, max	44.2	73.2	29.0	55.3
	50% Evaporated (°C)	80.0, max	63.3	116.5	53.2	72.9
	90% Evaporated (°C)	145.0–190.0	77.8	191.1	113.3	156.9
	Final boiling point (°C)	220.0, max	78.8	285.7	206.9	204.9
	Residue (% v/v)	2.0, max	0.4	2.8	2.4	1.0
	Octane numbers					
correlation to ASTM D2699/2700	Motor Octane Number	82.0, min	77.4	87.2	9.8	82.2
	Research Octane Number	Not specified	89.8	98.4	8.6	95.0
	Anti-knocked Index	87.0, min	84.6	91.4	6.8	88.6
	Hydrocarbon composition					
correlation to ASTM D1319	Saturates (% v/v)	Not specified	4.2	68.5	64.3	38.8
	Olefins (% v/v)	45.0, max	0.0	29.9	29.9	19.0
	Aromatics (% v/v)	38.0, max	7.1	26.4	19.3	15.8

one gasoline to another, because the basic originating refinery processes are quite similar. ^{13}C NMR chemical shifts follow the same principles as those of ^{1}H NMR, although the typical range of chemical shifts is much larger than for ^{1}H (by a factor of about 20). In general, classes of compounds (not individual ones) are associated with typical spectral regions, i.e., aromatic chemical shifts can be associated with peaks at 110–150 ppm, while 50–80 ppm can be associated to alcohol or R–CH$_2$–O compounds and the region between 10 and 50 ppm contains signals mainly due to cycloalkanes (naphthenes) and normal- and iso-paraffins [31].

It is clear that visual inspection of spectroscopic profiles is not efficient in identifying the presence of adulterant solvents in gasoline (Fig. 2) and, therefore, to distinguish if commercial gasoline is meeting or failing Brazilian specification. Any attempt to distinguish between gasoline samples must consider numerous peaks and requires the application of a chemometric classification technique. Therefore, pattern-recognition chemometric approach is a very useful tool and is often employed for gasoline discrimination. In this work, we chose the entire ^{13}C NMR spectrum (except CDCl$_3$ and TMS signals) for the SIMCA analysis because the choice of a large number of peaks allows us to achieve a more reliable classification model [4,6,9,22]. In this way, recently, D'Ávila and coworkers [4] and Monteiro et al. [6] have distinguished intentionally adulterated gasoline samples by organic solvents for routine quality control, based on the application of ^{1}H NMR-PCA and ^{1}H NMR-HCA exploratory models or based on the average group molecular weight approach and relative-content concept involving aromatics, olefinics and paraffinics, also including ethanol and benzene contents.

The SIMCA method was selected since it permits the classification of an unknown sample on the basis of rules defined by a training set. Additionally, gasoline samples' quality proceeding from physicochemical parameters established by ANP Regulation 309 (as supervisioned class) was established in the data matrix for the SIMCA analysis to be performed. In the development of SIMCA algorithm, 100 gasoline samples were used to compose the training set and the remaining 50 samples were used as external prediction set. The prediction set selection was performed through hierarchical cluster analysis (HCA) of all representative gasoline samples. The dendrogram, results in three different clusters, in which a proportional number of samples were selected from each cluster.

Moreover, the probability threshold of the algorithm was based on a 95% confidence level, while several pre-treatments and preprocessing were tested, and the best results were obtained when the logarithmical and autoscale were applied. The autoscale preprocessing was very important because it allowed the attribution of the same importance for all spectral regions. In SIMCA model, the 3D class projection (Fig. 3) provides a visual evaluation of the degree of class separation. To create this object, a 3-factor principal component analysis was performed on the entire training set during the SIMCA processing. It was also possible to see reasonable tendency segregations between samples in the scores hyperboxes. In addition, a close examination of the SIMCA 3D results showed an overlapping between gasoline samples in the PCA space. The coordinates of a bounding ellipse (based on the standard deviations of the scores in each principal component direction) for each category are projected into this 3-factor principal component space; they form a confidence interval for the distribution of the category.

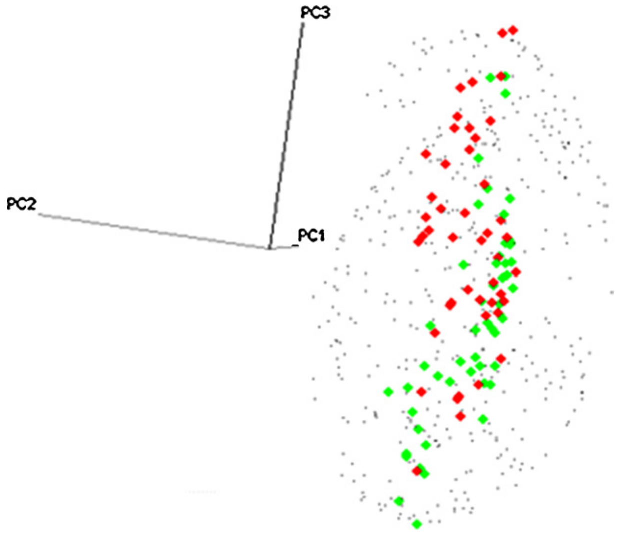

Fig. 3. SIMCA class 3D projections of samples in the training set on score plots. Note: green and red points represent conform and nonconform class, respectively. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.).

Table 2
Absolute errors in classification obtained by SIMCA.

Samples Class	Absolute error			
	Training set		Prediction set	
	Type I	Type II	Type I	Type II
Conform class	0	0	0	5
Nonconform class	0	1	0	3

Table 3
Physicochemical parameter values associated with ANP Regulation 309 for misclassified gasoline samples in the training and prediction sets by the SIMCA model. Entries in bold font indicate parameters nonconform to ANP specifications.

Samples	Physicochemical parameters associated with ANP Regulation 309													
	Density	T10	T50	T90	FBP	MON	RON	AI	Benzene	Saturates	Olefins	Aromatics	AE	Residue
Misclassified samples in the training set by SIMCA model														
13 April	0.7558	55.0	73.2	151.8	199.8	83.5	97.3	90.4	0.40	38.1	16.9	13.7	**35**	0.9
Misclassified samples in the prediction set by SIMCA model														
19 April	0.7447	49.2	71.4	151.2	197.6	82.2	95.4	88.8	0.47	33.2	25.6	15.6	25	0.9
1 May	0.7567	63.2	74.9	161.4	195.9	**81.3**	93.6	87.5	0.17	47.7	9.0	18.2	26	1.0
24 May	0.7566	53.1	73.7	173.2	**221.0**	82.4	95.5	89.0	0.41	37.5	23.2	15.7	24	0.6
15 June	0.7484	52.5	72.5	154.4	187.3	82.0	94.5	88.3	0.31	37.7	23.4	13.7	25	1.0
21 June	0.7497	51.2	71.6	153.4	199.6	82.5	95.8	89.2	0.44	35.0	24.3	14.4	**28**	1.1
22 June	0.7522	50.5	70.3	153.6	197.4	**81.7**	94.2	88.0	0.39	45.6	15.0	14.9	25	0.8
21 July	0.7453	55.2	72.2	155.7	193.4	**81.6**	93.8	87.7	0.31	41.9	22.4	10.8	25	1.1
19 July	0.7501	54.7	71.9	159.1	207.6	82.4	95.5	89.0	0.44	33.7	22.9	16	25	0.7

T10, T50 and T90—distillation temperatures required to reduce the volume of the sample to 10, 50 and 90% of its original value; FBP—final boiling point; MON—motor octane number; RON—research octane number; AI—anti-knock index; AE—anhydrous ethanol content.

Fig. 3 shows the score points for two categories (conform and nonconform) and the corresponding confidence intervals suggested by the single pixel grey points.

The SIMCA absolute errors in classification algorithm model could be of two types: Type I: object not included in its own class and Type II: object included in a wrong class. Table 2 summarizes the error in classification pointed out by full cross-validation of SIMCA algorithm. As it can be seen in Table 2, while Type I error was not observed, a significant number of Type II was obtained in the commercial gasoline samples, in both, conform and nonconform classes.

In SIMCA model training set, three principal components accounted approximately 70.0% of the total within set variance and all samples correctly classified, except for one sample (13 April). The misclassification may be associated to anhydrous ethanol (AE) physicochemical parameter; measured according to NBR 13992 standard procedure (Table 3). Hence, 99.0% of the samples were correctly classified by application of the SIMCA method. Based on these findings, it could be concluded that the modelling power of the training set was satisfactory.

Lastly, 50 new samples – the external prediction set – were used to evaluate the model. While all samples were clearly well segregated, eight of them were apparently misclassified according to the SIMCA model: five nonconform samples were classified as conform to ANP regulations and three samples conformed were classified as nonconform by SIMCA (Table 3). The misclassifications may be associated mainly to motor octane number (MON) physicochemical parameter (Table 3). Another misclassification physicochemical parameter was related to FBP and AE values. In MON values cases, the physicochemical results were not conclusive, because the values were very close to the limits established by ANP Regulation 309 and were certainly within the confidence limits of the method used (0.5 for MON). In this parameter, three samples (1 May; 22 June; 21 July) showed values between 81.3 and 81.9, while the minimum permitted value is 82.0. The same characteristics were obtained for samples 24 May and 21 June, where FBP temperature was 221.0 °C, while the established temperature is 220.0 °C, and AE content was 28% (v/v), while the established percentage is between 24 and 26% (v/v). Therefore, none of these parameters can be considered significantly different from the limiting values when the confidence limits are taken into account.

In contrast, three samples (19 April; 15 June; 19 July) that were fully conformed to ANP Regulation 309 were misclassified by the SIMCA model. Based on these findings, 92.0% of the samples in the prediction set were correctly classified by application of the SIMCA method. From this, it may be concluded that the modelling power was satisfactory and perfectly acceptable. Therefore, ^{13}C NMR fingerprintings and pattern-recognition SIMCA multivariate chemometric analysis supplied enough information to identify the slight differences between conform and nonconform gasoline, allowing the evident distinction between these two groups. Such results were in agreement with physicochemical analyses and proved that ^{13}C NMR-SIMCA algorithm allows the segregation of commercial gasoline based on its quality.

4. Conclusions

An analytical method, based on pattern-recognition SIMCA chemometric analysis of ^{13}C NMR spectroscopic fingerprinting, has been developed in order to determine the quality specified by ANP Regulation 309 of Brazilian commercial gasoline. ^{13}C NMR technique has a high potential to determine the quality of Brazilian commercial gasoline and research shows that the resulting spectroscopic fingerprints associated with the SIMCA model classification were satisfactory for screening the quality of gasoline samples. Finally, this work pointed out that ^{13}C NMR-SIMCA algorithm, as an alternative analytical methodology, offers an appealing procedure for government agency laboratories to control the quality of commercial automotive gasoline. This method can be applied in routine quality control, in view of possible automation, given that it allows analyses of a great number of samples, and employs only one NMR dedicated instrument.

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