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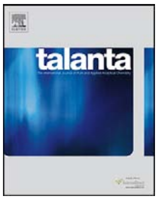

Screening Brazilian commercial gasoline quality by hydrogen nuclear magnetic resonance spectroscopic fingerprintings and pattern-recognition multivariate chemometric analysis

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ABSTRACT

The identification of gasoline adulteration by organic solvents is not an easy task, because compounds that constitute the solvents are already in gasoline composition. In this work, the combination of Hydrogen Nuclear Magnetic Resonance (^{1}H NMR) spectroscopic fingerprintings with pattern-recognition multivariate Soft Independent Modeling of Class Analogy (SIMCA) chemometric analysis provides an original and alternative approach to screening Brazilian commercial gasoline quality in a Monitoring Program for Quality Control of Automotive Fuels. SIMCA was performed on spectroscopic fingerprints to classify the quality of representative commercial gasoline samples selected by Hierarchical Cluster Analysis (HCA) and collected over a 6-month period from different gas stations in the São Paulo state, Brazil. Following optimized the ^{1}H NMR-SIMCA algorithm, it was possible to correctly classify 92.0% of commercial gasoline samples, which is considered acceptable. The chemometric method is recommended for routine applications in Quality-Control Monitoring Programs, since its measurements are fast and can be easily automated. Also, police laboratories could employ this method for 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, whose boiling point range 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 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 a content of anhydrous ethanol between 20 and 25%, an amount not encountered in any other country [3].

The Brazilian Government's recent suspension of the state monopoly on fuel production and distribution has given rise to significant changes in the market. This event has opened up enormous opportunities both for established oil companies, newcomers, fuel dealers and gas stations, operated by national or foreign companies. This competition leads to a substantial variation of the price of fuel, while the quality of the product is not necessarily guaranteed [4].

Generally, quality control of fuels is ensured through the establishment of technical specifications, which vary in 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]. However, these specifications can be modified inadvertently through inadequate transport, handling and storage or through adulteration with some substances [6,7]. Unfortunately, the adulteration of automotive gasoline is becoming a common practice because of economic issues. In fact, fuel adulteration has worried the Brazilian Government 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 excess 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 are observed. Likewise low cost, lower tax rates and similar chemical composition are factors that contribute to their use in adulteration [8].

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Currently, in Brazil, a commercial gasoline quality is controlled by several technical specifications (namely physicochemical parameters) established by the Regulation ANP n° 309 [9]. All these specifications are obtained by analytical protocols covered by international guides, mainly from the American Society for Testing and Materials (ASTM International) [10]. 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 [10,11]. Using this methodology, previous studies have shown that physicochemical parameters are not enough to identify adulterations unless chemometrics techniques had been employed. Only adulterations using high levels of anhydrous ethanol, aromatic solvents or heavy aliphatic hydrocarbons can be identified by physicochemical parameters [4,13]. Thus, new alternative analytical methods must be developed to monitor such adulterations. Likewise, simple, fast and efficient methods to certify the quality and authenticity of the commercial fuels are desirable and, therefore recommended for routine applications in quality-control monitoring programs.

Usually, amongst all analytical techniques, gas chromatographic methods are employed for establishing adulteration in gasoline [5,11,14–18]. However, chromatographic techniques are generally slow, time-consuming and expensive for the analysis of a large number of samples, making impracticable its in routine application [19,20]. On the other hand, spectroscopy methods are quite suitable for such determinations [7,21,22]. Especially, nuclear magnetic resonance (NMR) spectroscopy has become a powerful tool for gasoline analysis without pre-treatment [19,20,23,24]. Besides that, ^{1}H NMR measurements are fast and can be easily automated, allowing the analysis of a large number of samples in a short period of time and, therefore recommended for routine applications in quality-control monitoring programs. In general, the spectrum is subdivided into regions, each of which is associated with a specific molecular substructure, for example, to aromatic, olefinic, and aliphatic hydrogens [24,25]. A huge amount of data in NMR fingerprinting is produced, and chemometric analysis is frequently needed to extract desired information. Chemometrics, which is the application of mathematical, statistical, and logical–mathematical methods to chemical issues, is capable of treating large quantities of information and has been used in different areas [26–29]. In this field, the pattern-recognition methods are divided into exploratory analysis, and classification algorithms. The first one is constituted by two techniques: Hierarchical Cluster Analysis (HCA) and Principal Component Analysis (PCA); while the last one is constituted by two algorithms: K-Nearest Neighbor (KNN) and Soft Independent Modeling of Class Analogy (SIMCA). Exploratory analysis (HCA and PCA) shows that the samples tend to separate themselves into clusters, indicating that analysis using classification algorithms (SIMCA or KNN) ought to succeed. Thus, the next stage of analysis will be to build classification models that can be used to predict which category a sample originates from. A survey of current literature demonstrates the utilization of these methods applied to the analysis of fuel to detect adulteration, especially, gasoline fuel [4,6–8,11–16,30,31]. Moreover, in regard to Brazilian commercial gasoline, many authors have studied its adulteration with the addition of petrochemical solvents [4,6–8,11–14,30]. Thus, the use of ^{1}H NMR fingerprintings coupled with pattern-recognition methods can be very useful for quality control of gasoline and other fuels. For our knowledge, this is the first application of pattern-recognition multivariate SIMCA chemometric analysis to ^{1}H NMR spectroscopic fingerprintings derived from commercial gasoline samples.

2. Experimental

2.1. Physicochemical parameters

The gasoline samples were provided by a laboratory responsible for monitoring the quality of automotive fuels, in particular, gasoline, ethanol and diesel oil. 2400 gasoline samples, collected randomly from different gas stations in São Paulo state, Brazil, over 6 months, were stored in polyethylene terephthalate flasks and transported in refrigerated boxes, following official ANP procedures [32,33]. 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 Regulation ANP n° 309, namely, atmospheric distillation temperatures required to reduce the original volume of the sample to 10%, 50% and 90%, distillation, final boiling point and distillation residue (ASTM D86) [34], relative density (ASTM D4052) [35], motor octane number, research octane number and anti-knock index (correlation to ASTM D2699/D2700) [36,37] and percentage (v/v) of benzene (ASTM D6277) [38], anhydrous ethanol (NBR 13992) [39] and hydrocarbons (saturates, olefins and aromatics—correlated to ASTM D1319) [40]. 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). From the physicochemical parameters it was possible to select representative gasoline samples by exploratory analysis (Hierarchical Cluster Analysis, HCA) for further ^{1}H NMR analyses.

2.2. ^{1}H NMR analyses

All ^{1}H NMR spectroscopic fingerprintings 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 fingerprinting 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 and 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. 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 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 this, SIMCA is a well-known multivariate supervised pattern-recognition method that constructs models using samples preassigned to a category, i.e., in this case, conform (meeting Brazilian specification) and nonconform (failing Brazilian specification).

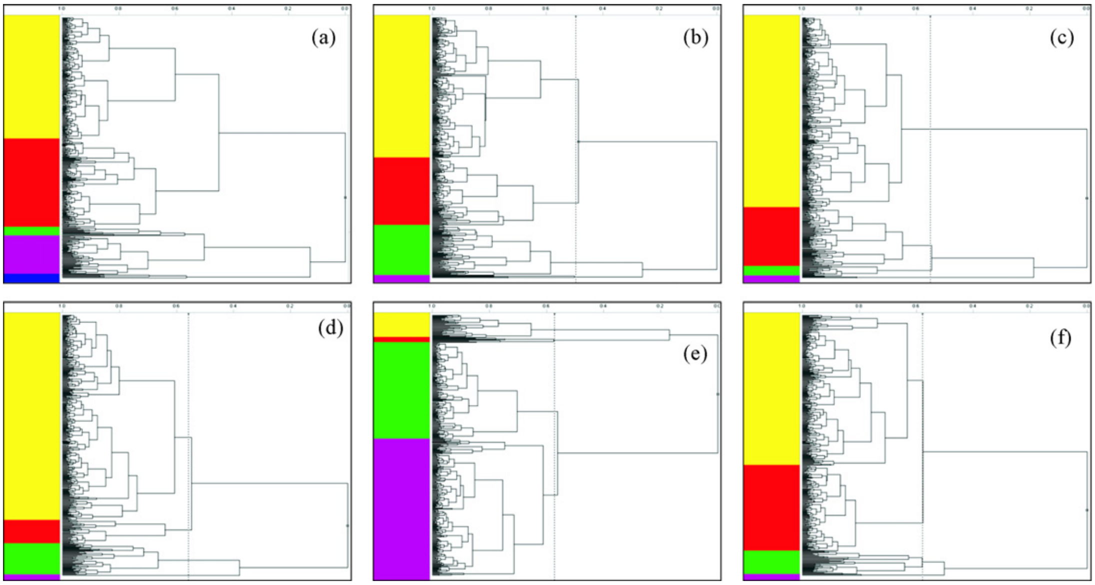

Fig. 1. Dendrograms for the selection of the 25 representative monthly gasoline samples that exhibited least similarity: (a) April, (b) May, (c) June, (d) July, (e) August and (f) September.

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 samples. 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, 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) [41] 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 ^{1}H NMR analysis.

SIMCA chemometric method was applied in order to build a screening model of multivariate pattern-recognition technique, which describes different classes of samples based on classification rules 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. To apply SIMCA modeling, ^{1}H NMR spectroscopic fingerprints of 150 representative gasoline samples were shifted to right or left as needed, with the TMS signal as the reference. ^{1}H 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 profile. These spectra profiles were saved as ASCII files and transferred to a PC for data analysis. The data matrix ($26\,713 \times 150 \times 2$; chemical shifts × representative gasoline samples × preassigned categories: conform and nonconform) were constructed and imported into Pirouette software (version 3.11, Infometrix Co., Woodinville, WA, USA) [41] for SIMCA algorithm. Each line in the matrix constitutes a sample, and the columns represent the number values obtained from the chemical shifts and intensities of the peaks. ^{1}H NMR spectra were normalized to 1-norm (the area under the sample profile is set equal to one), and the first derivative 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. ^{1}H 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, xylene, hexane, complex hydrocarbon mixtures, mineral spirits, kerosene, rubber solvent, petrochemical naphtha, diesel, and thinner, and these 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. Each monthly dendrogram, 25 representative gasoline samples that exhibited least similarity were selected for ^{1}H NMR analysis, maintaining the representatively of the dataset. Summary of physicochemical parameters values of representative commercial gasoline samples are presented in Table 1.

^{1}H NMR spectrum fingerprinting of gasoline is very complex, showing peaks almost in all spectral regions. A typical spectrum of Brazilian gasoline is shown in Fig. 2. From these it is not possible to see that many compounds present in adulterating solvents are also present in gasoline. Also, all spectroscopic fingerprints (Fig. 3)

Table 1
Summary of representative gasoline physicochemical parameters and its specification according to Regulation ANP n° 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, max (°C)	65.0, max	44.2	73.2	29.0	55.3
	50% Evaporated, max (°C)	80.0, max	63.3	116.5	53.2	72.9
	90% Evaporated, max (°C)	145.0–190.0	77.8	191.1	113.3	156.9
	Final boiling point, max (°C)	220.0, max	78.8	285.7	206.9	204.9
	Residue, max (% v/v)	2.0, max	0.4	2.8	2.4	1.0
	Octane numbers					
Correlation to ASTM D2699/2700	Motor octane number, min	82.0	77.4	87.2	9.8	82.2
	Research octane number, min	Not specified	89.8	98.4	8.6	95.0
	Anti-knocked index, min	87.0	84.6	91.4	6.8	88.6
	Hydrocarbons 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

are very similar from one gasoline to another, because the basic originating refinery processes are quite similar. Previous studies have made a detailed description about assignments of gasoline spectrum [19–23]. In general, classes of compounds (not individual ones) are associated with specific spectral regions. For example, aromatic compounds can be associated with peaks at 6.7–8.0 ppm, [21] and the region between 0.5 and 2.05 ppm contains signals mainly due to cycloalkanes (naphthenes) and normal and isoparaffins [19].

Clearly, visual inspection of spectroscopic profiles is not efficient in identifying the presence of adulterant solvents in gasoline (Fig. 3) and, therefore, to distinguish commercial gasoline 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 tool very useful and is often employed for gasoline discrimination. In this work, we chose the entire ^{1}H 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 models [7,11,15]. In this way, recently, Monteiro et al. [7] distinguish intentionally adulterated gasoline samples by organic solvents from ^{1}H NMR-PCA and ^{1}H NMR-HCA exploratory models, samples, which showed a tendency to meet in the nonconform group with the increase of the solvent concentration.

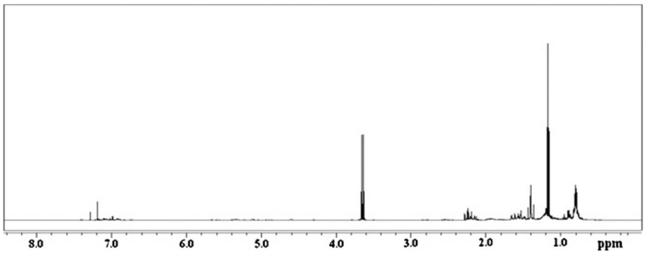

Fig. 2. ^{1}H NMR spectroscopic fingerprinting of a typical Brazilian commercial gasoline sample ($CDCl_3$, 500 MHz).

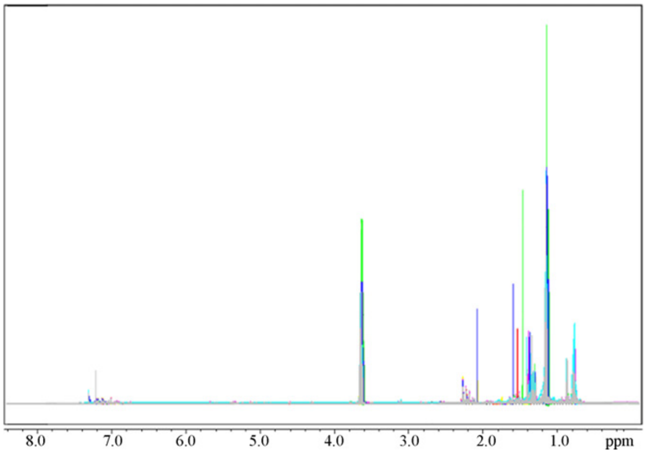

Fig. 3. Typical ^{1}H NMR spectroscopic fingerprints of all representative commercial gasoline samples ($CDCl_3$, 500 MHz).

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 Regulation ANP n° 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 (Fig. 4). As can be seen in Fig. 4, the dendrogram results in three different clusters (represented by *a*, *b* and *c*). In each cluster, a proportional number of samples were selected, such that in cluster *a* there were 32 samples, cluster *b*: 10 samples and cluster *c*: 8 samples.

Moreover, the probability threshold of the algorithm was based on a 95% confidence level, while several pretreatments and pre-processing were tested, and the best results were obtained when the first derivative and autoscaled were applied. The autoscale pre-processing was very important because it allowed the attribution of the same importance for all spectral regions. In SIMCA model, the 3D class projection (Fig. 5) provides a visual evaluation of the degree of class separation. To create this object, a three-factor principal component analysis was performed on the entire training set during the SIMCA processing. It was also possible to see a relative good segregation between samples in the scores hyperboxes. Also, a close examination of the SIMCA 3D results showed a slight overlap between few 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 pro-

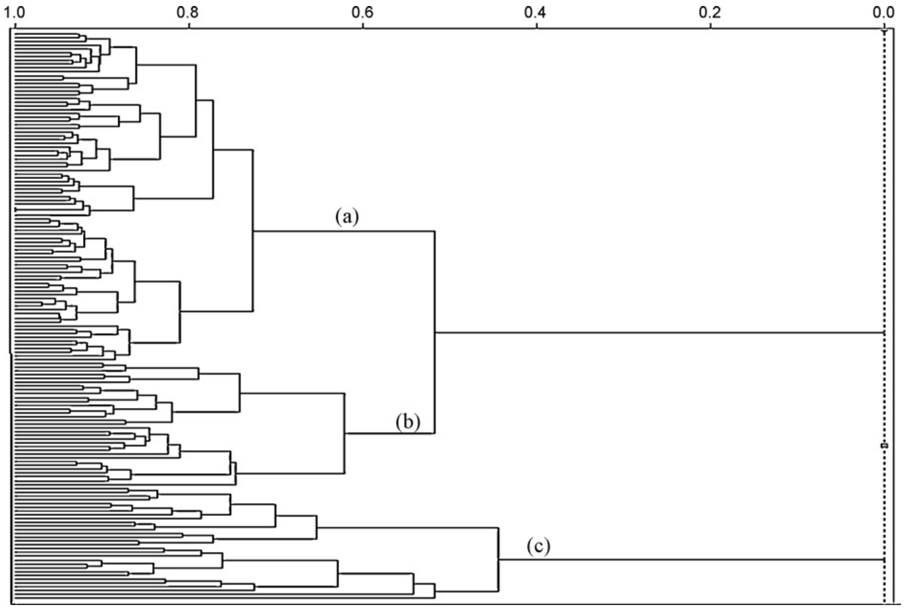

Fig. 4. Dendrogram for the prediction set selection of 50 representative samples of the dataset: (a) 32 samples, (b) 10 samples and (c) 8 samples.

jected into this three-factor principal component space; they form a confidence interval for the distribution of the category. Fig. 5 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 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, mainly, nonconform samples.

In SIMCA model training set, three principal components accounted approximately 70.0% of the total within-set variance and correctly classified all samples, except for a few ones. The misclassifications may be associated to final boiling point (FBP) and motor octane number (MON) physicochemical parameters, measured and correlated according to ASTM standard procedures (Table 3). Hence, 94.0% of the samples were correctly classified by application of the SIMCA method. Based on these findings, it may be concluded that the modeling power of the training set was satisfactory.

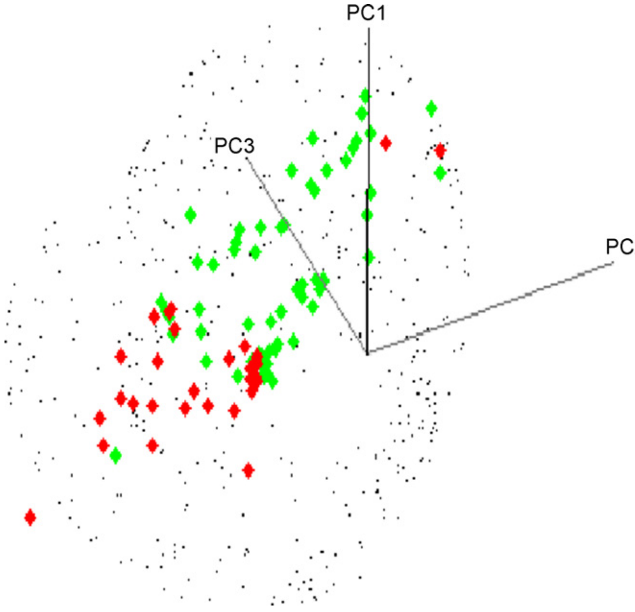

Fig. 5. SIMCA class 3D projections of samples in the training set on score plots. *Note*: Green and red points represents conform and nonconform classes, respectively. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of the article.)

Lastly, 50 new samples, the external prediction set, were used to evaluate the model. While all samples were clearly well segregated, seven of them were apparently misclassified according to the SIMCA model: six nonconform samples were classified as conform to ANP regulations and one sample conformed to ANP specifications was classified as nonconform by SIMCA (Table 3). As in the training set model, the misclassifications may be associated mainly to motor octane number (MON) physicochemical parameter (Table 3). Another misclassification physicochemical parameter was related to FBP, T90 and AE values. In MON values cases, the physicochemical results were not conclusive, because the values were very near to the limits established by Regulation ANP n° 309 and were certainly within the confidence limits of the method used (0.5 for MON). In this parameter, three samples showed values between 81.4 and 81.9, while the minimum permitted value is 82.0. Therefore, none of these parameters can be considered significantly different from the limiting values when the confidence limits are taken into account. In contrast, sample 20-June had a FBP temperature of 230.6 °C and samples with anhydrous ethanol (AE) content between 28 and 44%, which significantly exceed the allowed limits, clearly misclassifying them according to the SIMCA model. Furthermore, sample 5-May fully conforms to Regulation ANP n° 309, but was misclassified by the SIMCA model. Based on these findings, 92.0% of the samples in the prediction set were correctly classified by application of

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	1	0	1
Non-conform class	0	5	0	6

Table 3
Physicochemical parameter values associated with Regulation ANP n° 309 for misclassified gasoline samples in the training and prediction sets by the SIMCA model. Entries in bold and italic font indicate parameters non-conform 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														
20 – April	0.7572	61.4	74.7	176.4	202.6	***81.2***	93.6	87.4	0.25	44.8	15.0	13.9	26	1.2
24 – April	0.7560	58.5	73.0	172.7	210.6	***81.8***	94.6	88.2	0.40	44.5	16.5	14.7	25	0.9
11 – May	0.7379	52.6	71.5	153.3	200.8	82.5	95.3	88.9	0.48	39.1	20.1	15.9	26	0.9
10 – June	0.7540	53.7	72.5	166.6	***270.8***	82.4	95.5	89.0	0.44	32.6	26.6	15.1	25	1.2
23 – June	0.7553	57.3	72.6	167.5	208.9	***81.8***	94.6	88.2	0.42	45	14.9	16.1	25	0.6
11 – July	0.7526	55.4	72.7	161.9	***232.7***	82.4	95.5	89.0	0.43	35.3	24.1	15.3	26	***2.6***
Misclassified samples in the prediction set by SIMCA model														
14 – April	0.7465	52.2	72.5	171.3	203.7	***81.9***	94.4	88.2	0.42	41.4	18.9	16.0	24	1.0
3 – May	0.7527	54.0	73.8	160.1	204.0	83.2	96.7	90.0	0.45	32.7	25.9	14.1	***28***	0.7
5 – May	0.7472	55.1	72.3	153.4	189.9	82.8	95.5	89.2	0.37	34.6	24.6	16.0	25	0.7
10 – May	0.7581	56.1	74.8	***134.8***	194.7	***80.9***	94.6	87.8	0.32	55.2	0.0	10.4	***44***	0.7
20 – June	0.7522	55.3	72.8	161.8	***230.6***	82.0	95.0	88.5	0.39	38.2	22.0	14.5	25	1.4
6 – August	0.7556	53.4	72.2	157.9	201.3	***81.7***	95.4	88.8	0.32	28.5	28.0	18.1	25	0.9
8 – August	0.7616	56.9	74.5	176.0	207.6	***81.4***	95.2	88.3	0.29	28.4	28.6	17.6	25	1.2

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.

the SIMCA method. From this it may be concluded that the modeling power was satisfactory and perfectly acceptable. Therefore, ^{1}H 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. These results proved that ^{1}H NMR-SIMCA algorithm allow the segregation commercial gasolines into their quality.

4. Conclusions

An analytical method, based on pattern-recognition SIMCA chemometric analysis of ^{1}H NMR spectroscopic fingerprinting, has been developed in order to determine the quality specified by Regulation ANP n° 309 of Brazilian commercial gasoline. The ^{1}H NMR technique has a high potential to determine the quality of Brazilian commercial gasoline and 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 ^{1}H NMR-SIMCA algorithm, as alternative analytical methodology, offers an appealing procedure for commercial automotive gasoline quality control by government agency laboratories. 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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