

# Study of Brazilian Gasoline Quality Using Hydrogen Nuclear Magnetic Resonance ( $^1\text{H}$ NMR) Spectroscopy and Chemometrics

Marcos R. Monteiro,<sup>\*,†</sup> Alessandra R. P. Ambrozini,<sup>†</sup> Luciano M. Lião,<sup>‡</sup> Elisângela F. Boffo,<sup>§</sup> Leila A. Tavares,<sup>§</sup> Márcia M. C. Ferreira,<sup>||</sup> and A. Gilberto Ferreira<sup>§</sup>

Centro de Caracterização e Desenvolvimento de Materiais, Departamento de Engenharia de Materiais, Universidade Federal de São Carlos, Rodovia Washington Luiz, km 235, CEP 13560-971, São Carlos, São Paulo, Brazil, Instituto de Química, Universidade Federal de Goiás, Campus Samambaia, CP 131, CEP 74001-970, Goiânia, Goiás, Brazil, Departamento de Química, Universidade Federal de São Carlos, Rodovia Washington Luiz, km 235, CEP 13560-605, São Carlos, São Paulo, Brazil, and Instituto de Química, Universidade de Campinas, Cidade Universitária, CEP 13083-970, Campinas, São Paulo, Brazil

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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 use of hydrogen nuclear magnetic resonance ( $^1\text{H}$  NMR) with a statistical approach for identifying gasoline adulteration by organic solvents is described. Both principal component analysis (PCA) and hierarchical cluster analysis (HCA) from NMR data of 47 commercial samples allowed the distinction between conform and nonconform samples. The  $^1\text{H}$  NMR–PCA and  $^1\text{H}$  NMR–HCA models were evaluated through the analyses of 21 intentionally adulterated samples, which showed a tendency to meet in the nonconform group with the increase of the solvent concentration.

## 1. Introduction

Gasoline is a petroleum-derived product constituted by a complex mixture of liquid aliphatic and aromatic hydrocarbons, ranging from  $\text{C}_4$  to  $\text{C}_{12}$  carbon atoms, whose boiling point range is 30–225 °C. A typical gasoline is predominantly a mixture of paraffins (alkanes), naphthenes (cycloalkanes), aromatics, and olefins (alkenes), 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 chemical composition of gasoline.<sup>1,2</sup> In Brazil, the gasoline used as fuel in internal combustion engines (called gasoline C) may have a content of anhydrous ethanol between 20 and 25%.

Generally, quality control of fuels is ensured through the establishment of technical specifications. However, these specifications can be modified inadvertently through inadequate transport, handling, and storage or through adulteration with some substances.<sup>3,4</sup> Unfortunately, the adulteration of automotive gasoline is becoming a common practice because of economic issues. In 2006, 10% from the 24.0 billion L of the commercial-

ized gasoline was adulterated with organic solvents.<sup>5</sup> In fact, fuel adulteration has worried the Brazilian National Agency of Petroleum, Natural Gas, and Biofuels (ANP) not only for quality control reasons but also for tax evasion. Adulteration involving the addition of organic solvents, such as light aliphatic ( $\text{C}_4$ – $\text{C}_8$ ), heavy aliphatic ( $\text{C}_{13}$ – $\text{C}_{15}$ ), and aromatic hydrocarbons, is one of the possibilities that is observed. Especially, benzene, toluene, xylenes, hexane, complex hydrocarbon mixtures, mineral spirits, kerosene, rubber solvent, petrochemical naphtha, diesel, and thinner have been used to carry out the adulteration.<sup>3,6–9</sup> The low cost, lower tax rates, and similar chemical composition between solvents and gasoline are factors that contribute to their use in adulteration.<sup>9</sup> Actually, most of the compounds that compose organic solvents are already in gasoline, but their amounts are limited. The excessive amount of these solvents in gasoline may lead to engine damage, rubber degradation, and environmental hazards, as well as tax evasion.<sup>4,6,7</sup>

In Brazil, several physicochemical parameters, established by ANP regulation number 309/2001, are employed to the quality control of gasoline, including the determination of color, relative density, temperatures equivalent to 10, 50, and 90% distilled volume, final evaporation point, flash point, octane numbers (MON and RON), benzene, etc. However, it is not always possible to identify gasoline adulteration using these tests because many solvents are very similar to gasoline, and

\* To whom correspondence should be addressed. Telephone: +55-16-33518844. Fax: +55-16-33518850. E-mail: monteiro@ccdm.ufscar.br.

<sup>†</sup> Departamento de Engenharia de Materiais, Universidade Federal de São Carlos.

<sup>‡</sup> Instituto de Química, Universidade Federal de Goiás.

<sup>§</sup> Departamento de Química, Universidade Federal de São Carlos.

<sup>||</sup> Instituto de Química, Universidade de Campinas.

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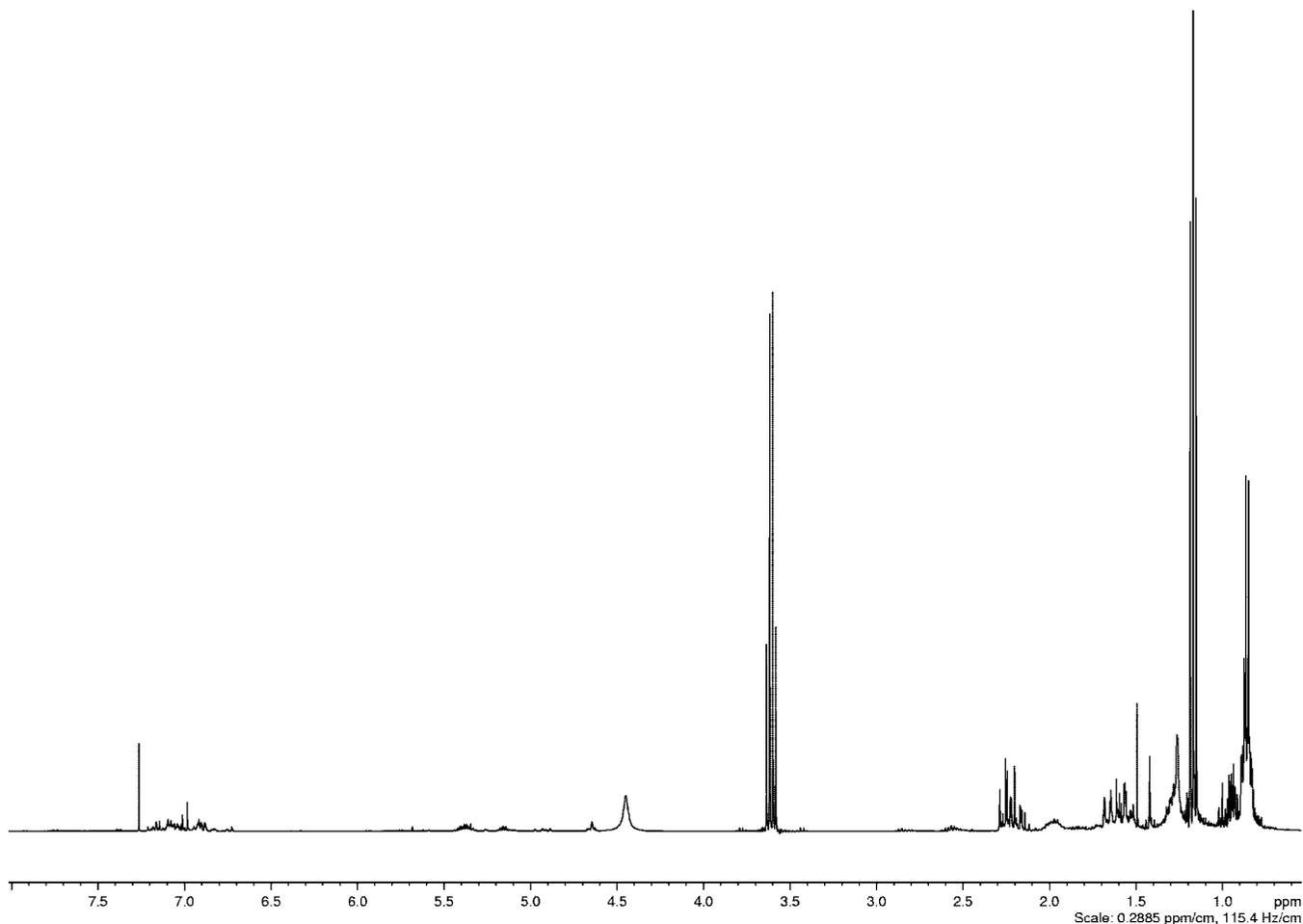
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**Figure 1.**  $^1\text{H}$  NMR spectrum of a typical gasoline sample ( $\text{CDCl}_3$ , 400 MHz).

consequently, physicochemical parameters are usually not efficient for detecting adulteration.<sup>2,10,11</sup> Actually, some works have shown that physicochemical measurements are not enough to identify most of adulterations unless chemometric techniques had been employed.<sup>5</sup> In general, only adulterations using high levels of aromatic solvents or heavy aliphatic hydrocarbons can be identified by physicochemical parameters.<sup>6,7,12</sup> Recently, the Brazilian government determined the use of solvent markers to help their identification in gasoline. However, few laboratories are authorized to analyze such markers, and the procedure has high cost to the country.<sup>2,10,11</sup> Thus, new analytical methods must be developed to monitor such adulterations.

Usually, chromatographic methods are employed for establishing adulteration in gasoline. Frequently, gasoline and related petroleum products are analyzed by gas chromatography.<sup>2,6-8,10,13-20</sup> However, chromatographic techniques are generally slow, time-consuming, and expensive for the analysis

of a large number of samples.<sup>8,13,21,22</sup> On the other hand, spectroscopy methods are quite suitable for such determinations.<sup>1,4,9,21,23-35</sup> Especially, nuclear magnetic resonance (NMR)

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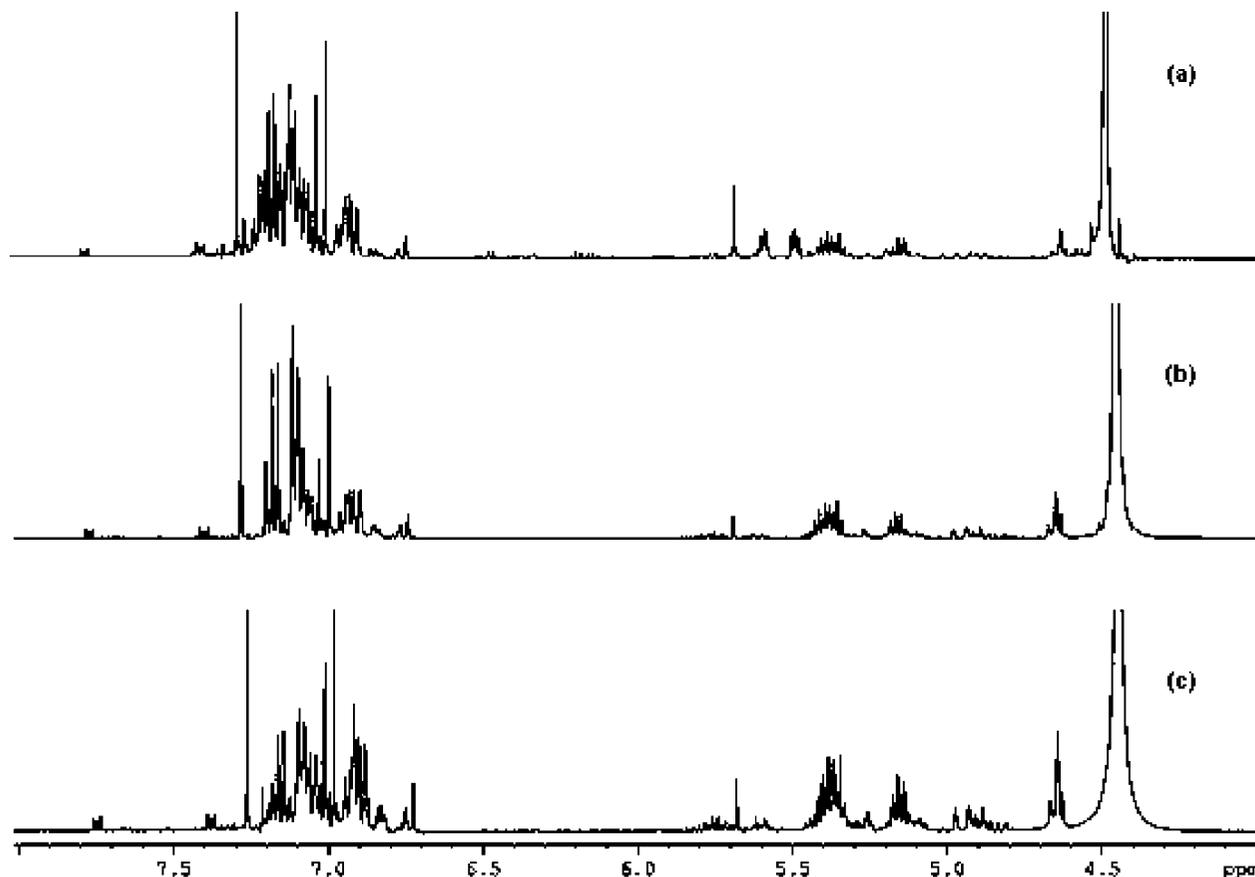


Figure 2. Expanded region of  $^1\text{H}$  NMR spectra of (a and b) nonconform and (c) conform gasoline.

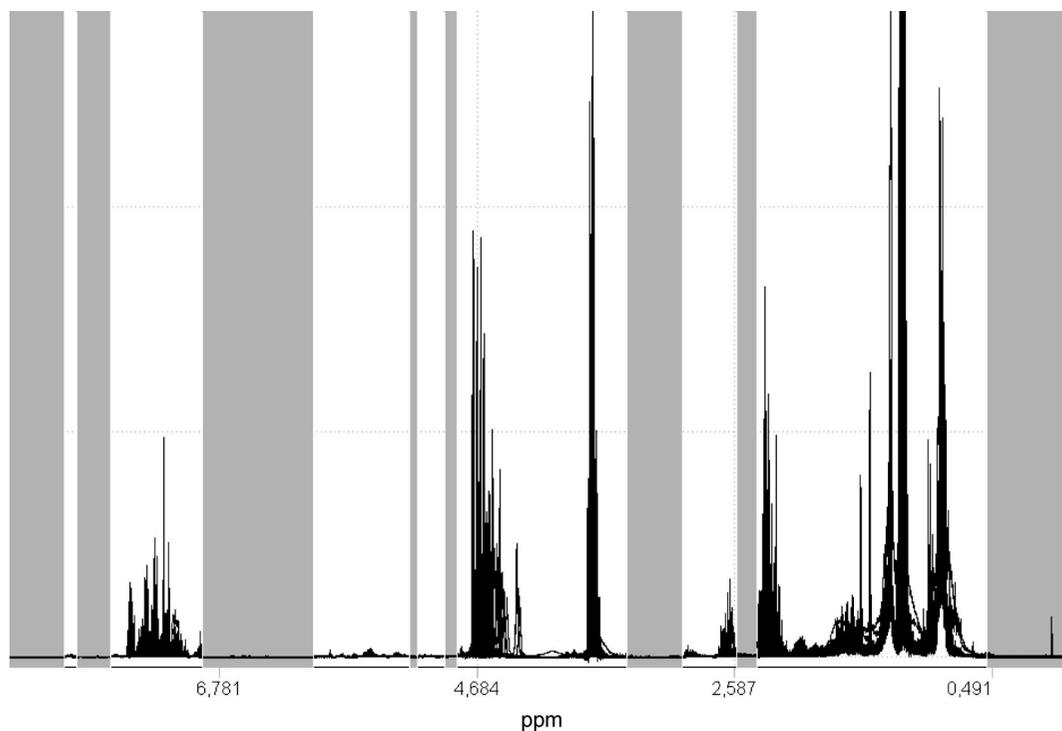


Figure 3. Selected spectral regions used in statistical analyses (excluded regions are shown in gray).

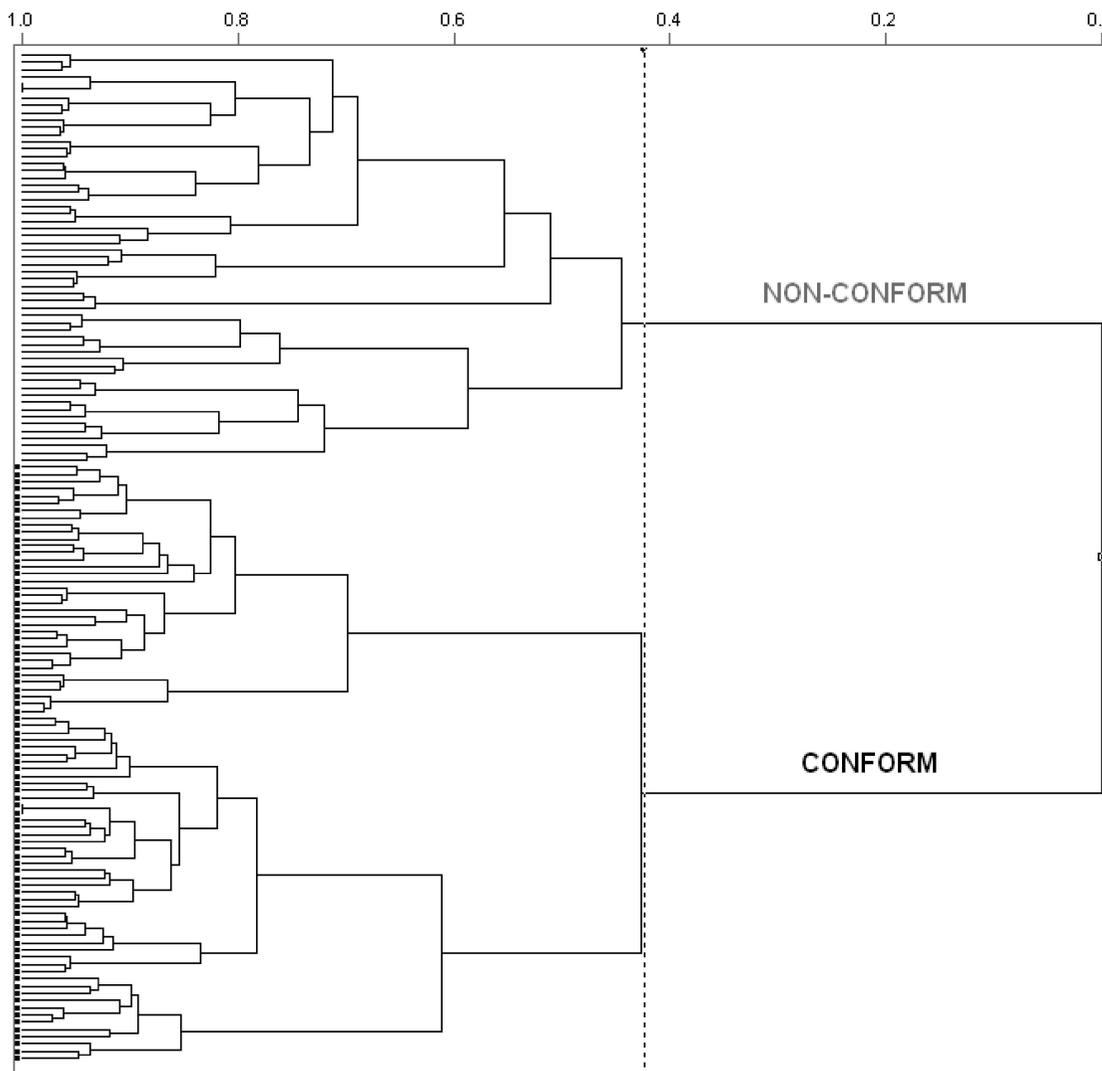
spectroscopy has become a powerful tool for gasoline analysis without the need of any physical separation or pretreatment.<sup>13,16,22,36–38</sup> Besides that,  $^1\text{H}$  NMR measurements are fast and can be easily

automated, allowing the analysis of a large number of samples in a short period of time. In fact, because of complexity spectral and strong spectral overlapping, few single compounds in gasoline (benzene and oxygenates) can be individually identified and quantified by the analysis of a single  $^1\text{H}$  NMR spectrum. In general, the spectrum is subdivided into regions, each of which is

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**Figure 4.** HCA dendrogram obtained from  $^1\text{H}$  NMR data of gasoline samples (similarity index: 0.424).

associated with a specific molecular substructure, for example, to aromatic, olefinic, and aliphatic hydrogens.<sup>13,16,36,37</sup> A huge amount of NMR data 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.<sup>39</sup> In fact, several studies have demonstrated that chemometric techniques are very useful to the analysis of gasoline and other petrochemical products.<sup>1–5,10,11,14,15,17,19,20,25,30–32,34,35,40,41</sup> Thus, the use of NMR together with chemometrics can be very useful for quality control of gasoline and other fuels.

In this work, a reliable  $^1\text{H}$  NMR method using multivariate statistical analyses, especially hierarchical cluster analysis (HCA) and principal component analysis (PCA), was developed for evaluating gasoline quality. Such analyses allowed the discrimination between conform and nonconform samples, which was in agreement with the physicochemical results. The  $^1\text{H}$  NMR–PCA and  $^1\text{H}$  NMR–HCA classification model efficiencies were confirmed through the analyses of some conform gasoline samples intentionally adulterated with alkyl-

benzene-9, “aliphatic solvent”, toluene, xylenes, hexane, varsol, and turpentine.

## 2. Experimental Section

**2.1. Material.** A total of 47 gasoline samples were randomly acquired in different gas stations in São Paulo state, in Brazil. The commercial solvents used (alkylbenzene-9, “benzene”, toluene, xylenes, hexane, varsol, and turpentine) were kindly supplied by a paints and varnishes industry. It is important to mention that the  $^1\text{H}$  NMR analyze of the “benzene” showed that, in fact, this solvent was mainly composed by aliphatics. Therefore, we used the denomination “aliphatic solvent” for it.

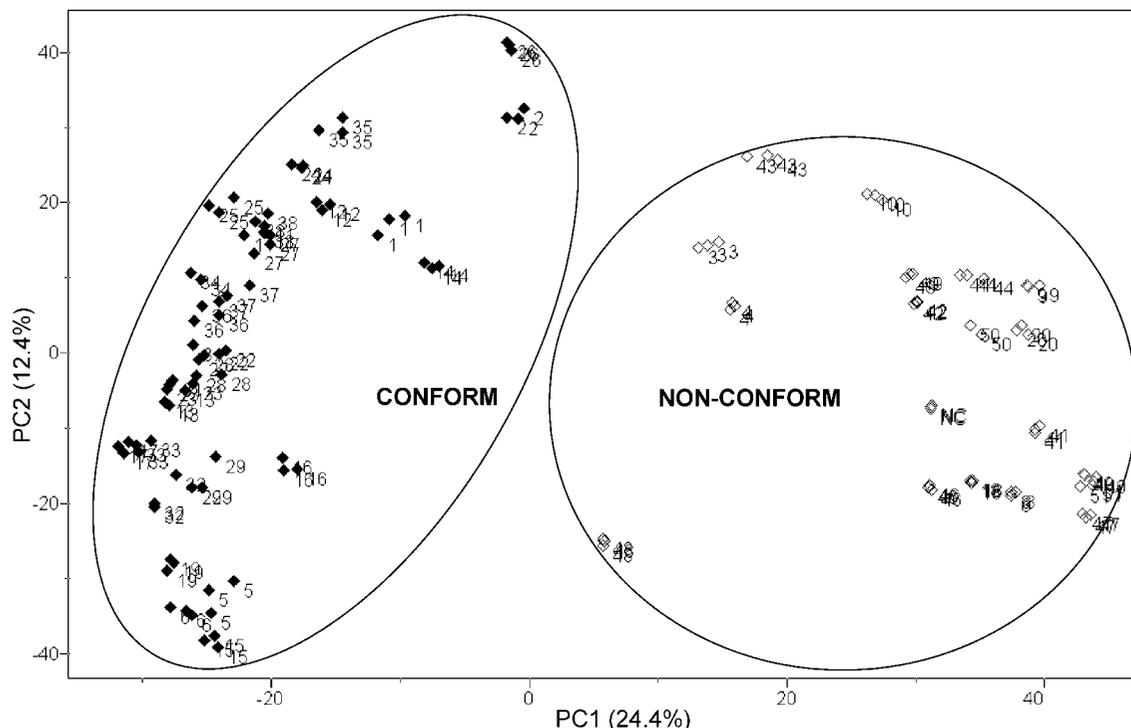
**2.2. Gasoline Samples Collection.** Gasoline samples were stored in polyethylene terephthalate flasks and transported in refrigerated boxes below 10 °C, according to ANP procedures. These samples were previously analyzed by some physicochemical parameters established in the ANP regulation 309, namely, aspect, color, density, distillation, octane numbers (MON and RON), and percentage of benzene, anhydrous ethanol, and hydrocarbon. According to these results, the samples were classified in two groups: conform (meeting Brazilian specification) and nonconform (failing Brazilian specification). All of them were selected for  $^1\text{H}$  NMR analyses and were used to create the data set. Subsequently, one conform gasoline sample was used in the preparation of intentionally adulterated samples.

**2.3. Adulterated Sample Preparation.** Seven groups of purposely adulterated samples were prepared in our laboratory using one “standard” conform gasoline and 5, 10, and 20% (v/v) of individual

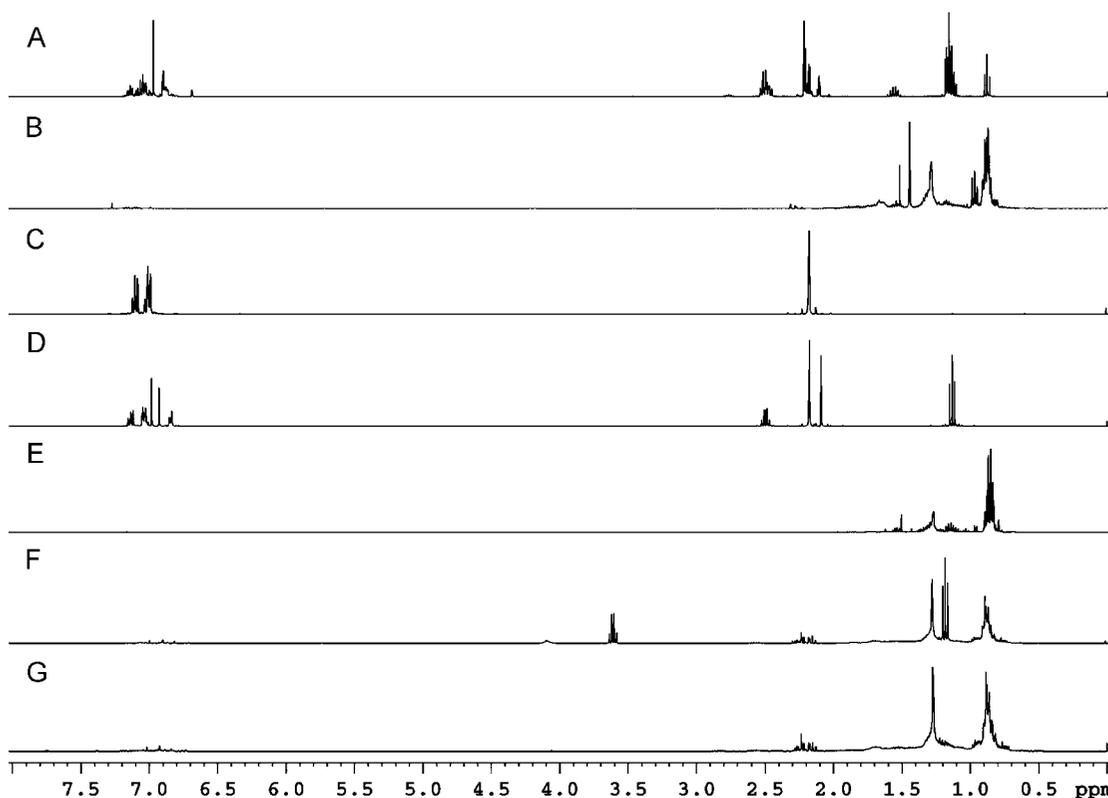
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**Figure 5.** PCA scores plot (PC1 versus PC2) obtained from  $^1\text{H}$  NMR data of gasoline samples, 36.8% of the total variance (NC = “standard” nonconform gasoline).

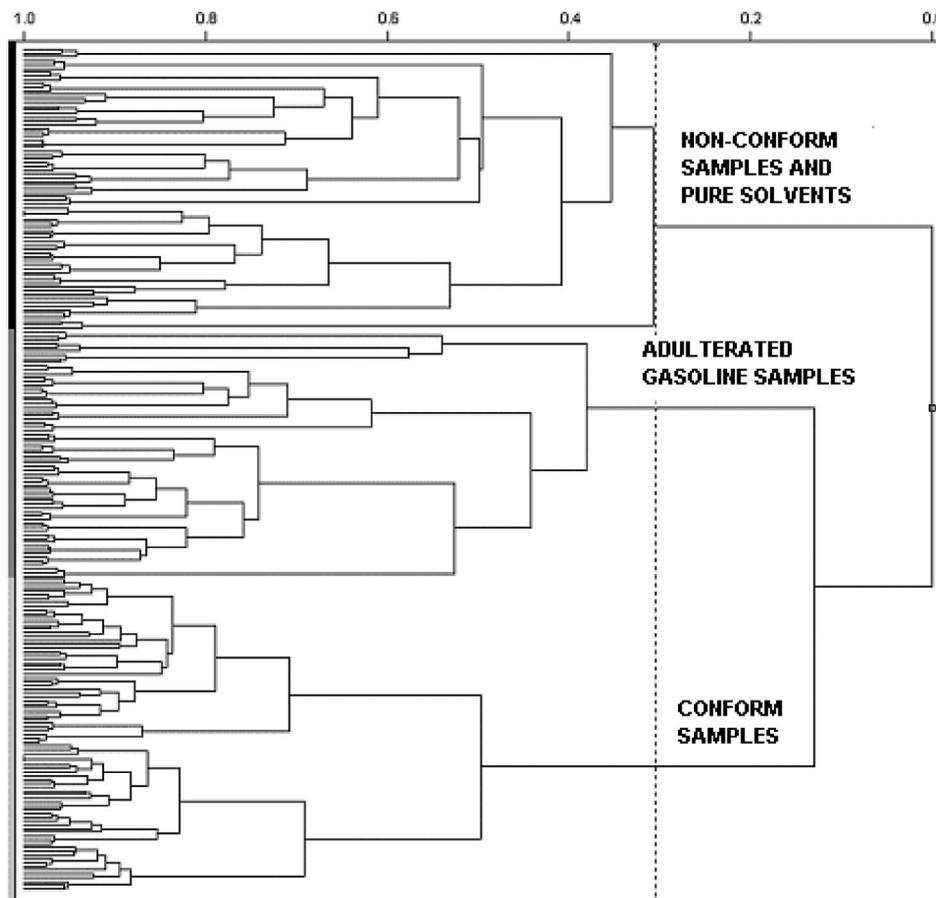


**Figure 6.**  $^1\text{H}$  NMR spectra of solvents ( $\text{CDCl}_3$ , 400 MHz): (A) AB-9, (B) “aliphatic solvent”, (C) toluene, (D) xylenes, (E) hexane, (F) turpentine, and (G) varsol.

organic solvents. The solvents used were alkylbenzene-9, “aliphatic solvent”, toluene, xylenes, hexane, varsol, and turpentine. Such samples were used to test the quality of the discrimination performed by the statistical approach (HCA and PCA).

**2.4. Physicochemical Analyses.** According to standards and specific techniques, aspect (visual inspection), color (visual inspection), density (ABNT NBR 7148, ASTM D 1298), distillation

profile (ASTM D 86), octane numbers (MON, motor octane number; and RON, research octane number) (infrared spectroscopy), antiknock indices (infrared spectroscopy), and percentage of benzene (ASTM D 6277), anhydrous ethanol (ABNT NBR 13992), and hydrocarbon (infrared spectroscopy) were determined for all samples, and the results were compared to the ANP specifications.



**Figure 7.** HCA dendrogram obtained from  $^1\text{H}$  NMR data of gasoline samples, intentionally adulterated gasoline samples, and organic solvents (similarity index = 0.304).

The instruments employed in the analyses were an automatic distiller (W. Herzog HDA628), a digital densimeter (Anton Paar DMA4500), and an infrared analyzer (Petrospec GS-1000).

**2.5. NMR Analyses.** All  $^1\text{H}$  NMR experiments were acquired in triplicate and at room temperature on a Bruker DRX 400-9.4 T spectrometer, using a 5 mm inverse-detection probehead with z-gradient. The spectra were obtained at 400.21 MHz for  $^1\text{H}$ , using  $\text{CDCl}_3$  as the solvent and tetramethylsilane (TMS) as the internal standard. For each analysis, 500  $\mu\text{L}$  of gasoline sample was dissolved in 200  $\mu\text{L}$  of solvent. The spectra were obtained using  $90^\circ$  rf pulse (8.5  $\mu\text{s}$ ), a spectral width of 3811 Hz, 8 transients with 64 000 data points, an acquisition time of 8.6 s, and relaxation delays of 1 s. They were processed with 32 000 data points and using an exponential weighing factor corresponding to a line broadening of 0.1 Hz. The phase and baseline were manually corrected using the Bruker software.

**2.6. Statistical Data Analyses.** First of all, the  $^1\text{H}$  NMR spectra of 75 samples (47 commercial samples, 21 intentionally adulterated gasoline, and 7 solvents) were shifted to right or left as needed, with the TMS signal as the reference. Then, such spectra were saved as ASCII files and transferred to a PC for data analysis. The data matrix were constructed using the Origin software (version 5.0, Microcal, Northampton, MA) and, thus, the matrix (4099  $\times$  225) was imported into the Pirouette software (version 3.11, InfoMetrix, Woodinville, WA) for PCA and HCA.<sup>42</sup> 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. Because the 75 samples were analyzed in triplicate, there are 225 lines in the matrix. The 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-

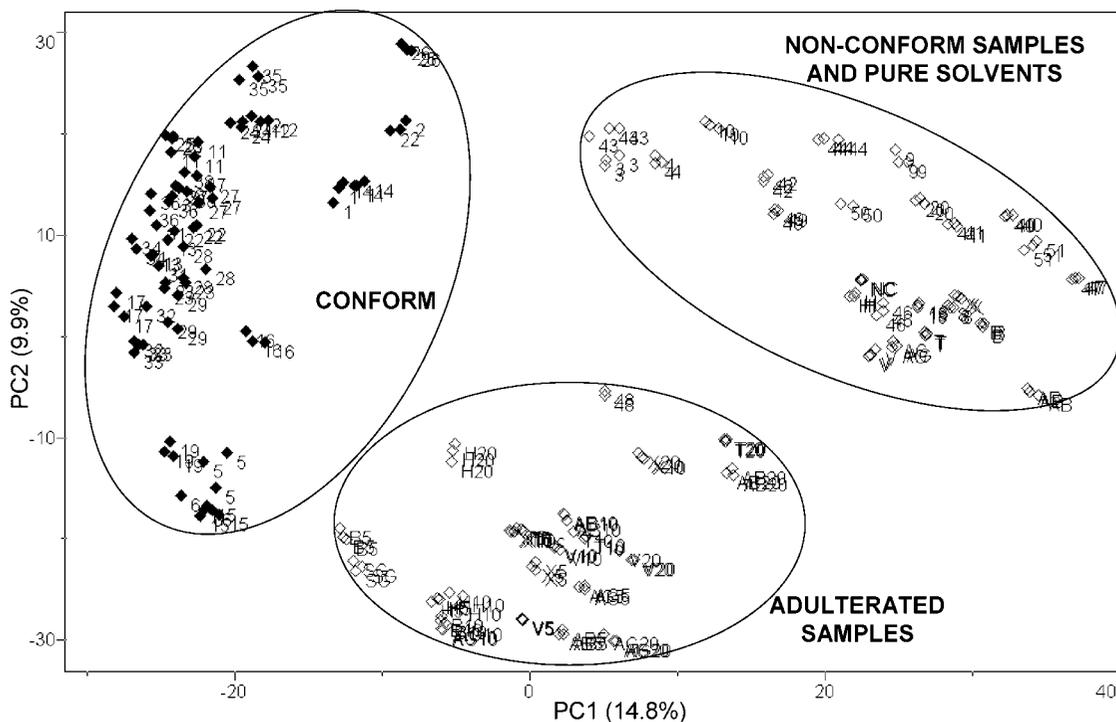
centered and scaled to unity variance, was applied to give each variable equal weight, and therefore, large and small peaks were treated with equal emphasis. PCA was applied to the data set for exploring the data and for feature selection, excluding noises,  $\text{CDCl}_3$ , and TMS regions. The ethanol peaks ( $\text{CH}_2$  in the 3.67–3.58 ppm range, *q*, and  $\text{CH}_3$  in 1.2–1.15 ppm, *t*) were also selected for the construction of the matrix. In HCA, the Euclidean distances among samples were calculated and transformed into similarity indices ranging from 0 to 1 using the incremental linkage method.

### 3. Results and Discussion

$^1\text{H}$  NMR spectrum of gasoline is very complex, showing peaks almost in all spectral regions. A typical spectrum of Brazilian gasoline is shown in Figure 1. Some works made a detailed description about assignments of gasoline spectrum.<sup>13,16,22,36–38</sup> 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,<sup>36</sup> and the region between 0.5 and 2.05 ppm contains signals mainly due to cycloalkanes (naphthenes) and normal- and iso-paraffins.<sup>13</sup>

Clearly, a simple visual inspection of conform (meeting Brazilian specification) and nonconform (failing Brazilian specification) gasoline spectra (Figure 2) is not enough to distinguish them. In this figure, a nonconform gasoline seems to be more similar to a conform than to a nonconform one. Therefore, statistical approach is a tool very useful and is often employed for gasoline discrimination. In this work, we chose the entire  $^1\text{H}$  NMR spectrum (except noises,  $\text{CDCl}_3$ , and TMS regions) for the statistical analysis because the choice of a large number of peaks allows us to achieve a more reliable clas-

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**Figure 8.** PCA scores plot (PC1 versus PC2) obtained from  $^1\text{H}$  NMR data of gasoline samples, intentionally adulterated gasoline samples, and organic solvents, 24.7% of the total variance (AB, AB-9; AG, turpentine; B, “aliphatic solvent”; H, hexane; T, toluene; X, xylenes; V, varsol; and SG, “standard” conform gasoline used for preparing adulterated samples).

sification model.<sup>2</sup> The selection of the regions was also based on PCA-loading graphs. The ethanol peaks were included in the data for the construction of the matrix. However, statistical analyses were carried out excluding such peaks, and the classification was identical to the previous one. The selected spectral regions are illustrated in Figure 3, which shows overloaded spectra of conform and nonconform gasolines (the excluded regions are shown in gray).

A total of 47 gasoline samples, collected in different gas stations of Brazil, were first submitted to physicochemical analyses (aspect, color, density, distillation profile, octane numbers, antiknock indices, and percentage of benzene, anhydrous ethanol, and hydrocarbon), which allowed their discrimination as conform and nonconform samples. Distillation profile, MON, antiknock indices, and percentage of anhydrous ethanol were the main off-specification parameters obtained for the nonconform samples.

The same samples were submitted to  $^1\text{H}$  NMR spectroscopy, and the spectral data were analyzed by methods of multivariate exploratory analysis: HCA (Figure 4) and PCA (Figure 5).

Several pretreatments were tested, and the best results were obtained when the first derivative and normalization were applied to the samples. The resulted data were autoscaled. This autoscale preprocessing was very important because it allowed the attribution of the same importance for all spectral regions.

In the HCA analysis, the Euclidean distance was used as metric and an incremental linkage method was employed. The resultant dendrogram (Figure 4) was useful to obtain preselected profiles of high similarity. Figure 4 shows two main clusters, which represent two distinct groups separated for the high similarity of their compositions. Each group was constituted of similar samples in relation to their spectral data. With a similarity index of 0.424, the data were discriminated in a conform gasoline sample group and a nonconform one.

Similarly to HCA, PCA analysis allowed the distinction between conform and nonconform groups. The PCA scores plot,

obtained from the first two principal components (PC1 and PC2), indicated similarity among the samples; similar samples tended to form clusters. PC1 described 24.4% of the total variance, while PC2 described 12.4%; the two PCs together express 36.8% of the original information. In this way, PC1 versus PC2 scores plot (Figure 5), obtained from NMR data of the 47 commercial gasoline, shows the conform samples with negative scores and the nonconform samples with positive scores. Figure 3 shows that both intensity and chemical shifts of the peaks, especially those related to aromatics, alkenes, and ethyl- and methylbenzenes compounds, allowed the discrimination between conform and nonconform gasolines.

Therefore,  $^1\text{H}$  NMR data and statistical analyses 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.

We also chose the same  $^1\text{H}$  NMR spectral regions (Figure 3) to the statistical analysis of intentionally adulterated samples. Therefore, the quality models obtained by  $^1\text{H}$  NMR–HCA and  $^1\text{H}$  NMR–PCA was evaluated through analyses of some conform gasoline contaminated (individually) with alkylbenzene-9 (AB-9), “aliphatic solvent”, toluene, xylenes, hexane, varsol, and turpentine. The NMR spectra of these solvents (Figure 6) showed that they have peaks in the same regions as gasoline, because many compounds present in the solvents also belong to gasoline. This coincidence between gasoline peaks and those relate to some compounds present in solvents was expected, because solvents are also petroleum-derived and most of their compounds are already in gasoline but in limited concentrations.

The dendrogram and the PC1 versus PC2 scores plot obtained from NMR data of the 47 commercial gasoline samples, intentionally adulterated gasoline samples, and pure organic solvents are shown in Figures 7 and 8, respectively.

The dendrogram obtained from HCA (Figure 7) showed that, with a similarity index of 0.304, three distinct groups could be identified: one group related to nonconform gasoline and pure solvents, another group related to intentionally adulterated samples, and the last group related to conform gasoline.

With regard to the PCA analysis (Figure 8), the first two PCs captured 24.7% of the variance. PC1 described 14.8% of the total variance, while PC2 described 9.9%. These statistical results indicated a tendency of migration of the adulterated samples from the negative score region, where conform samples are located, to the positive score area, where nonconform gasoline samples and pure organic solvents are clustered. This tendency is directly related to the increase of the organic solvent concentration in the gasoline. Figure 8 provides evidence that 5% of adulteration is quite difficult to be detected. Except for the AB5 sample, all purposely adulterated samples with 5% of solvent were with negative scores. Also, light solvents, such as hexane and "aliphatic solvent", were not detected up to 20%. In fact, some works demonstrated that the detection of the adulteration is only possible if the solvent concentration will have a specific value. Generally, if the quantity of adulterant added is not very high, not even the most sophisticated techniques can be used to qualify or quantify the added solvent.<sup>12</sup> For example, Dhole and Ghosal<sup>43,44</sup> verified that the detection of gasoline adulteration by kerosene is only possible if its concentration is close to 5%. Similar results were also obtained by Gaião et al.<sup>33</sup> However, Pedrosa et al.<sup>19</sup> developed a gas chromatography (GC)  $\times$  GC-flame ionization detector (FID) method using multiway partial least-squares regression (N-PLS), which allowed the identification of kerosene, white spirit, and thinner in concentrations upper than 3.3%. Lately, de Godoy et al.<sup>20</sup> also described the use of GC  $\times$  GC-FID and chemometrics to determine kerosene in gasoline in minimum concentrations of 2.08%. Moreira et al.<sup>8</sup> determined (through GC analyses) that gasoline adulteration is possible to detect when the solvent is added over 5.5% for aromatic hydrocarbons and over 28% for light aliphatic hydrocarbons. Besides that, the authors pointed out that the adulteration by heavy aliphatic hydrocarbons is easier to detect. Subsequently, Wiedemann et al.<sup>7</sup> have shown that gasoline adulteration by aromatic and light aliphatic hydrocarbon solvents is only possible to be detected when the solvent addition exceeds 19.5% for aromatics and 28% for light

aliphatics. On the other hand, Pereira and co-workers,<sup>9</sup> employing Fourier transform infrared (FTIR) spectroscopy and PCA-linear discriminant analysis (LDA), demonstrated that solvent concentrations up to 8% are enough to identify gasoline adulteration by solvents. Recently, Skrobot et al.<sup>11</sup> showed that samples containing a low solvent concentration (<6%, v/v) were not easily distinguished from pure gasoline in a GC-PCA analysis. These authors also pointed out that gasoline adulteration by organic solvent is, in general, performed in concentrations higher than 2% (v/v).

Finally, the results from this work pointed out that NMR-PCA and NMR-HCA are suitable tools for evaluating gasoline adulteration by organic solvents; especially, the adulteration by heavy aliphatic hydrocarbons can be detected even in low concentrations, such as 5%.

#### 4. Conclusions

The detection of gasoline adulteration by organic solvents is difficult because both are petrochemical fractions. In general, physicochemical analyses are not enough to detect such a type of gasoline adulteration. Thus, the search for new analytical methodologies for the quality control of gasoline is necessary.

In this work, we intended to develop an analytical methodology based on chemometric analyses of  $^1\text{H}$  NMR spectral data to identify the presence of solvents in gasoline. The results indicated that the use of  $^1\text{H}$  NMR spectroscopy associated with multivariate techniques is quite useful as a tool for identifying gasoline adulteration by organic solvents. Both PCA and HCA analyses of NMR data allowed the distinction between conform and nonconform samples. The  $^1\text{H}$  NMR-HCA and  $^1\text{H}$  NMR-PCA quality models were evaluated through the analyses of 21 intentionally adulterated samples, which showed a tendency to meet in nonconform group with the increase of solvent concentration. Therefore, the combination of NMR spectroscopy with chemometric methods offered an appealing procedure for the quality control of automotive gasoline.

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