



## Prediction of the physicochemical properties of gasoline by comprehensive two-dimensional gas chromatography and multivariate data processing

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### ABSTRACT

The estimation of physicochemical parameters such as distillation points and relative densities still plays an important role in the quality control of gasoline and similar fuels. Their measurements according to standard ASTM procedures demands specific equipments and are time and work consuming. An alternative method to predict distillation points and relative density by multivariate analysis of comprehensive two-dimensional gas chromatography with flame ionization detection (GC × GC-FID) data is presented here. Gasoline samples, previously tested according to standard methods, were used to build regression models, which were evaluated by external validation. The models for distillation points were built using variable selection methods, while the model for relative density was built using the whole chromatograms. The root mean square prediction differences (RMSPD) obtained were 0.85%, 0.48%, 1.07% and 1.71% for 10, 50 and 90% v/v of distillation and for the final point of distillation, respectively. For relative density, the RMSPD was 0.24%. These results suggest that GC × GC-FID combined with multivariate analysis can be used to predict these physicochemical properties of gasoline.

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### 1. Introduction

Gasoline is a petroleum-derived fuel constituted mainly by a mix of hydrocarbons from C<sub>4</sub> to C<sub>12</sub>, with distillation range from 30 °C to 220 °C, also containing traces of oxygenates and other minor compounds such as sulfur, nitrogen and metal containing compounds [1]. The exact composition of gasoline depends on the nature of the crude oils from which it originates, variations in the conditions in which the gasoline is removed from the distillation tower, transportation, storage time, which can lead to volatilization losses, the end use for which it is intended and the legislation of the country where production and distribution are located [2]. In Brazil, the gasoline commercially available (Type C) consists of “raw” gasoline (Type A, obtained directly after refining and not available for the consumer) with 25 ± 1% (v/v) of anhydrous ethanol as anti-knocking agent. In 1995, the end of the state monopoly of fuel production and distribution caused significant changes in the fuel market in Brazil. Since then, the number of distribution companies and gas stations has increased, so com-

petition has increased causing great price variation [3]. However, some companies are increasing profits by adulterating gasoline, which can lead to mal-functioning and failure of components of the engine, increases the emissions of harmful pollutants and tax revenue losses. The solvents most used in these adulteration are ethanol in quantities greater than those legally prescribed, and petrochemical organic solvents, such as light aliphatic, heavy aliphatic and aromatic hydrocarbons, due to the large differences between the prices of gasoline and the costs of these substances [4].

The quality control of gasoline in Brazil is performed by the Brazilian National Oil, Gas and Biofuel Agency (Agência Nacional do Petróleo, Gás Natural e Biocombustíveis—ANP). The official ANP control consists of physicochemical testing and gas chromatographic (GC) analysis. The procedure of physicochemical tests is based on American Society for Testing and Materials (ASTM) methods, and includes measurements of relative densities, temperatures equivalent to 10%, 50% and 90% of distilled volume, final evaporation point, octane numbers, amount of anhydrous ethanol, among others [5]. However, to perform these tests large amounts of the samples are required, qualified professionals are fundamental and most of the procedures require manual operations, which can be tedious and where operational errors can happen. Since

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1999 the ANP runs a nationwide fuel quality program, including more than 20 contract laboratories in universities and technological centers. This program collects and tests gasoline samples from retailers. In 2001, the ANP begun to introduce markers, that are easily identified through ECD detectors, in all solvents, national or imported, sold in Brazil for non-fuel applications. Marked solvents added to gasoline can be detected by GC analysis; however, this approach is expensive and demands a substantial network to audit the production and distribution of solvents. Obviously, non-marked adulterants available through the black market are undetectable by this approach [6]. In May 2009, according ANP statistics, 126 of 6290 samples of gasoline were classified as not conforming in Brazil, in which 54.0% of the cases were excess of ethanol, where a simple liquid-liquid extraction can flag the adulteration and 16.7% of the cases were detected in distillation curve analyses [7]. Gas chromatography (GC), an obvious choice for studies on fuel adulteration, has been widely used to evaluate the quality of the gasoline [3,8–12]. Ré-Poppi et al. [13] made screening analysis of Brazilian gasoline by GC-FID: linear retention indexes were calculated and individual components of the gasoline samples were characterized using detailed hydrocarbon analysis software. However, due to the complexity of gasoline and of the potential adulterants, evaluation of gasoline adulteration through conventional GC is not a trivial task. The number of possible individual compounds in petrochemical samples increases with the boiling point; for example, there are 75 isomers for C<sub>10</sub> hydrocarbons and 4347 isomers for C<sub>20</sub> hydrocarbons. Of course, not all isomers will be present in all samples, but it is clear that no single GC operation can come up with a full separation. To avoid co-elution among compounds present in gasoline samples, a technique more efficient than GC is required to resolve the problem [14].

Comprehensive two-dimensional gas chromatography (GC × GC) has revealed a huge potential for investigating complex mixtures, such as petroleum products or natural products, due to its resolution power, and it could be an interesting alternative in the present example. In GC × GC, two capillary columns are connected in series with a transfer device, defined as a modulator, located between the columns. Most often, the first column is a non-polar phase to separate compounds mainly by volatility differences, and the second column is a more polar phase to separate first dimension co-eluting species by polarity differences. The resulting two-dimensional chromatogram can have thousands of resolved peaks sorted according to their volatility and polarity properties. Besides the resolution achievable, the main advantages of GC × GC over conventional GC are the so-called chromatographic structure, as well as a significant improvement on detection limits of individual analytes. Moreover, because of the modulation of the chromatographic bands, the peak heights of the peaks increase when compared to conventional 1D-GC and, therefore, the signal-to-noise ratios and number of detected compounds also is enlarged [15,16]. Micyus et al. [17] analyzed aromatic compounds in gasoline using GC × GC equipped with a flame ionization detector (FID). Compared to GC-FID and to GC coupled to mass spectrometry (GC-MS), the amount of information obtained in a GC × GC chromatogram is considerably larger. As a consequence, the adoption of chemometric strategies for processing and interpretation of GC × GC data is desirable. Recently, de Godoy et al. [18] and Pedroso et al. [19] used multivariate analysis of data obtained from GC × GC in studies of flagging gasoline adulteration with some of the solvents more employed to this criminal practice.

In this paper, we describe the use of chemometric modeling to correlate the physicochemical properties measured according to ASTM standard procedures and GC × GC data. The algorithms

used to build the models were partial least squares (PLS), synergy interval partial least squares (siPLS) and genetic algorithm (GA).

## 2. Experimental

### 2.1. Chromatographic conditions

The gasoline analysis was performed using a lab-made GC × GC-FID prototype. This prototype is based on a HP-6890 GC-FID system (Hewlett-Packard, Wilmington, DE, USA) fit with a split-splitless injector and using H<sub>2</sub> (0.6 mL/min) as the carrier gas. This prototype uses a cryogenic modulator, which was designed based on devices previously described in the literature [20]. As cryogenic fluid, nitrogen cooled by LN<sub>2</sub> was employed, and the heating media was hot nitrogen. The flow of cold and hot nitrogen was toggled by two three-way Asco (Florham Park, NJ, USA) solenoid valves. The command of these valves and digitization of the FID signal was performed by a DAQPad-6015 16 bits AD/DA board controlled by self-made software developed using the LabView v.8.2 programming environment (National Instruments, Austin, TX, USA) and connected to an AMD Athlon 4600 GHz Dual Core personal computer. The column set employed was a 30 m × 0.25 mm × 0.25 μm HP-5 column (Agilent, Avondale, PA, USA) connected to a 1.0 m × 0.10 mm × 0.10 μm DB-wax column (J&W Scientific, Folsom, CA, USA). The modulation period was set to 4.0 s and the data acquisition rate was 100 Hz. For all runs the injection volume was 1.0 μL with 1:250 injector split ratio. The oven temperature program was: 40 °C → 3 °C/min → 120 °C → 10 °C/min → 220 °C; injector and detector temperatures were 250 °C.

### 2.2. Samples

A total of 51 type C gasoline samples with results of ANP tests were supplied by Unicamp Central Analytical Laboratory, CA-IQ/Unicamp (local ANP contract laboratory) and kept at 4 °C until use. The 51 samples of gasoline were separated into two groups by the Kennard Stone algorithm [21]: a calibration set consisting on 30 samples and a prediction set with 21 samples. The samples were collected in gas stations of Campinas-SP-Brazil and cities around. The temperature range of the distillation points was 49.3–55.2 °C at 10% v/v of distilled, 70.1–74.9 °C at 50% v/v of distilled, 147.5–166.8 °C at 90% v/v of distilled and 189.3–209.3 °C at the final point of the distillation. The density range was 738.2–761.3 kg/m<sup>3</sup>.

### 2.3. Data processing

The raw chromatograms were generated and stored as ASCII vector files. All calculations and graph generation were performed on a MatLab 6.5 platform (MathWorks, Natick, MA, USA) using the packages PLS\_Toolbox 4.21 (Eigenvector Technologies, Manson, USA) and iToolbox 1.1 (Chemometrics Group-KVL, Copenhagen, Denmark).

## 3. Theory

### 3.1. Partial least squares (PLS)

Partial least squares (PLS) regression is a method for building regression models between independent variables (called **X**), usually the instrumental measurement, and dependent variables (called **y**). The method decomposes the calibration matrix **X** and the vector **y** as can be seen in Eqs. (1) and (2). After that, the algorithm

finds the maximum covariance between  $\mathbf{X}$  and  $\mathbf{y}$  [22].

$$\mathbf{X} = \sum_{z=1}^z t_z p_z^T + \mathbf{E} \quad (1)$$

$$\mathbf{y} = \sum_{z=1}^z u_z q_z^T + \mathbf{E} \quad (2)$$

where  $t_z$  and  $u_z$  are scores vectors,  $p_z$  and  $q_z$  are loadings vectors,  $z$  is the number of latent variables and  $\mathbf{E}$  is the residual matrix.

### 3.2. Synergy interval partial least squares (siPLS)

In some cases, only one or more intervals of the instrumental data set provide more reliable PLS regressions. Therefore, Norgaard et al. [23] proposed a method called interval partial least squares (iPLS). It splits the data set into a number of intervals given by the analyst and for each interval a PLS model is calculated, the interval with the lowest root mean square error of cross-validation (RMSECV) is selected. One year later, Munck et al. [24] proposed a method called synergy interval partial least squares (siPLS). As in iPLS, it splits the data set and then calculates all possible PLS model combinations of two, three or four intervals. The combination of intervals with the lowest RMSECV is selected. The RMSECV is calculated as described in Eq. (3).

$$\text{RMSECV} = \sqrt{\frac{\sum_{i=1}^n (y_{\text{cvpred}(i)} - y_{\text{ref}(i)})^2}{n}} \quad (3)$$

where  $y_{\text{cvpred}(i)}$  is the value predicted through cross-validation,  $y_{\text{ref}(i)}$  is the reference value and  $n$  is the number of samples.

### 3.3. Genetic algorithm (GA)

Genetic algorithm (GA) is a method of variable selection for PLS regression based on Darwin evolutive theory [25]. It finds the subset of independent variables most consistent with the dependent variables. The basic operations of GA are: codification of the variables, creation of the initial population, selection, crossover and mutation. In the codification of variables, it is considered that the “chromosome” has “ $p$ ” genes, where each “gene” represents one of the variables of the analytical signal. Then, the “chromosome” will have the same number of variables as contained in this signal. After that, each “gene” of the “chromosome” is codified with the binary code (0, 1). If the “gene” is “0” the variable is not selected. Otherwise, if its value is “1”, the variable is selected. A population with “ $n$ ” “chromosomes” is created and then the best “chromosomes” are selected. In the crossover stage, which can be single or double, two “chromosomes” previously selected are combined to give origin to two new “chromosomes”. The “mutation” occurs after the crossings, and only a small percentage of “chromosomes” suffer “mutation” in some of their “genes” (Fig. 1). This operation eliminates the possibility of all “chromosomes” having a gene with the same value (1 or 0), which will result in a “gene” where no possible crossing could modify it, leading to a less heterogeneous system. The steps of selection, crossing and “mutation” are iteratively repeated until a convergence criterion is reached [25].

## 4. Results and discussion

A representative 1D-GC chromatogram of a gasoline sample is shown in Fig. 2(a), in which the most intense peaks are located in the beginning of the chromatogram. Because of the high amount (25% v/v) of ethanol present in type C gasoline, some co-elution with low boiling point hydrocarbons should be present; the same occurs between aromatic and aliphatic or alicyclic hydrocarbons. Fig. 2(b)

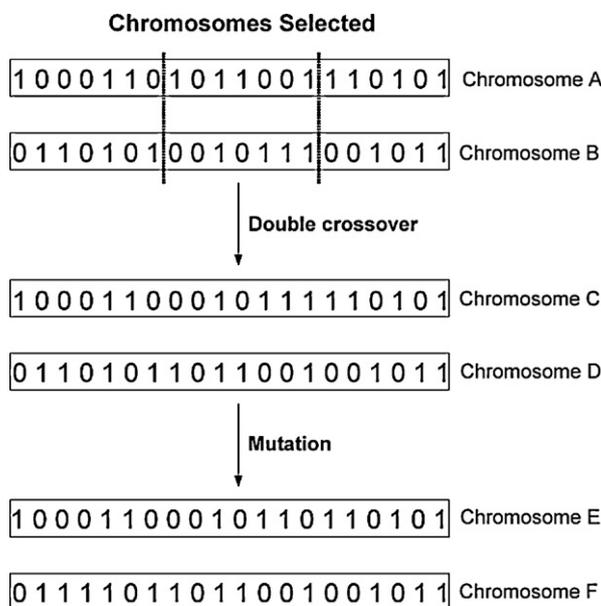


Fig. 1. Double-crossover and mutation of two codified chromosomes previously selected from a population.

shows the unfolded GC  $\times$  GC chromatogram of the same gasoline sample, in which the increment in signal intensity, when compared to 1D-GC chromatogram, is observed. The increment in signal intensity led to more precise data, which is important in chemometric studies. Slices corresponding to the modulation period of the raw modulated GC  $\times$  GC data were aligned side-by-side and converted to a three-dimensional plot (the GC  $\times$  GC chromatogram), displayed as top-down view. This three-dimensional GC  $\times$  GC chromatogram is shown in Fig. 2(c), where the chromatographic structure is clearly visible. In Fig. 2(c), the band enclosing peaks of aliphatic, alicyclic and cyclic hydrocarbons (S) can be seen, as well as benzene (B), toluene (T), ethylbenzene (E), xylenes (X), naphthalene (N), that was wrapped-around, a group of monoaromatics with C3, C4 and C5 substitution and ethanol (Et). The information contained in the raw modulated chromatogram, Fig. 2(b), is the same as

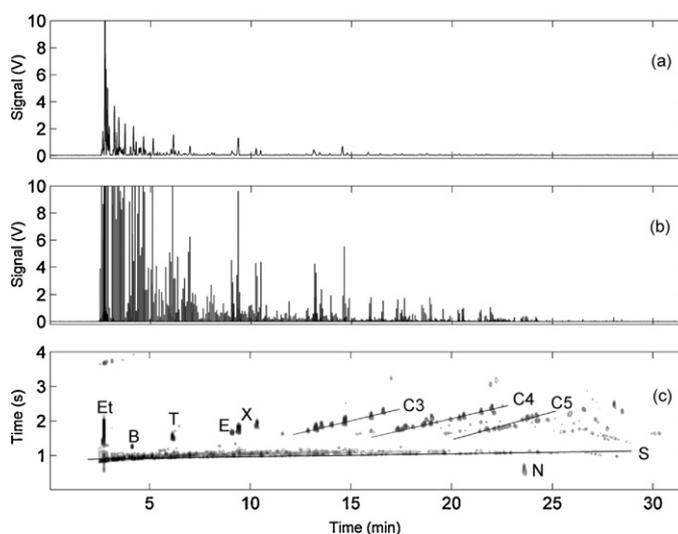
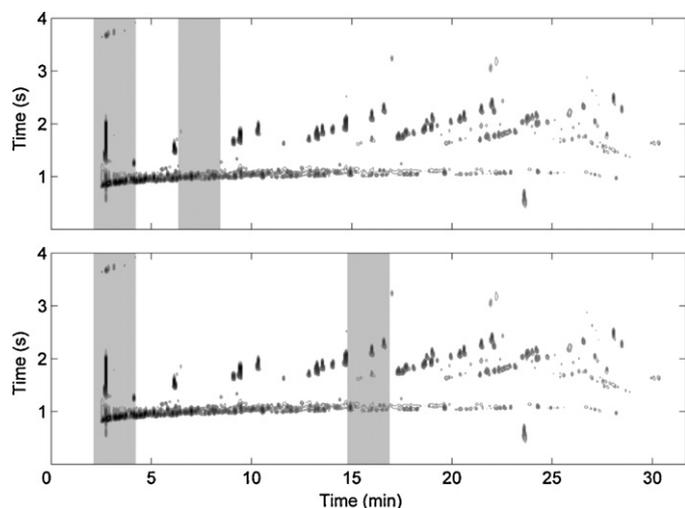


Fig. 2. Representative chromatograms of gasoline: (a) conventional GC-FID, (b) unfolded GC  $\times$  GC-FID, (c) GC  $\times$  GC-FID. Band identification: Et=ethanol, B=benzene, X=xylyne isomers, N=naphthalene, C3=benzene C<sub>3</sub>-substituted, C4=benzene C<sub>4</sub>-substituted, C5=benzene C<sub>5</sub>-substituted and S=saturated hydrocarbons (aliphatic, alicyclic and cyclic hydrocarbons).



**Fig. 3.** Typical GC  $\times$  GC chromatogram of gasoline showing the selected intervals (dark areas) by siPLS for 10% v/v (top) and 50% v/v (bottom) of distillation.

that of the GC  $\times$  GC chromatogram, Fig. 2(c); however, visual information is only obtained with the latter. For this project, the raw modulated GC  $\times$  GC chromatograms were unfolded and analyzed without pre-processing.

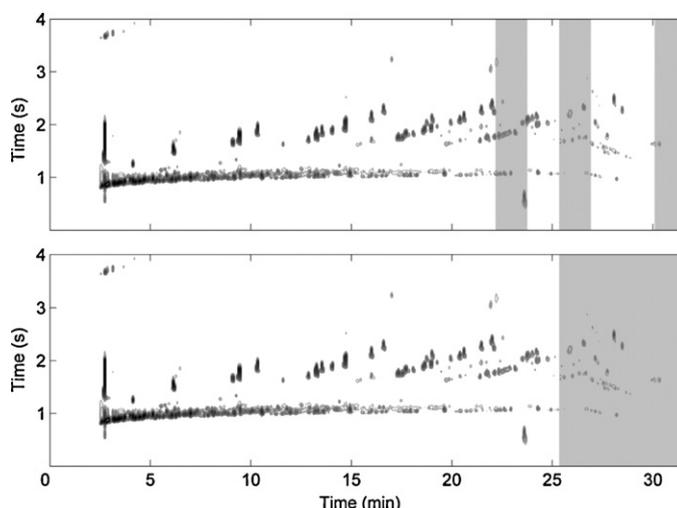
#### 4.1. Distillation points

The boiling point at 10, 50 and 90% v/v of distillation and the final point of distillation of gasoline is an important test used by ANP to evaluate the quality of gasoline. These points of distillation allow controlling the volatilization of light, intermediate and heavy gasoline fractions and the formation of residues during the gasoline combustion process inside the engine. The ANP utilizes the ASTM D86 procedure to make this test. There is a Brazilian standard method for the atmospheric distillation called ABNT NBR 9619 that is equivalent to the ASTM procedure. The boiling point for each percentage of distillation is not related to the whole chromatogram. It is related to the compounds that boil in the respective temperature regions and present concentration variance among the samples, therefore variable selection methods were used to build these models.

##### 4.1.1. 10 and 50% v/v of distillation

The calibration models for boiling point at 10 and 50% v/v of distillation were fashioned using siPLS and after that the genetic algorithm was applied. The number of latent variables, intervals, combinations and GA configurations were optimized by analyzing the RMSECV. The final prediction results were expressed as the root mean square error of prediction (RMSEP), Eq. (4), and the root mean square prediction difference (RMSPD), Eq. (5).

In siPLS models the data set was divided into fifteen intervals with two combinations for 10 and 50% v/v of distillation. The intervals selected in each model are shown in Fig. 3. The optimal GA configurations, which were the same for both models, presented the follow values: 256 population size; double crossover; 1% mutation rate; 200 generations and 30% of convergence. For the 10% v/v of distillation model, the RMSEP and the RMSPD values were 0.4 °C and 0.8%, respectively. The model for boiling point at 50% v/v of distillation presented 0.3 °C and 0.5% for RMSEP and RMSPD, respectively. The RMSEP previously published in the literature obtained using 1D-GC and PLS was 3.3 °C for the 10% v/v of distillation model and 5.8 °C for the 50% v/v of distillation model [12]. The standard method ASTM D86 reproducibility limits for the temperatures of 10 and 50% v/v are 3.20 °C and 1.88 °C, respectively.



**Fig. 4.** Typical GC  $\times$  GC chromatogram of gasoline showing the selected intervals (dark areas) by siPLS for 90% v/v of distillation (top) and distillation final point (bottom).

Therefore, the prediction results obtained in the proposed method are in accordance with the reproducibility value established in the norm.

$$\text{RMSEP} = \sqrt{\frac{\sum_{i=1}^n (y_{\text{pred}(i)} - y_{\text{ref}(i)})^2}{n}} \quad (4)$$

$$\text{RMSPD} = 100 \sqrt{\sum_{i=1}^n \frac{(y_{\text{pred}(i)} - y_{\text{ref}(i)})^2}{(y_{\text{ref}(i)})^2} \times \frac{1}{n}} \quad (5)$$

where  $y_{\text{pred}(i)}$  is the predicted value for sample  $i$ ,  $y_{\text{ref}(i)}$  is the reference value for this sample and  $n$  is the number of samples.

##### 4.1.2. 90% v/v of distillation and final point

The calibration models for boiling points at 90% v/v of distillation and final point of distillation were also built using siPLS. The siPLS model for 90% v/v of distillation were built using twenty intervals with three combinations, while for the distillation final point fifteen intervals with three combinations were used. The intervals selected for these models are shown in Fig. 4.

For these models each interval of the data had fewer chromatographic signals than for 10 and 50% v/v of distillation, as can be seen in Figs. 3 and 4. Therefore, GA was not used to select variables in the selected intervals by siPLS to build the models. The RMSEP and RMSPD values obtained were 1.5 °C and 1.1% for the 90% v/v of distillation model, respectively, and 2.1 °C and 1.7% for the final point of distillation model, respectively. The RMSEP previously published using 1D-GC and PLS was 10.1 °C for 90% v/v of distilled model and 10.5 °C for final point of distillation model [12]. The standard method ASTM D86 reproducibility limits for the temperatures of 90% v/v and at the final point are 4.1 °C and 6.8 °C, respectively. Thus, the prediction results obtained in the proposed method are in accordance with the reproducibility value established in the norm.

Therefore, the four points of the curve of distillation for gasoline used by ANP to evaluate the quality of the fuel can be predicted through GC  $\times$  GC and multivariate analysis, which require only 1.0 mL of the sample while the ANP procedure uses 100 mL of the sample and the ANP procedure is experimentally more complicated than the method proposed. Nowadays, with the use of automatic equipments, the ANP procedure is much easier than it used to be. Therefore, the evaluation of gasoline distillation curve using these automatic equipments is not experimentally complicated. It is experimentally comparable to the method proposed, because

both methods require one or more technicians with a few time of training to operate the equipment and both need some specialized assistance occasionally.

#### 4.2. Density

Another important test used by ANP to analyze gasoline is density. The procedure to perform this test is ASTM D4052. The Brazilian method equivalent to the ASTM procedure to determine the density of gasoline samples is the ABNT NBR14065 method. Differently from distillation points, the density is related to the whole chromatogram, because it depends on the entire composition of the sample. Thus, PLS was used to build the calibration model. The RMSEP and the RMSPD obtained were 1.7 kg/m<sup>3</sup> and 0.2%, respectively. The RMSEP previously published using 1D-GC and PLS was 4.3 kg/m<sup>3</sup> [12]. The reproducibility limit established in the ASTM D4052 norm is 2.0 kg/m<sup>3</sup>. Therefore, the RMSEP value obtained in the proposed method is in accordance with the reproducibility limit of the ASTM norm.

Although the test to determine density of gasoline carried out by ANP has a simple procedure and it is a faster test in comparison to gas chromatographic analysis, the chemometric model for density of gasoline were fashioned using the same chromatographic runs as the distillation points. Thus, both the distillation points and the density of a gasoline sample can be determined with only one GC × GC chromatogram.

#### 5. Conclusions

An alternative to the ASTM tests for distillation curve and relative density of gasoline samples is proposed. The advantages of more chromatographic information from GC × GC-FID over conventional GC-FID were combined with multivariate data processing to build the prediction models. The distillation models were created using variable selection chemometric tools, because the distillation points are not related to the whole GC × GC chromatogram, but to the compounds that boil in the respective temperature windows and present concentration variance among the samples. The results obtained with GC × GC-FID and multivariate analysis with selection of variables presented lower values for RMSEP than the previously reported multivariate analysis of GC-FID. The relative density model was built using the whole GC × GC chromatograms and it also presented lower RMSEP than the previous model built with GC-FID. All models were validated with a sample set of prediction. Therefore, the distillation points and the relative density of a gasoline sample can be predicted with only one GC × GC-FID run, which require lower sample volumes than the ANP procedure and does not involve manual operations, like the ANP tests.

In this work, the chemometric models were built using samples collected in gas stations of Campinas-SP-Brazil and cities around. The results obtained showed the capability of the models to predict some of the tests used by ANP to evaluate the gasoline quality of samples of that region. Although the methodology proposed in

this work were performed with samples of Campinas-SP-Brazil and cities around, it can be extended to the whole country since the calibration step be done using samples collected in the region of interest.

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#### References

- [1] M.M. Fonseca, M.I. Yoshida, I.C.P. Fortes, V.M.D. Pasa, J. Therm. Anal. Cal. 87 (2007) 499.
- [2] E.V. Takeshita, R.V.P. Rezende, S.M.A.G.U. de Souza, A.A.U. de Souza, Fuel 87 (2008) 2168.
- [3] V.L. Skrobot, E.V.R. Castro, R.C.C. Pereira, V.M.D. Pasa, I.C.P. Fortes, Energy Fuels 19 (2005) 2350.
- [4] P.J.S. Barbeira, R.C.C. Pereira, C.N.C. Corgozinho, Energy Fuels 21 (2007) 2212.
- [5] Agência Nacional do Petróleo, Gás Natural e Biocombustíveis (ANP). <<http://www.anp.gov.br>>, Regulation 309 of 27 December 2001 (accessed 15.07.10).
- [6] M.R. Monteiro, A.R.P. Ambrozini, L.M. Lião, E.F. Boffo, L.A. Tavares, M.M.C. Ferreira, G. Ferreira, Energy Fuels 23 (2009) 272.
- [7] Agência Nacional do Petróleo, Gás Natural e Biocombustíveis (ANP). <[http://www.anp.gov.br/doc/conheca/boletim.qualidade/2009/BQ\\_05\\_09.pdf](http://www.anp.gov.br/doc/conheca/boletim.qualidade/2009/BQ_05_09.pdf)>, 2009 (accessed 15.07.10).
- [8] L.S. Moreira, L.A. d'Avila, D.A. Azevedo, Chromatographia 58 (2003) 501.
- [9] V.L. Skrobot, E.V.R. Castro, R.C.C. Pereira, V.M.D. Pasa, I.C.P. Fortes, Energy Fuels 21 (2007) 3394.
- [10] D.L. Flumignan, G.C. Anaia, F.de.O. Ferreira, A.G. Tininis, J.E. de Oliveira, Chromatographia 65 (2007) 617.
- [11] D.L. Flumignan, A.G. Tininis, F.de.O. Ferreira, J.E. de Oliveira, Anal. Chim. Acta 595 (2007) 128.
- [12] D.L. Flumignan, F.de.O. Ferreira, A.G. Tininis, J.E. de Oliveira, Chemom. Intell. Lab. Syst. 92 (2008) 53.
- [13] N. Ré-Poppi, F.F.P. Almeida, C.A.L. Cardoso, J.L. Raposo Jr., L.H. Viana, T.Q. Silva, J.L.C. Souza, V.S. Ferreira, Fuel 88 (2009) 418.
- [14] J.M. Davis, C. Samuel, J. High Resol. Chromatogr. 23 (2000) 235.
- [15] M. Adahchour, J. Beens, R.J.J. Vreuls, U.A.T. Brinkman, Trends Anal. Chem. 25 (2006) 726.
- [16] C. von Muhlen, C.A. Zini, E.B. Caramão, P.J. Marriott, J. Chromatogr. A 1105 (2006) 39.
- [17] N.J. Micyus, J.D. McCurry, J.V. Seeley, J. Chromatogr. A 1086 (2005) 115.
- [18] L.A.F. de Godoy, E.C. Ferreira, M.P. Pedroso, C.H.de.V. Fidélis, F. Augusto, R.J. Poppi, Anal. Lett. 41 (2008) 1603.
- [19] M.P. Pedroso, L.A.F. de Godoy, E.C. Ferreira, R.J. Poppi, F. Augusto, J. Chromatogr. A 1201 (2008) 176.
- [20] M. Pursch, P. Eckerle, J. Biel, R. Streck, H. Cortes, K. Sun, B. Winniford, J. Chromatogr. A 1019 (2003) 43.
- [21] R.W. Kennard, L.A. Stone, Technometrics 11 (1969) 137.
- [22] R.G. Brereton, Analyst 125 (2000) 2125.
- [23] L. Norgaard, A. Saudland, J. Wagner, J.P. Nielsen, L. Munck, S.B. Engelsen, Appl. Spectrosc. 54 (2000) 413.
- [24] L. Munck, J.P. Nielsen, B. Moller, S. Jacobsen, I. Sondergaard, S.B. Engelsen, L. Norgaard, R. Bro, Anal. Chim. Acta 446 (2001) 169.
- [25] D.E. Goldberg, Genetic algorithms in search, in: Optimization and Machine Learning, Addison-Wesley Publishing Company, Boston, 1989.