Article

Brazilian Gasoline Quality: Study of Adulteration by Statistical Analysis and Gas Chromatography

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A adição de solventes orgânicos (hidrocarbonetos alifáticos pesados, alifáticos leves e hidrocarbonetos aromáticos) na gasolina brasileira é muito freqüente, e esta prática ilícita prejudica a qualidade da gasolina. Neste trabalho, as adulterações por solventes orgânicos de amostras de gasolina foram analisadas. Para a caracterização e comparação destas amostras, alguns parâmetros físico-químicos foram selecionados como fator para análise estatística hierárquica multivariada (*Cluster Analysis*). Entretanto estes parâmetros não foram eficientes para detectar todos os tipos de adulteração, em particular a adulteração por hidrocarbonetos alifáticos leves e mistura dos mesmos com hidrocarbonetos aromáticos. Este tipo de adulteração é melhor detectada através da análise do perfil cromatográfico destas amostras. A Cromatografia Gasosa (CG) deve ser usada para uma melhor detecção de gasolinas adulteradas. O uso das propriedades físico-químicas de amostras de gasolina na análise estatística multivariada juntamente com os perfis cromatográficos é um método eficiente e viável à detecção da adulteração.

The addition of organic solvents (heavy aliphatic, light aliphatic and aromatic hydrocarbons) in Brazilian gasoline is unfortunately very frequent, and this illicit practice does not guarantee gasoline quality. Organic solvent adulterations of gasoline samples have been investigated. For characterization and comparison of these samples, physico-chemical parameters were selected as the factor for hierarchic multivariate analysis (Cluster Analysis). However, these parameters are not efficient to detected all kinds of adulteration. Gas Chromatographic (GC) analysis can be used as a procedure to improve the detection of adulterated gasoline. More detailed information of their compositions was revealed. The use of physico-chemical properties of gasoline samples for hierarchic multivariate analysis and gas chromatographic fingerprints is a practicable method to adulteration detection.

Keywords: gasoline, statistical analysis, gas chromatography, hierarchic cluster analysis, adulteration

Introduction

The Brazilian fuel market has gone through great changes in last years with the end of state production.[1] Liberalization has opened vast opportunities for both established firms and news entrants into the Brazilian oil industry. Reduction of barriers to entry in the distribution sector, such as permitting 'white flag" service stations (service stations not operating under the trademark of a particular distributor) and liberalizing distributions and resale margins, have radically alternated this segment of the industry. In the beginning of the 1990's, only 14 distributions firms were in operation. In 1998, the number increased to 171. In May 2002 alone, the Brazilian National Petroleum Agency (ANP) granted 231 licenses for new distributions.[2]

Immediately, with the end of the distribution monopoly and the state production, which lead to an increase number of fuel deals, and fuel gas station, the opening of the market, a stronger competition with ensuing great price variation. However, fuel quality has not being guaranteed.[1]

Gasoline is a complex mixture of several hundred of liquid, volatile and inflammable petroleum derived compounds, ranging from C_4 to C_{12} carbon atoms and boiling points in the range of 30 – 225 °C. In Brazil, gasoline can be "A" or "C" type. Gasoline "A" is derived

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directly from refinery and "C" type is the gasoline "A" with the addition of 24% ± 1 ethanol (% v/v).[3]

The most important solvents used for adulterating gasoline are: light aliphatic hydrocarbons (C_4-C_8), heavy aliphatic hydrocarbons (C_{13}-C_{15}) and aromatic hydrocarbons. Many of their compounds are already in gasoline. This illicit practice occurs because the solvent addition in the gasoline does not pay tax, so the prices go down.[4]

High boiling compounds, when added to gasoline, increase knock and engine wear and may make starting difficult; low boiling compounds may cause vapor lock.[3-5] The addition of solvents may lead to engine malfunction, rubber corrosion and environmental hazards, besides tax evasion, since industrial solvents and fuels have different taxation.[6]

Nowadays, many physical and chemical properties are utilized in quality-control tests for gasoline by the Brazilian National Petroleum Agency (ANP regulation number 309/2001), and these tests include measurement of relative density, temperatures equivalent to 10%, 50% and 90% distilled volume, final evaporation point, flash point, octane numbers (MON and RON), antiknock indices (AI) values, benzene etc. However, after all these measurements, many samples are approved but in reality they are adulterated.[1-3]

The multivaried statistical analysis (Clusters Analysis), has being used in many areas as control of pollution, biotechnology and biochemistry; therefore it has as objective to relate how much distinct samples are similar in accordance with comparison of parameters previously defined. It is a very important tool advances in order to understand and improve the results.[7-11]

The literature is replete with articles on the gas chromatographic analysis of gasoline and related petroleum products. Retention index databases and computer software for the detailed analysis of gasoline are available from commercial sources.[12-17] Gas chromatographic classification of liquid petroleum products is a well-established technique. Basic parameters used to distinguish different classes of products include boiling point range, aliphatic and aromatic hydrocarbon content, relative concentration of major versus minor components, and the presence of additives. Gas chromatography has also been used to compare liquid petroleum products within a given classification.[18] Our group has published previous chromatographic data on gasoline samples.[19, 20]

In this work, detection of organic solvent gasoline adulteration by statistical approach and gas chromatography analysis of Brazilian samples are described. The physico-chemical parameters and gas chromatographic fingerprints were used to detect organic solvent adulterated gas station gasoline samples in comparison with intentionally adulterated gasoline. This procedure is a powerful methodology in this intent.

Experimental

Material

The commercial solvents used were donated by Carbono S.A chemistry industry, and their commercial names are Carbosolv SB (light aliphatic hydrocarbons), Carbosolv AB-9 (aromatic hydrocarbons) and Carbosolv A-70 (heavy aliphatic hydrocarbons).

Sample preparation

A group of 22 intentionally adulterated samples were prepared in our laboratory. Each sample consist of 39% (v/v) gasoline "A" type (deriving from oil refineries), 22% (v/v) of ethanol and commercial organic solvents in a total of 39% (v/v). Two distinct gasoline "A" type were used: Reduc and Manguinhos. Solvents were heavy aliphatic, light aliphatic and aromatic hydrocarbons. The detailed compositions of these samples are shown in Table 1.

Sample collection

Gasoline samples were obtained from different gas stations in the State of Rio de Janeiro. These samples were previously analyzed by the ANP regulation physico-chemical parameters and solvent marker detection by GC with ECD detector according to ANP regulation (number 274/2001), so twenty adulterated samples (samples 29 - 30 and 33 - 50) and two non-adulterated samples (samples 31 and 32) were selected for this work.

Gas Chromatography (GC)

The gas chromatographic (GC) analyses were carried out on a Hewlett-Packard 5890 series II gas chromatography equipped with a flame ionization detector. Injection of samples was performed at the split mode using a Hewlett-Packard 7673 auto sampler. The column used was a fused-silica capillary column DB-5 (60 m x 0.25 mm i.d, film thickness of 1 μm; J & W, USA). Injector and detector temperatures were maintained at 270 °C. Oven temperature was programmed as follows: initial temperature of 40 °C with an isothermal period of 15 min; temperature program rate, 4 °C /min; final temperature 220 °C. Hydrogen was used as carrier gas. Split ratio was 1/70 and the injected sample volume was 1.0 μL.

Table 1. Composition of samples (in % v/v) prepared in laboratory

Sample N[o.]	Gasoline from oil refinery[a]	Light aliphatic hydrocarbons	Aromatic hydrocarbons	Heavy aliphatic hydrocarbons	Ethanol
1	X	0	0	0	22
2	X	0	0	39.0	22
3	X	0	39.0	0	22
4	X	0	19.5	19.5	22
5	X	39.0	0	0	22
6	X	19.5	0	19.5	22
7	X	19.5	19.5	0	22
8	X	13	13	13.0	22
9	Y	0	0	0	22
10	Y	0	0	39.0	22
11	Y	0	39.0	0	22
12	Y	0	19.5	19.5	22
13	Y	39.0	0	0	22
14	Y	19.5	0	19.5	22
15	Y	19.5	19.5	0	22
16	Y	13	13	13.0	22
17	X	28.0	5.5	5.5	22
18	X	5.5	28	5.5	22
19	X	5.5	5.5	28.0	22
20	Y	28.0	5.5	5.5	22
21	Y	5.5	28	5.5	22
22	Y	5.5	5.5	28.0	22

[a] **X**: Manguinhos Refinery; **Y**: Duque de Caxias Refinery (REDUC).

Physico-chemical parameters

Standard specification tests were determined for all samples as follows: ASTM Distillation percentages (10%, 50%, 90% and 98%), Motor Octane Number (MON; ASTM D 2700), Research Octane Number (RON), antiknock indices [AI = (MON+RON)/2; ASTM D 2700 and D 2699], Ethanol percentage (NBR 13992), color and clarity and the results were compared by the Brazilian National Petroleum Agency regulation limits. Automatic distillation equipment Herzog HDA 627 for ASTM D 86 and NBR 9619 and an infrared analyzer, Petrospec GS 1000, were used for determined the parameters (Table 2). Those results were also used as a parameter in the statistical analysis. The GS-1000 use the technology of spectroscopy with the wavelengths in the "Infrared" through the comparison of the spectra of the olefinic, parafinic and aromatic compounds (method FIA ASTM D 1319), as well as the oxygenate ones, MethylTetraButhylEther (MTBE), Ethanol and others, containing in the electronic memory of GS- 1000, being possible the determination of MON and RON, through mathematically advanced models.

Statistical data analysis

Cluster analysis sorts a set of objects X, described by several variables, into "homogeneous" clusters. The usual approach is to compute a measure of association, or similarity, for every pair of objects, by means of the values of the variables describing these objects. Then, a hierarchical clustering method is used.

Statistical (99 Edition) software for cluster analysis and complete linkage method was used. Similarity index value were calculated by following equation; similarity$_{a.b}$ = 1- $d_{a.b}$/ d_{max}, where $d_{a.b}$ is the Euclidian distance of sample a and b and d_{max} the largest Euclidian distance in the data set. For cluster analysis, seven physico-chemical data from each gasoline sample were used as the factors.[12,21-24]

Results and Discussion

The distribution of compounds in a typical gasoline sample chromatogram derived from the Reduc and Manguinhos oil refineries is shown in Figure 1. The hydrocarbons in gasoline consist primarily of light aliphatic hydrocarbons (butane, pentane, methylpentane, hexane, methylhexane, heptane) and aromatic compounds (toluene, xylenes, trimethylbenzenes).

Cluster Analysis result was obtained with the selected physico-chemical data from the 22 intentionally adulterated gasoline and 22 gas station samples. The quantity and type of the organic solvent used in the intentionally adulterated gasoline samples are described in Table 1. Seven parameters for each gasoline sample were used for cluster analysis: MON, RON, AI, temperature of distillation at 10%, 50%, 90% and 98%. Figure 2 shows a

Table 2. Physico-chemical properties of all analyzed samples[a]

Samples	Dist. Temp. 10% (ºC)	Dist. Temp. 50% (ºC)	Dist. Temp. 90% (ºC)	Dist. Temp. 98% (ºC)	Residue	RON	MON	AI
1	62.0	71.0	146.0	187.0	1.2	91.4	82.6	87.0
2	71.0	130.0	204.0	230.0	2.4	84.3	79.3	81.8
3	72.0	138.0	163.0	177.0	1.0	98.4	89.1	93.8
4	71.0	134.0	178.0	225.0	1.6	93.1	83.9	88.5
5	62.0	70.0	122.0	178.0	1.4	93.0	83.0	88.0
6	68.0	80.0	181.0	224.0	1.2	92.0	82.0	87.0
7	65.0	78.0	163.0	178.0	1.1	93.9	84.2	89.1
8	68.0	95.0	176.0	209.0	2.0	91.0	82.6	86.8
9	60.0	63.0	149.0	186.0	1.8	95.3	83.6	89.4
10	70.0	146.0	205.0	238.0	1.6	86.0	80.4	83.2
11	71.0	149.0	167.0	189.0	1.4	100.4	89.4	94.9
12	70.0	145.0	180.0	219.0	2.4	95.0	84.8	89.9
13	61.0	70.0	145.0	196.0	1.4	88.9	81.5	85.2
14	65.0	74.0	185.0	229.0	1.6	87.5	81.0	84.3
15	62.0	75.0	163.0	189.0	1.4	96.4	85.7	91.1
16	61.0	81.0	177.0	220.0	1.6	93.7	84.0	88.9
17	67.0	74.0	158.0	198.0	1.4	92.5	82.5	87.5
18	70.0	124.0	168.0	195.0	1.3	96.2	86.4	91.3
19	70.0	121.0	190.0	219.0	2.4	87.3	80.6	84.0
20	63.0	74.0	170.0	203.0	1.4	91.4	82.8	87.1
21	67.0	123.0	168.0	204.0	1.4	98.6	87.2	92.9
22	69.0	132.0	192.0	231.0	1.6	89.4	81.9	85.2
29	67.0	77.0	191.0	231.5	1.4	90.0	83.2	86.6
30	64.0	77.5	198.0	235.0	1.5	91.8	82.7	87.2
31	55.5	72.5	166.5	212.0	1.3	95.7	83.6	89.7
32	58.0	73.0	172.5	211.0	1.4	95.6	83.4	89.5
33	70.0	77.0	144.0	229.0	1.5	98.4	84.9	91.7
34	68.0	78.0	199.0	231.0	1.4	92.4	82.7	87.5
35	63.0	74.0	204.5	242.5	1.3	89.9	81.8	85.8
36	64.0	75.0	173.0	212.0	1.6	89.0	80.8	84.9
37	65.0	78.0	176.0	223.0	1.5	93.3	82.0	87.6
38	67.0	75.5	195.0	230.0	1.6	91.0	80.9	86.0
39	60.0	75.0	185.5	227.0	1.4	95.9	83.6	89.8
40	61.0	76.0	172.5	215.0	1.3	91.5	81.7	86.6
41	72.0	77.0	150.0	190.0	1.1	93.9	86.1	88.7
42	69.0	76.0	164.0	200.0	1.5	92.8	82.5	87.7
43	73.5	98.0	190.0	225.0	1.5	91.4	81.7	86.5
44	66.0	82.0	192.5	229.0	1.8	90.5	80.1	85.3
45	64.0	79.0	170.5	206.0	1.2	91.6	80.8	86.2
46	70.0	99.0	190.0	224.0	1.4	91.9	81.8	86.9
47	63.0	78.0	179.0	226.5	1.5	91.4	79.8	85.6
48	69.0	82.0	198.5	231.0	1.7	90.2	81.7	86.0
49	71.0	118.0	177.5	199.0	1.2	89.7	79.7	84.7
50	66.5	81.5	202.5	236.0	1.6	91.9	81.9	86.9

[a]Regulated by ANP; Distillation Temperature (Dist. Temp.*)* (max): 10% - 65 ºC, 50% - 80 ºC and 90% -145 to 190 ºC; Final Point (FP is equal to 98%), 220 ºC; Residue, 2.0 mL; MON minimum value, 82.0; Antiknock Indices (AI) minimum value, 87.0.

dendrogram that is divided in distinct groups separated for the high similarity of their compositions. Each group is constituted of similar samples in relation to the values of the measured parameters. The data set was classified into four groups where the level of similarity index values is 0.5. The characteristics of the four groups were:

First group

Gasoline samples adulterated mainly with approximately one third each hydrocarbon solvent

(aromatic, light and heavy aliphatic): Gasoline from Manguinhos and Reduc refineries with addition of 13% of aromatic, light aliphatic and heavy aliphatic hydrocarbons (samples 13 and 16); 28% light aliphatic hydrocarbons and 5.5% heavy aliphatic and aromatic hydrocarbons (samples 20), and 19.5% of light and heavy aliphatic hydrocarbons (samples 6 and 14).

Second group

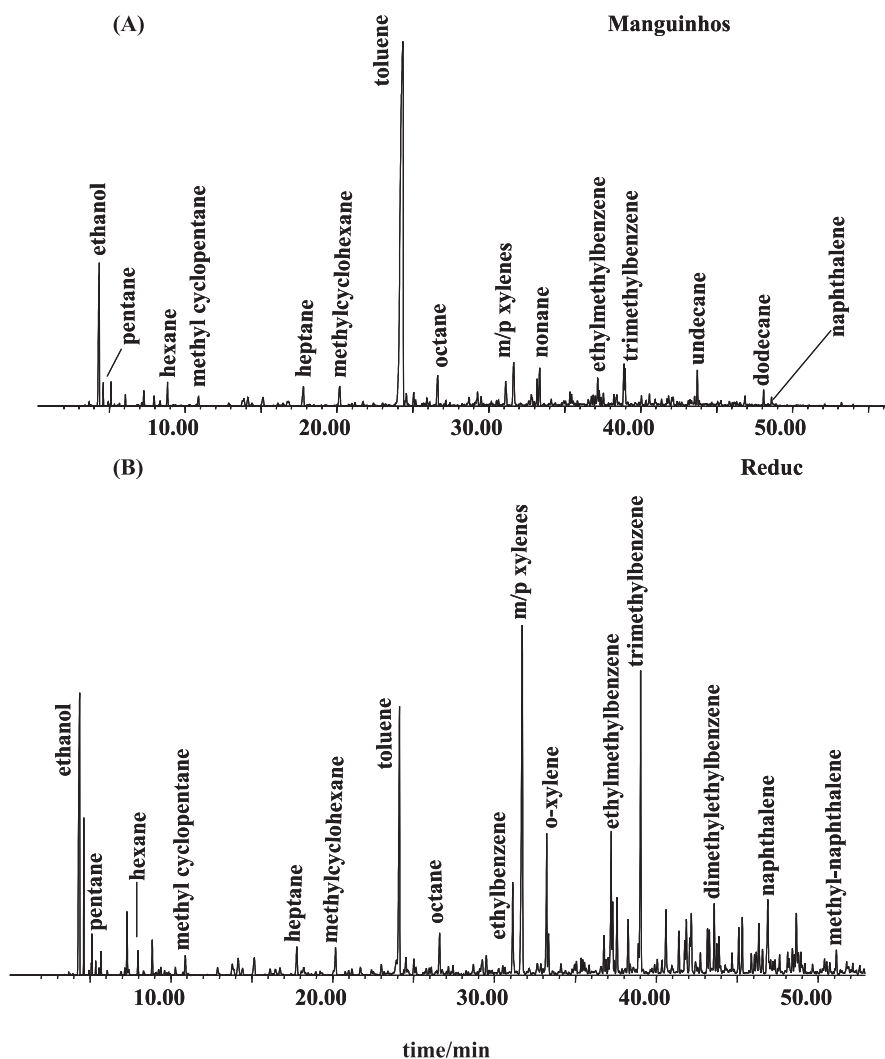Gasoline samples adulterated with 28% up to 39%

Figure 1. A typical gas chromatogram from Manguinhos (A) and Reduc (B) oil refineries gasoline samples.
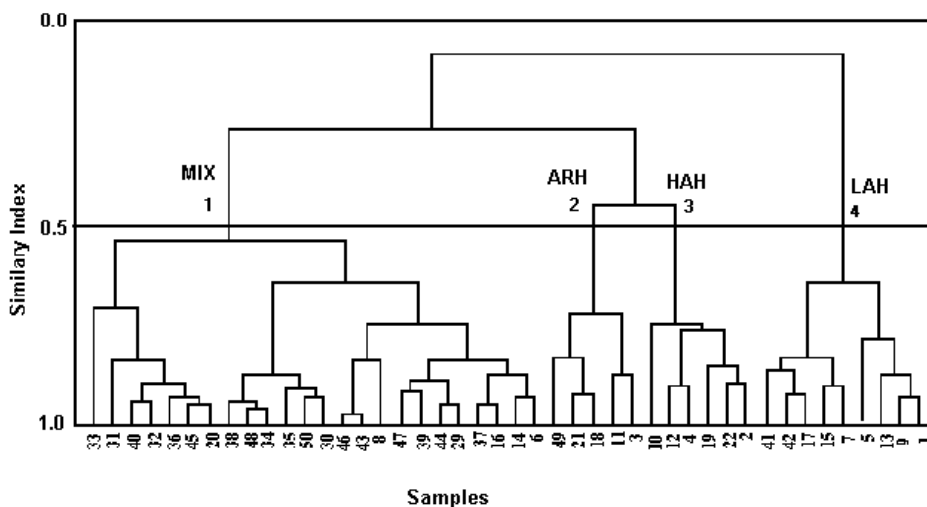

Figure 2. Dendrogram resulting from hierarchical cluster analysis with physico-chemical data from all studied gasoline samples, 20 intentionally adulterated and 22 gas station and 2 oil refineries gasoline samples. Four groups are found: MIX, mixture of solvents; ARH, aromatic hydrocarbons; HAH, heavy aliphatic hydrocarbons and LAH, light aliphatic hydrocarbons.

aromatic hydrocarbon solvent: samples 3 and 11, gasoline samples from Manguinhos and Reduc refineries with addition of 39% aromatic hydrocarbons; samples 18 and 21, gasoline samples with 28% aromatic hydrocarbons, 5.5% light and heavy aliphatic hydrocarbons and a gas station sample 49.

Third group

Gasoline samples adulterated with 19% up to 39% heavy aliphatic hydrocarbon solvent: samples 2 and 10, gasoline samples from Manguinhos and Reduc refineries with addition of 39% heavy aliphatic hydrocarbons; samples 19 and 22, gasoline with 28% heavy aliphatic hydrocarbons, 5.5% light aliphatic and aromatics hydrocarbon; samples 4 and 12, gasoline samples with 19.5% heavy aliphatic and aromatic hydrocarbons.

Fourth group

Gasoline samples adulterated with 19% up to 39% light aliphatic hydrocarbon solvent: gasoline samples from Manguinhos and Reduc refineries with addition of 39% light aliphatic hydrocarbons (samples 5 and 13); with addition by 28% light aliphatic hydrocarbons (sample 17); with addition of 19.5% light aliphatic and aromatic hydrocarbons (samples 7 and 15), standard gasoline samples by Manguinhos and Reduc refineries (samples 1 and 9) and gas station samples (sample 41 and 42). The refineries samples and these adulterated samples were grouped together (samples 5, 7, 13, 15, 41 and 42 are adulterated). This case is showed at the chromatographic fingerprints in Figure 3. It is interesting to observe the significant relative abundance of light aliphatic hydrocarbon in samples 41 and 42.
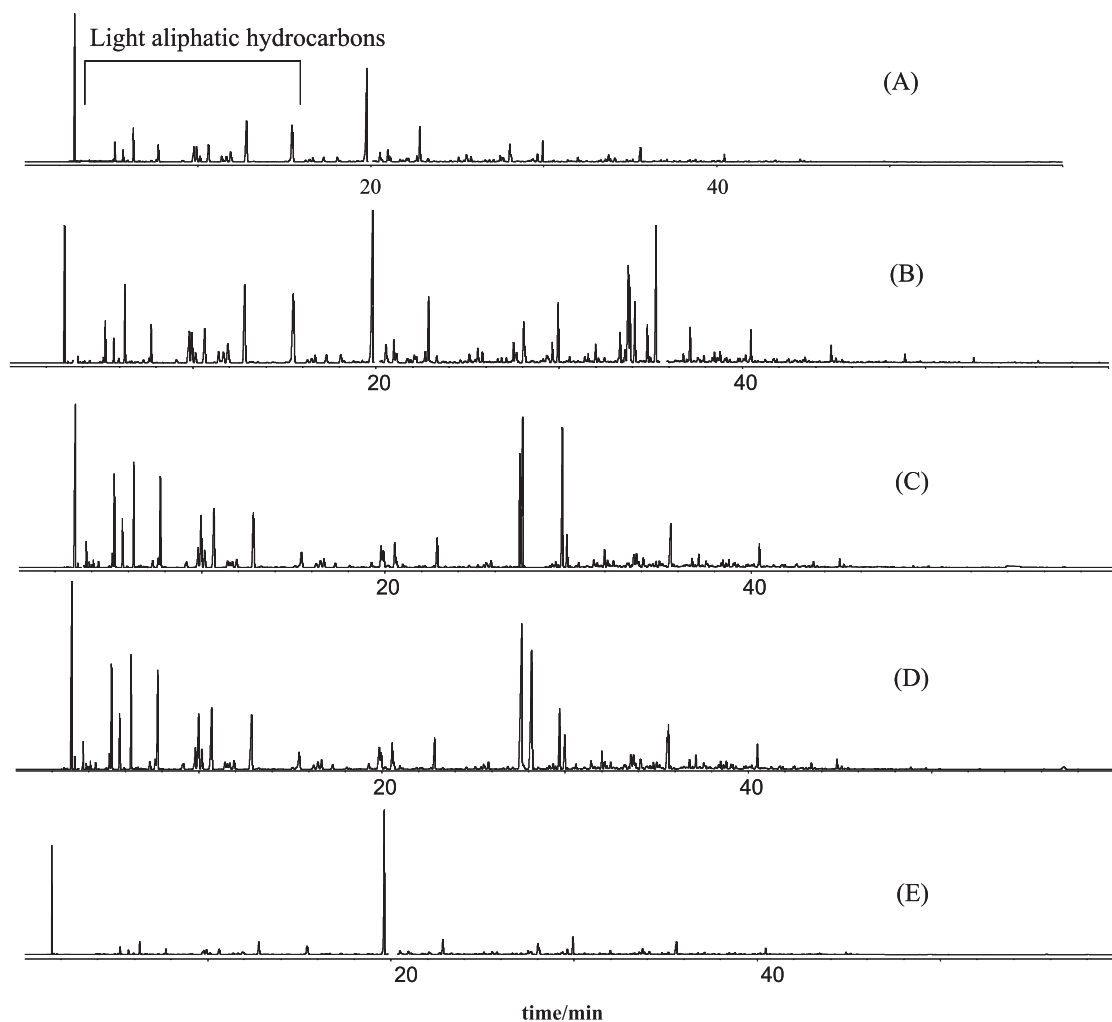

Figure 3. Gas chromatograms of gasoline samples with emphasis in the light aliphatic hydrocarbon adulteration: (A) sample 5, Manguinhos with 39% light aliphatic hydrocarbon; (B) sample 17, Manguinhos with 28% light aliphatic hydrocarbon, (C) gas station sample 41 (D) gas station sample 42 (E) sample 1, Manguinhos refinery. They are classified in the same group by cluster analysis, Figure 2. It seems by the gas chromatographic fingerprints comparison that the gas station samples 41 and 42 are adulterated with more than 39% of light aliphatic hydrocarbon solvent.

Figure 4 shows chromatographic fingerprints of gas station samples. Only one gas station sample, sample 49, was considered adulterated by high level of aromatic hydrocarbons, besides the low MON and AI values, Group 2. This type of adulteration is easier to be detected even without any statistical analysis, only by the physico-chemical parameters analysis (ANP regulation). Furthermore, is the type of adulteration less used. This case is showed at the gas chromatographic fingerprint in Figure 4C.

None of the gas station gasoline samples was classified in the Group 3, high level of heavy aliphatic hydrocarbons. This may be explained by the fact that the organic compounds in this type of solvent are not common constituents of gasoline samples (paraffin with more than twelve carbon atoms, normally nC_{13}-nC_{15}) and so, none adulterated gas station gasoline sample with this type of solvent was found. This situation is illustrated at the gas chromatographic fingerprints in Figure 4D.

So, the majority of the analyzed gas station gasoline samples were classified in one type of adulteration: mixture of the three solvents (aromatic, light aliphatic and heavy aliphatic hydrocarbons).

Samples 31 and 32, approved by ANP regulation, were also classified in the first group. These samples were considered adulterated by hydrocarbon solvent, using the present analysis, although being approved previously only by physico-chemical parameters analysis. Their gas chromatographic fingerprints are illustrated at Figures 4A and 4B.
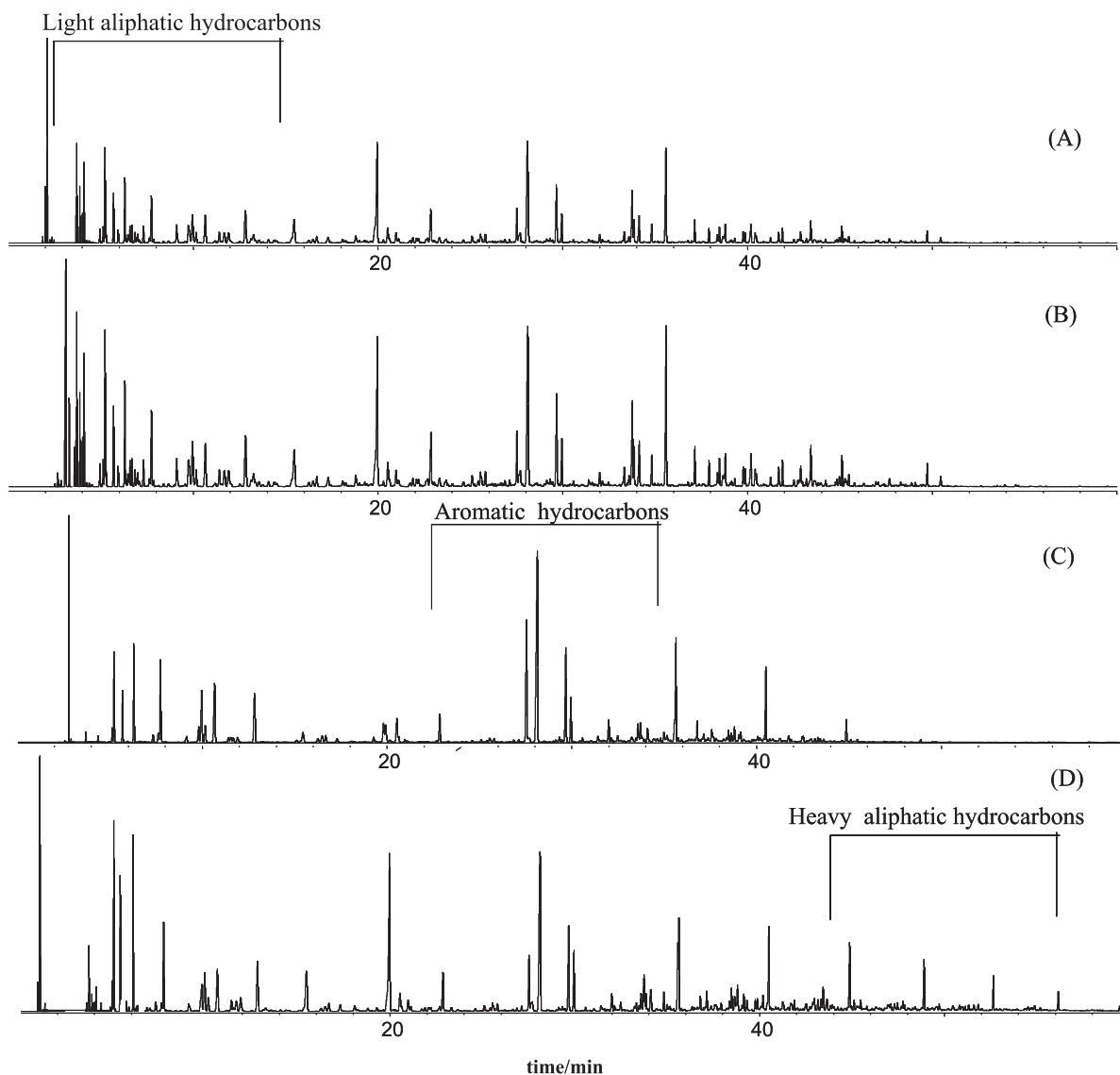

Figure 4. Select gas chromatographic fingerprints of gas station gasoline samples: (A) sample 31, (B) sample 32, (C) samples 49 and (D) sample 45.

Conclusions

The solvent adulteration detection is a very difficulty task, because their compounds are also in the original gasoline composition.

Today, the detection of adulterated gasoline presents problems as some samples are approved but in reality they are adulterated. The fact is that analysis based on ANP regulation can be improved.

Using the present procedure, it could be observed by Cluster Analysis that some sample considered approved only by the physico-chemical analyses (ANP regulation) were reproved. These two samples (31 and 32) are adulterated with a mixture of solvents. This conclusion was confirmed by the gas chromatographic fingerprint analysis *i.e.*, a more detailed analysis of the gasoline sample.

So, besides all the physico-chemical analyses currently used by the ANP regulation, it is also recomended a cluster analysis with these physico-chemical parameters. This practice will reduce the number of gas station gasoline samples approved when they are adulterared. The cluster analysis indicates not only that the gasoline sample is adultareted but also with which type of solvent. If remain some doubt, it is recomended a more refined analysis, the gasoline gas chromatographic fingerprints of selected samples.

Acknowledgements

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