Adulteration detection of Brazilian gasoline samples by statistical analysis

L.S.M. Wiedemann[a], L.A. d'Avila[b], D.A. Azevedo[a],*

[a]Departamento de Química Orgânica, Instituto de Química, Universidade Federal do Rio de Janeiro, Centro de Tecnologia,
Bl. A, S/603, Ilha do Fundão, 21949-900 Rio de Janeiro, Brazil
[b]Departamento de Processos Orgânicos, Escola de Química, Universidade Federal do Rio de Janeiro, Centro de Tecnologia,
Bl. E, S/201, Ilha do Fundão, 21949-900 Rio de Janeiro, Brazil

Abstract

Unfortunately, addition of organic solvents (heavy aliphatic, light aliphatic and aromatic hydrocarbons) in Brazilian gasoline is very frequent, and this illegal 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 together with gas chromatographic analyses data were proposed as the factors for multivariate analysis. Hierarchical clusters analysis was used to improve the detection of the type of solvent and their relative proportion used for this practice. More detailed information of their compositions was revealed. It was found that using physico-chemical properties of gasoline samples together with statistical analysis are a useful method to adulteration detection.
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1. 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. Reductions 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 [2].

Immediately, the end of the fuel distribution monopoly and the state production lead to an increasing number of fuel dealers and gas stations, the opening of the market for foreign companies, 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' types. Gasoline A is derived directly from refinery and C type is the gasoline A with the addition of $24\% \pm 1$ ethanol (% v/v) [3]. One of the great preoccupations with the gasoline quality is the illicit addition of organic solvents. The solvents normally used in this adulteration practice are aromatic hydrocarbons, light and heavy aliphatic hydrocarbons as well. In fact, the majority of these compounds are gasoline constituents [4].

Light aliphatic hydrocarbons, when added to gasoline, tend to reduce the departure of engine. Aromatic hydrocarbons need more energy to explode. Heavy aliphatic hydrocarbons increase knock, engine wear and increase the probability of more serious consequence [5,6]. The main consequences of this practice are: fiscal evasion, disloyal competition by fuel price, and potential hazards to the environmental and minor durability of the vehicle combustion motor.

Physical and chemical properties for gasoline are usually used in quality-control tests by the Brazilian National Petroleum Agency (ANP, regulation number 309/2001). These tests include measurement of relative density,

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* Corresponding author. Tel.: +55 21 2562 7488; fax: +55 21 226 03967.
E-mail address: debora@iq.ufrj.br (D.A. Azevedo).

temperatures equivalent to 10, 50, 90% of the distilled volume, final evaporation point, flash point, octane numbers (MON and RON), Anti-knock Indices values (AI), benzene and sulfur percentage etc. Despite all these measurements, many adulterated samples are approved [1,5].

The literature is full of articles on the gas chromatographic analysis of gasoline and related petroleum products [7,8]. Retention index databases and computer software for the detailed analysis of gasoline are available from commercial sources [9–16].

Clusters analysis has being used in many areas as control of pollution, biotechnology and biochemistry advances in order to understand and improve the obtained results [16–19]. Statistical classification together with gas chromatographic profiles has been previously used in the identification of impurities of methamphetamine tables [20].

In this paper, identification of organic solvent gasoline adulteration by gas chromatography and statistical approach analyses of Brazilian samples of gasoline are described.

2. Experimental

2.1. Material

The commercial solvents used named Carbosolv SB (light aliphatic hydrocarbons), Carbosolv AB-9 (aromatic hydrocarbons) and Carbosolv A-70 (heavy aliphatic hydrocarbons) were donated by Carbon SA chemistry industry.

2.2. Sample preparation

A group of 22 intentionally adulterated samples were prepared in our laboratory. Each sample consist of 39% gasoline A type (deriving from oil refineries), 22% of ethanol and 39% of commercial organic solvents. Two distinct gasoline A type were used: the one obtained from Reduc and the other from Manguinhos, both from PETROBRÁS SA, the Brazilian Oil Company. Solvents were heavy aliphatic, light aliphatic and aromatic hydrocarbons. The detailed compositions of these samples are shown in Table 1.

2.3. 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. Twenty adulterated samples (samples 29–30 and 33–50) and two non-adulterated samples (samples 31–32) were selected for this work.

2.4. Gas chromatographic analysis

The gas chromatographic (GC) analyses were carried out on a Hewlett–Packard 5890 series II gas chromatograph

Table 1
Composition of samples prepared in laboratory

Sample number	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).

equipped with a flame ionization detector. Injection of samples was performed at the split mode using a Hewlett–Packard 7673 autosampler. The column used was a fused-silica capillary column DB-5 (60 m × 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 initial isothermal period of 15 min; temperature program rate of 4 °C/min; final temperature. 220 °C. Hydrogen was used as carrier gas for all the GC analyses. Split ratio was 1/70 and the injected sample volume was 1.0 μL.

2.5. Physico-chemical parameters

Temperatures equivalent to 10, 50 and 90% of the distilled volume, final evaporation point, Motor Octane Number (MON), Research Octane Number (RON), Anti-knock Indices values [AI = (MON + RON)/2], ethanol percentage, color and aspect were determined for all samples. The results were compared with the Brazilian National Petroleum Agency regulation limits. Automatic distillers Herzog HDA 627 (ASTM D 86), and an infrared analyzer Petrospec GS 1000 were used for determined the MON, RON (Table 2).

The following set of data was obtained from the gasoline samples gas chromatograms: gas chromatographic relative integrated areas within a retention time range. Each gas

Table 2
Physico-chemical properties of all analyzed samples

Samples	Dist. temp. 10% (°C)	Dist. temp. 50% (°C)	Dist. temp. 90% (°C)	Dist. temp. 98% (°C)	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

Regulated by ANP; distillation temperature (dist. temp.) (max): 10%–65 °C, 50%–80 °C and 90%–145 to 190 °C; final point (FP=98%), 220 °C; residue, 2.0 mL; MON minimum value, 82.0; Antiknock Indices (AI) minimum value, 87.0.

chromatogram was divided in three parts, corresponding to the light aliphatic hydrocarbons (retention time—t_R—in the range of zero to 19 min), to the aromatic hydrocarbons (t_R in the range of 19–40 min) and to heavy aliphatic hydrocarbons (t_R in the range of 40–60 min). These results were also used as a parameter in the statistical analysis.

2.6. 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$_{ab}$= $1 - d_{ab}/d_{max}$, where d_{ab} is the Euclidian distance of samples a and b and d_{max} the largest Euclidian distance in the data set. For cluster analysis, 11 gasoline physico-chemical data from each gasoline sample were used as the factors.
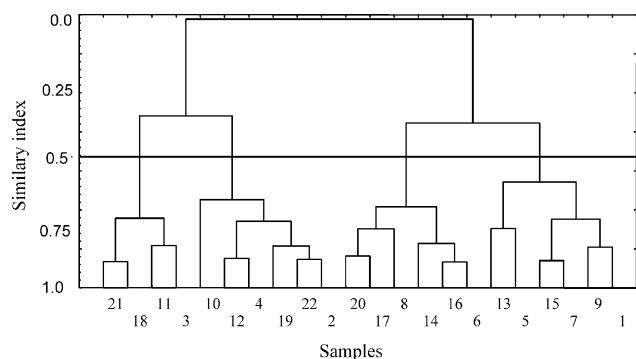
Fig. 1. Dendrogram resulting from hierarchical cluster analysis from 20 intentionally adulterated samples, where four groups are found.

3. Results and discussion

Previously, cluster analysis result was obtained from the 22 intentionally adulterated gasoline samples. The quantity and type of the organic solvent used in the adulteration are described in Table 1. Eleven parameters for each gasoline sample were used for cluster analysis: MON, RON, AI, percentage of benzene, percentage of distillation at 10, 50, 90 and 98%, percentage of light aliphatic hydrocarbons,

percentage of heavy aliphatic hydrocarbons and percentage of aromatic hydrocarbons (these three last parameter were taken from the gas chromatographic fingerprints, see Section 2). The resultant dendrogram shown in Fig. 1 were useful in order to get preselected profiles of high similarity. The data set was classified into four groups where the level of similarity index values is 0.5. Representative chromatograms for those groups are shown in Fig. 2. The characteristics of the four groups were as follows.

The first group. Gasoline samples adulterated with 28–39% 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.

The second group. Gasoline samples adulterated with 19–39% 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 hydrocarbons and aromatics hydrocarbons; samples 4 and 12, gasoline samples with 19.5% heavy aliphatic and aromatic hydrocarbons.
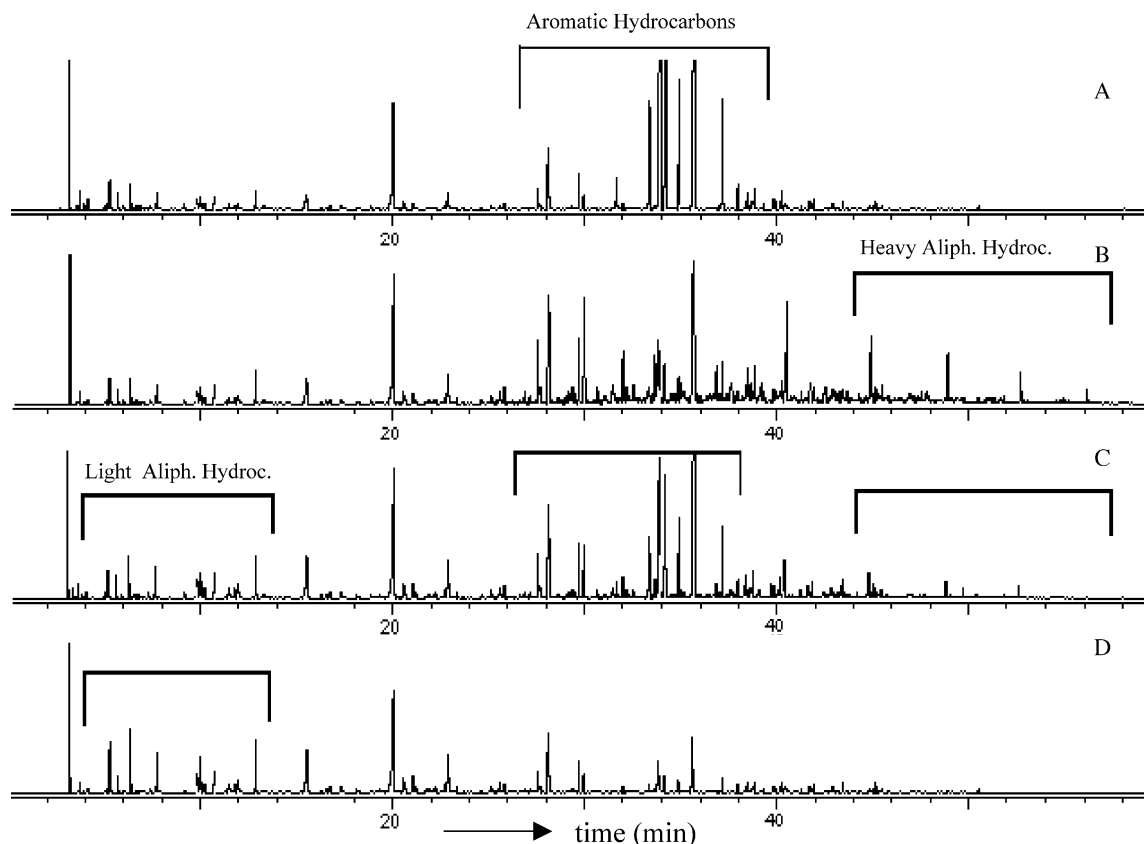

Fig. 2. Gas chromatograms of intentionally adulterated gasoline samples: (A) sample 11, (B) sample 10, (C) sample 16 and (D) sample 13. These samples were classified in different group by cluster analysis, Fig. 1.

The third 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 17 and 20), and 19.5% of light and heavy aliphatic hydrocarbons (samples 6 and 14).

The fourth group. Gasoline samples adulterated with 19–39% light aliphatic hydrocarbon solvent: gasoline samples from Manguinhos and Reduc refineries with addition of 39% light aliphatic hydrocarbons (samples 5 and 13); with addition of 19.5% light aliphatic and aromatic hydrocarbons (samples 7 and 15), and standard gasoline samples by Manguinhos and Reduc refineries. The refineries samples and these adulterated samples were grouped together. This is a fact to point out, since three more parameters than that considered by ANP regulation were used in this statistical analysis and even though the good gasoline samples and the adulterated ones with light aliphatic hydrocarbons were grouped together.

The 11 parameters of gasoline samples from the 22 gas stations were added to the data from the previous cluster analysis. Now the data set was also classified into four groups and the resulting dendrogram is shown in Fig. 3. The representative chromatograms for those groups are shown in Fig. 4.

If the level of similarity index value 0.6 were used, seven groups would be obtained. Furthermore, two groups would be formed only by gas station gasoline samples. In this way, a lower level of similarity index value 0.5 was used and four groups were obtained (Fig. 3). First group: mainly one-third of each solvent; second group: mainly heavy aliphatic hydrocarbons (19–39%); third group: mainly of aromatic hydrocarbons (28–39%) and the fourth

group: mainly of light aliphatic hydrocarbons (19–39%). The first group would be the more usable way of adulteration as is one of the most difficult of being detected. In this way, the majority of the collected gas station gasoline sample was classified in this group. Another difficult adulteration detection is whenever light aliphatic hydrocarbon are used as adulterating substances as these samples were grouped together with the reference gasoline samples from Manguinhos and Reduc. Representative chromatogram for this group is shown in Fig. 5. Many gas station gasoline samples analyzed have this group profile. Thus, these samples are considered adulterated mainly with light aliphatic hydrocarbon solvent. Samples 31 and 32, approved by ANP regulation, were also classified in this group, being considered really approved or adulterated by light aliphatic hydrocarbon solvent.

Only one sample, sample 49, was considered adulterated by high level of aromatic hydrocarbons, group 3. This type of adulteration is easier to be detected even without any statistical analysis, by the use of only a gas chromatographic fingerprint profile or by their physico-chemical characteristics. Furthermore, this type of adulteration is one of the less used adulteration practice.

None of the gas station gasoline sample was classified in the group 2, referring to high contents of heavy aliphatic hydrocarbon. This may be explained by the fact that compounds present in this type of solvent are not common constituents of gasoline samples (heavy aliphatic hydrocarbons with more than 12 carbon atoms, normally nC_{13}–nC_{15}). Thus, the majority of the analyzed gas station gasoline samples were classified in two type of adulteration: approximately one-third of each hydrocarbon solvents (aromatic, light and heavy aliphatic hydrocarbons) and with high level of light aliphatic hydrocarbon.
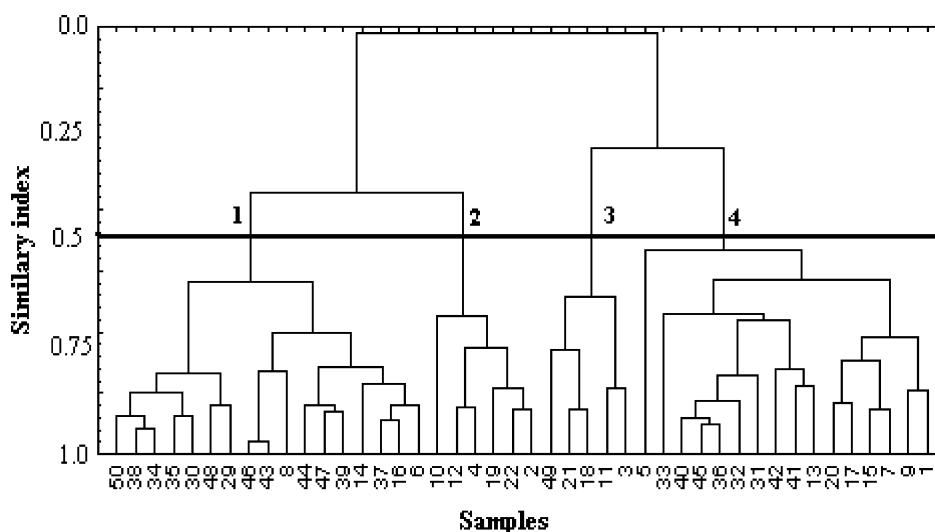

Fig. 3. Cluster diagram with data from 20 intentionally adulterated and more 20 gas station gasoline samples, where four groups are found.
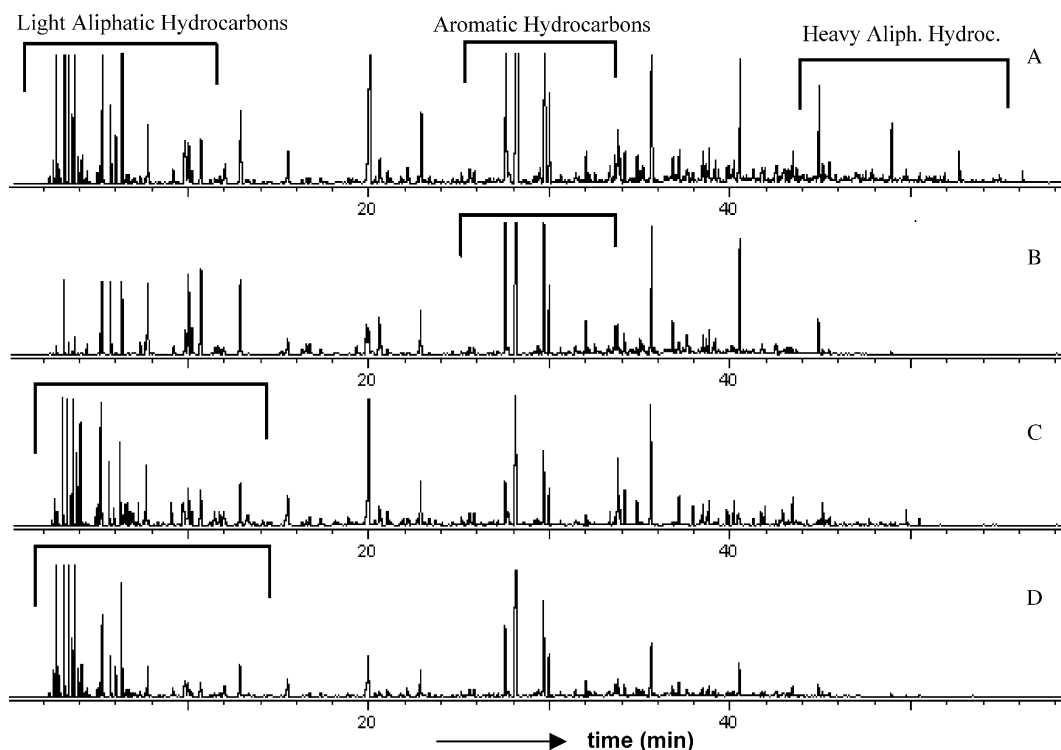
Fig. 4. Gas chromatograms of gas station gasoline samples: (A) sample 50, (B) sample 49, (C and D) samples 31 and 45. Each sample was classified in different group by cluster analysis, Fig. 3.
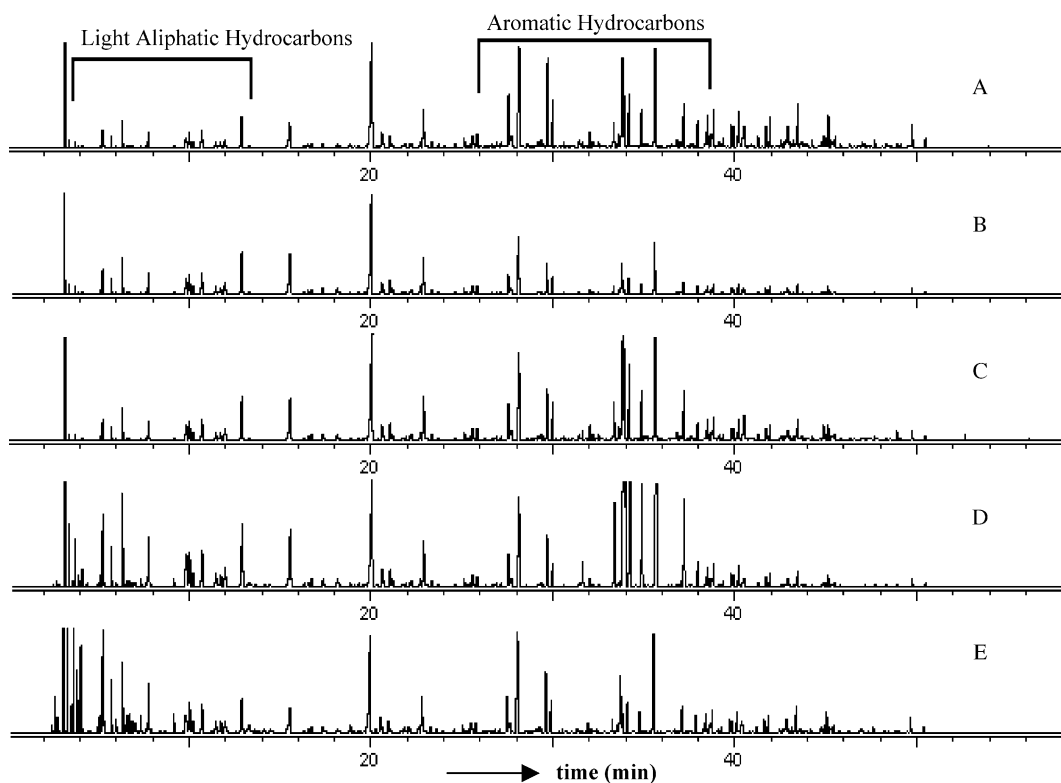

Fig. 5. Gas chromatograms of gasoline samples with emphasis in the light aliphatic hydrocarbon adulteration: (A) sample 9, Reduc; (B) sample 13, Reduc with 39% light aliphatic hydrocarbon (C) sample 20, Reduc with 28% light aliphatic hydrocarbon; (D) sample 15, Reduc with 19.5% light aliphatic and aromatic hydrocarbons and (E) sample 32 from gas station.

4. Conclusion

The detection of solvent adulteration by heavy aliphatic hydrocarbons is easier as these compounds are not present in the original gasoline composition. On the other hand, detection of aromatic and light aliphatic hydrocarbons is more difficulty because they are common compounds in gasoline composition. These type of adulteration is possible to be detected when the solvent addition exceed 19.5% for aromatics and 28% for lights. Adulteration by light aliphatic hydrocarbon solvent is the most difficulty to be detected, as its mixture with other solvent types as well. Analysis based on ANP regulation can be improved guarantying gasoline quality for all population. For this purpose, we considered the use of more parameters in cluster statistical analysis and have shown that this improved the results as more specific details were analyzed. Thus, more differences are found for samples and they can are better discriminated. Furthermore, hierarchical cluster analysis proved to be a very valuable tool for comparison and characterization of adulterated gasoline by illegal addition of organic solvent.

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