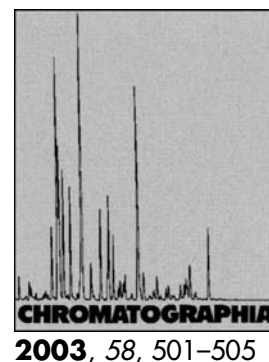


Automotive Gasoline Quality Analysis by Gas Chromatography: Study of Adulteration



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Key Words

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Gasoline
Adulteration
Organic solvents

Summary

The addition of organic solvents (light aliphatic, heavy aliphatic and aromatic hydrocarbons) in Brazilian gasoline is unfortunately very frequent, and this illicit practice impairs gasoline quality. Gas chromatography (GC) and gas chromatography coupled to mass spectrometry (GC-MS) analyses can be used as a procedure to improve the detection of adulterated gasoline. The results showed that adulterated samples and also the type of organic solvent used in adulteration can be detected by comparison of chromatographic profiles (standard samples versus adulterated samples). However, a single GC analysis can detect an adulterated gasoline, and so decrease the number of adulterated samples approved as presenting good quality.

Introduction

Gasoline is a mixture of liquid, volatile and inflammable petroleum-derived compounds, in the range of C₄–C₁₂ carbon atoms and boiling points in the range of 30 °C–225 °C. Gasoline “A” is derived directly from the refinery and “C” type is the gasoline “A” with the addition of 24% ± 1% of ethanol (% v/v) [1].

The end of the monopoly distribution and the State production has brought many changes in the Brazilian gasoline. One of them is the addition of illicit organic solvents in gasoline. The most

important solvents used in this adulterating practice are: light aliphatic hydrocarbons (C₄–C₈), heavy aliphatic hydrocarbons (C₁₃–C₁₅) and aromatic hydrocarbons. Most used solvents in adulteration are kerosene, diesel, toluene, xylenes, hexane and light naphthas. 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 [2].

High boiling compounds, when added to gasoline, increase knock and engine wear and may make starting difficult; low boiling compounds may

cause vapour lock [3,7]. 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 [5].

The detection of adulterated gasoline needs fast action by regulation agencies to protect consumers from the harms caused by the bad quality of gasoline, besides the possible hazards to the environment [4].

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 and sulfur percentage etc. However, after all these measurements, many samples are approved but in reality they are adulterated [3, 4].

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 [8–16]. 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

Table I. Composition of samples prepared in laboratory.

Sample No.	Gasoline from oil refinery*	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

* X-Manguinhos Refinery; Y-Duque de Caxias Refinery (REDUC).

presence of additives. The complete hydrocarbons type PIONA analyses (Paraffins, Iso-paraffins, Olefins, Naphtenes and Aromatics) of gasoline range products are generally carried out by multi-dimensional GC methods (ASTM D-5443). The olefin content is measured using the ASTM D-6298-98 method, which is also based on multi-dimensional GC [17, 18]. Though these methods have been standardized, yet they demand perfect instrumental conditions for accurate and reliable analyses. The ASTM D-3710 is also a standard test method for boiling range distribution of gasoline by gas chromatography. GC has also been used to compare liquid petroleum products within a given classification [8]. In these comparisons, the relative peak intensities are used to distinguish products containing the same components [6]. However, GC has not been used so extensively as a technique for detection gasoline adulteration because it is time consuming and expensive, for a large number of samples.

In this work, the gas station gasoline samples gas chromatographic profiles were used as a tool to detect organic solvent adulterated samples in comparison with purposely adulterated gasoline Type A samples. These chromatographic profiles in conjunction with the physico-chemical parameter analyses are a powerful methodology for this purpose.

Experimental

Material

The commercial solvents used were donated by Carbone 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 purposely adulterated samples were prepared in our laboratory. Each sample consist of 39% (v/v) gasoline Type A (deriving from oil refineries), 22% (v/v) of ethanol and a varying distribution to a constant total of 39% of commercial organic solvents. The solvents were heavy aliphatic, light aliphatic and aromatic hydrocarbons. The detailed compositions of these samples are shown in Table I.

Sample Collection

Gasoline samples were obtained from different gas stations in the State of Rio de Janeiro. These samples were previously analyzed by the physico-chemical parameters and 21 adulterated samples were selected for this work.

Gas Chromatographic Analysis

All samples were subjected to GC and GC-MS analyses. The GC and GC-MS operating conditions were as follows: HP 5890 gas chromatography and HP 5972 mass spectrometry detector (Agilent Technologies, Avondale, USA), ionization 70 eV, 60 m × 0.25 mm i.d capillary column coated with DB-5; $d_f = 1 \mu\text{m}$ (J & W Scientific, Folsom, CA, USA), temperature program 40 °C to 220 °C at 4 °C min with an initial isothermal period of 15 min at 40 °C. Helium was used as carrier gas for GC-MS and hydrogen for the GC analyses. The detector and injector temperatures were held at 270 °C, the split ratio was 1/70 and the sample volume 1.0 μL .

Structural assignments were performed with the help of the Wiley 275 standard mass spectra library.

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), Research Octane Number (RON), Antiknock Indices [$\text{AI} = (\text{MON} + \text{RON})/2$], Ethanol percentage, color and clarity and the results were compared by the Brazilian National

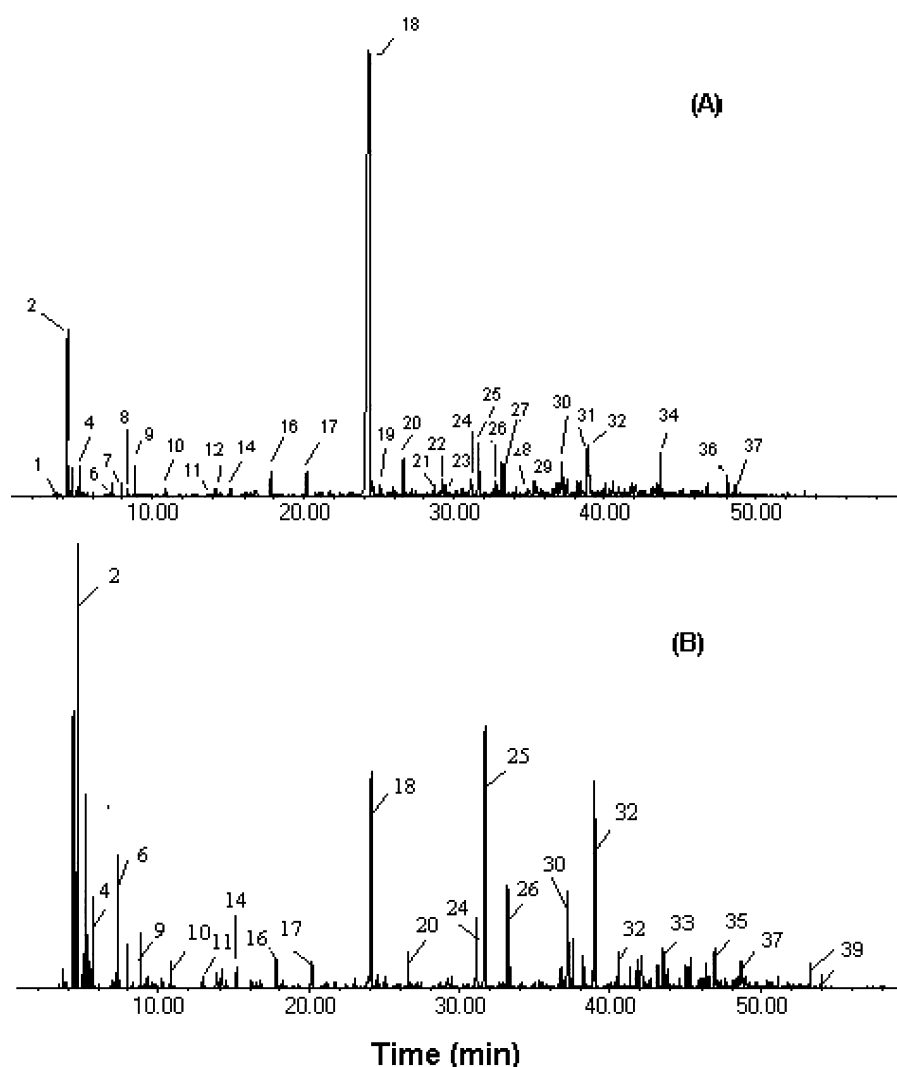


Figure 1. A typical gas chromatogram from Manguinhos (A) and Reduc (B) oil refineries gasoline samples.

Petroleum Agency regulation limits. Automatic distillation equipment Herzog HDA 627 for ASTM D 86 and an infrared analyzer, Petrospec GS 1000, were used.

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), with smaller amounts of olefinic hydrocarbons (pentenes, hexenes, heptenes, octenes, nonenes) as listed in Table II [6].

The chromatographic profiles of the spiked samples were obtained, and the samples derived from gas stations were compared with these laboratory chromatographic profiles.

Figure 2 shows gas chromatograms of standard and adulterated gasoline samples. The Figure 2A shows the REDUC oil refinery gasoline chromatogram; Figure 2B shows the chromatogram from gasoline doped with heavy aliphatic hydrocarbons solvent. It is observed an increase in the peaks height at 48–60 min region in comparison with the refinery sample (Figure 2A) because of the homologue paraffin series (nC_{13} – nC_{15}), recalling that typical gasoline hydrocarbon compounds are in the range of nC_4 – nC_{12} . Figure 2C showed an increase in the peaks height at the retention time range 33–36 min in comparison with the refinery sample; this

Table II. Gasoline main compounds identification and their respectively retention time (min).

No	compounds	t_R (min)
1	Butane	3.7
2	Ethanol	4.3
3	Pentene	4.9
4	Pentane	5.1
5	2,3-Dimethylbutane	5.4
6	2-Methylpentane	7.3
7	3-Methylpentane	7.9
8	Hexene	8.4
9	Hexane	8.8
10	Methylcyclopentane	10.9
11	Benzene	13.8
12	Cyclohexane	13.9
13	2,3-Dimethylpentane	14.1
14	3-Methylhexane	15.1
15	1,2-Dimethylcyclopentane	16.7
16	Heptane	17.8
17	Methylcyclohexane	20.2
18	Toluene	24.2
19	1,2-Dimethylcyclohexane	25.0
20	Octane	26.7
21	2,6-Dimethyl heptane	26.8
22	Ethylcyclohexane	27.0
23	Dimethylcyclohexane	27.1
24	Ethylbenzene	31.1
25	<i>m/p</i> -Xylenes	31.6
26	<i>o</i> -Xylene	33.2
27	Nonane	33.4
28	Dimethylbenzene	35.3
29	Propylbenzene	36.8
30	Ethylmethylbenzene	37.3
31	Decane	37.8
32	Trimethylbenzene	38.0
33	Dimethylethylbenzene	43.2
34	Undecane	43.8
35	Methylpropenylbenzene	46.8
36	Dodecane	48.1
37	Naphthalene	48.6
38	Tridecane	52.1
39	Methylnaphthalene	54.0
40	Tetradecane	55.1

region is typical for aromatic hydrocarbons. Figure 2D shows a gasoline with light hydrocarbon solvent, where it is observed an increase in the peaks height at region 0–20 min. The same was observed for the adulterated Manguinhos oil refinery gasoline samples chromatographic profiles (Figure 2E–2H).

Figure 3 shows chromatograms from gas station samples. It is easy to observe from the chromatogram that the gasoline shown in Figure 3A (gasoline sample – G1) was enriched with light aliphatic and with aromatic hydrocarbons, while the gasoline in Figure 3B (G2) and Figure 3D (G4) was enriched by the addition of three different solvent types (light aliphatic, heavy aliphatic and aromatic hydrocarbons). There is a homologue series (nC_{13} – nC_{15}) at the end of the gas chromatograms (48–60 min). Figure 3E (G5) shows aromatic hydrocarbon adulteration by a contribution in

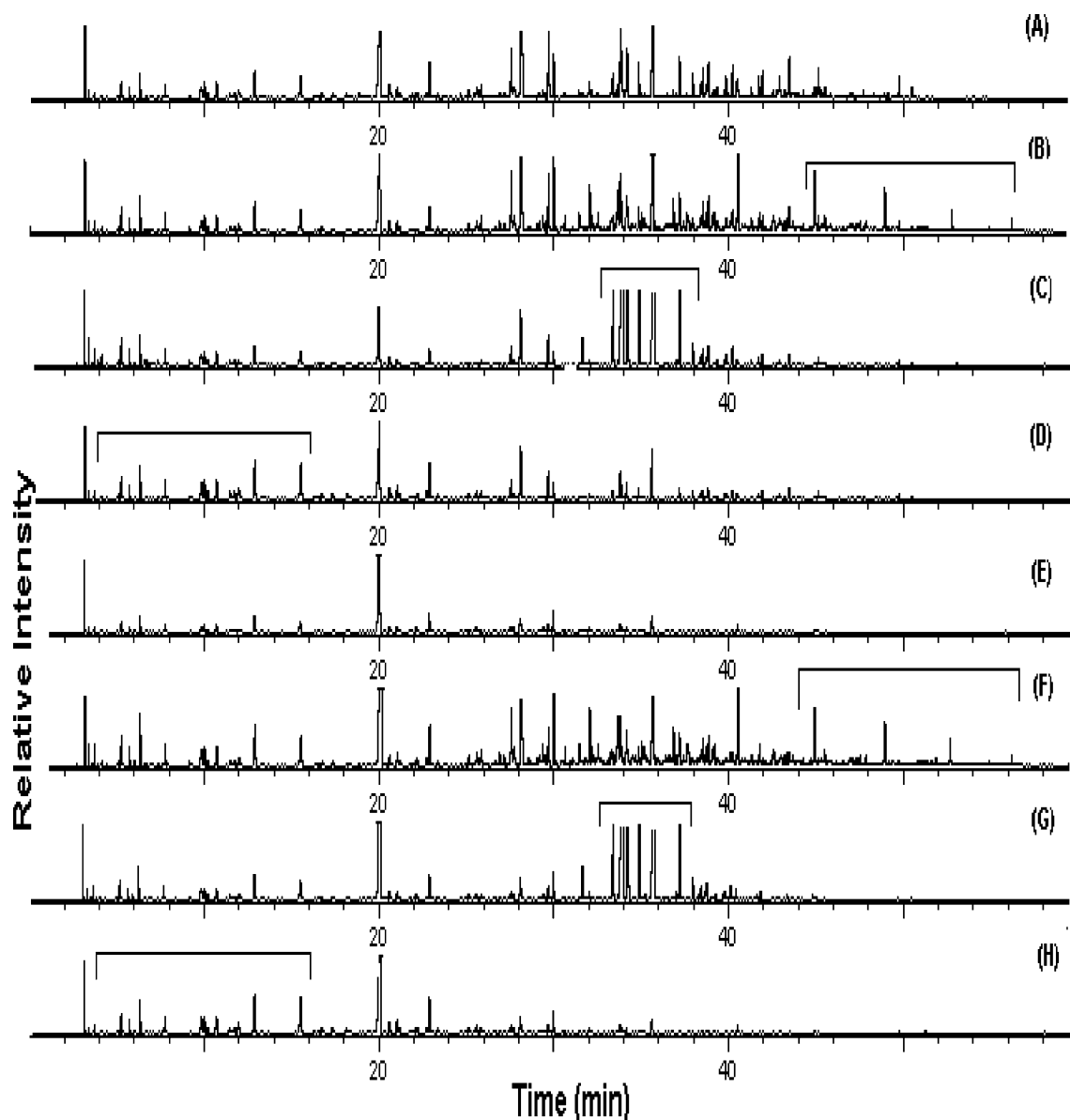


Figure 2. Comparison of gasoline gas chromatogram from Reduc (A) and Manguinhos (E) oil refinery, purposely adulterated Reduc (B) and Manguinhos (F) gasolines with 39% heavy aliphatic hydrocarbon solvent, Reduc (C) and Manguinhos (G) with aromatic hydrocarbon solvent and Reduc (D) and Manguinhos (H) light aliphatic hydrocarbon solvents.

the region 33–36 min. Figure 3C (G3) shows heavy aliphatic hydrocarbons with the homologue series (nC_{13} – nC_{15}) at the end of the gas chromatogram (48–60 min) more pronounced than that in the standard samples, being clearly adulterated with heavy aliphatic hydrocarbon solvent, although approved by standard physico-chemical analyses regulated by Brazilian Petroleum Agency. The distinct change in the chromatographic profile is bracketed for emphasis.

With the present results, it may be concluded that there is a real necessity to improve the present adulteration detec-

tion parameters (by ANP) and to guarantee better quality gasoline.

Conclusion

Solvent adulteration detection is difficult, because many of the solvent compounds are also in the original gasoline composition. Some samples approved by standard specification tests in reality are adulterated.

A better, rapid and easy way to detect the adulteration is to compare the gasoline sample gas chromatographic profiles

(standard samples versus gas station samples).

The detection of solvent adulteration by heavy aliphatic hydrocarbons is easier because these compounds are not present in the original gasoline composition. Otherwise, the detection of adulteration by aromatic and light aliphatic hydrocarbons is difficult because they are common constituents at gasoline. Furthermore, it is possible to detect when the solvent is added over 5.5% for aromatic hydrocarbons and over 28% for light aliphatic hydrocarbons. The adulteration by light aliphatic hydrocarbon solvent is the most difficult to detect.

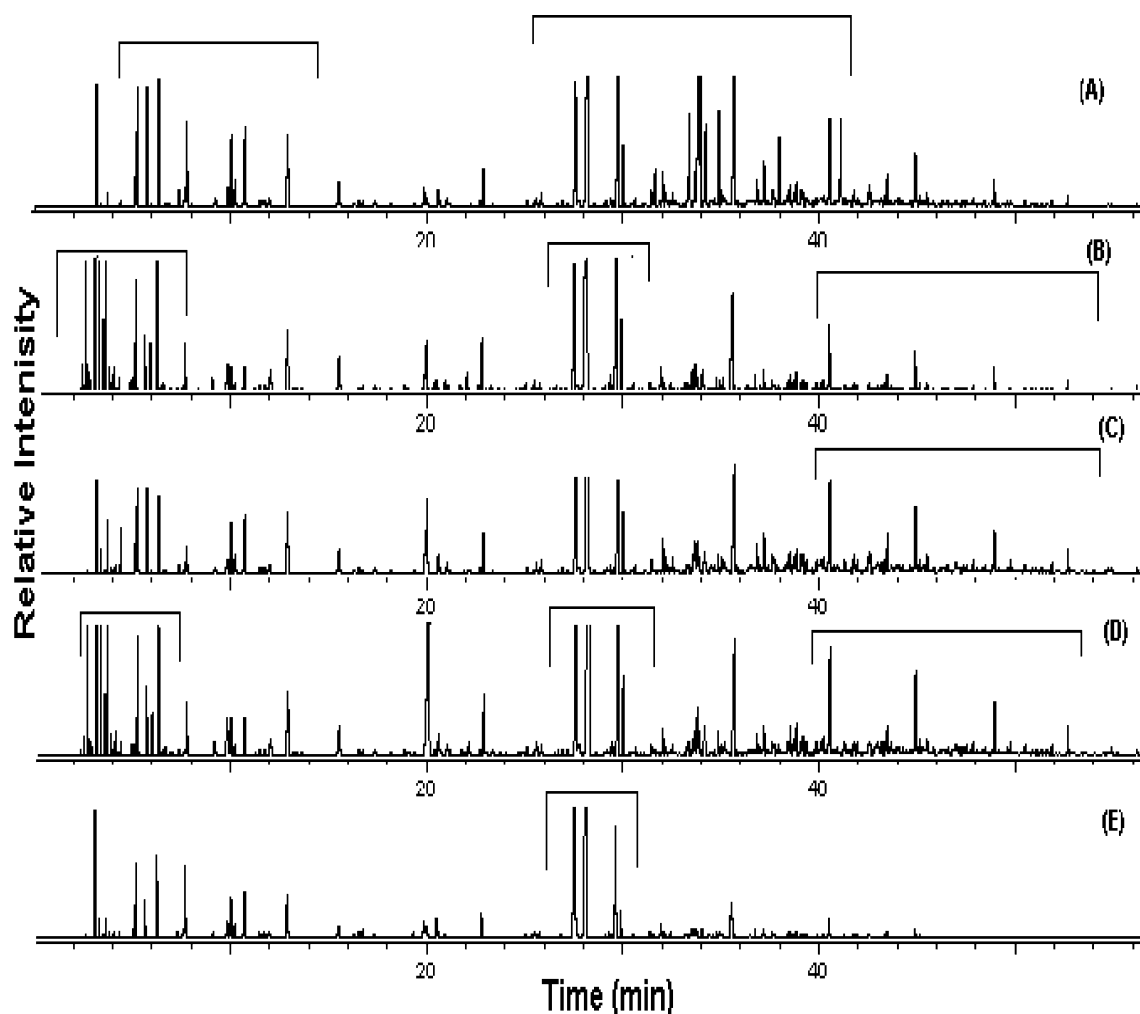


Figure 3. Gas chromatograms of gasoline samples deriving from gas station of Rio de Janeiro State, G1 (A), G2 (B), G3 (C), G4 (D) and G5 (E).

A national gas chromatographic profiles data file could be created with all standard gasoline samples commonly commercialized in Brazil.

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