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The Water Detection in Gasoline and Its Hydrocarbon Contents

Petrolde Su Tayini ve Hidrokarbon İçeriği

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Abstract

In this work a practical method is proposed for detection water contamination in gasoline. Methylene blue crystal was added to the gasoline samples and shaked, the blue colour developed in water phase indicating water contamination. Phthalate ester was detected by the GC/MS in the water contamined sample. Water contamination was found in one of the three samples tested.

The identified hydrocarbons by the GC/MS analysis were: 12 aliphatic, 21 aromatic compounds in normal and 9 aliphatic, 19 aromatic compounds in super type of gasoline.

Tetra ethyl lead which is usually added to gasoline, was also detected in all the samples.

Keywords: Water detection, super/normal gasoline, analysis hydrocarbons.

Introduction

Petroleum is a Latin word and orginated from petra, stone and oleum. It is a complex mixture of gaseous, liquid and solid hydrocarbons. The number of hydrocarbons in crude oil are approx. thousands. It contains small amounts of oxygen, sulfur and nitrogen.

Petroleum is fractioned into a series of products of gradually increasing boiling points. These are petroleum ether, gasoline, kerosene, furnace oil, gas oil, light, medium and heavy lubricating oils. Asphalt or coke remain in the still as a residue.

Gasoline is the chief fuel for motor cars and airplanes. It must be highly refined by removing the impurities. It is washed with an

organic lead to remove sulfur compounds. If the sulfur compounds were not removed, they would form sulfur dioxide and then sulfuric acid and these compounds in turn would cause serious corrosion of the crank- case or cylinders. The sulfuric acid after being used to purify petroleum, is separated as an acid sludge. It is washed first with water then with dilute alkali to remove the trace of acid. Finally gasoline is decolorized by filtration on fuller's earth.

When ordinary gasoline is subjected to high compression, it often causes a gas knock. It is possible to lessen this knocking by adding lead tetra ethyl to the gasoline, but it is carcinogenic and mutagenic effects on laboratory animals (Nadim *et al.*, 2001). To decrease the risk of lead poisoning a little ethylene dibromide is added to the gasoline. It prevents undesirable formation of lead oxide on engine valves. After Jan, 1 1996 the use of leaded gasoline for highway vehicles was banned in the United States (Thomas, 1995).

To specify the anti-knock quality of the hydrocarbons, iso-octane of a subtance with only very slight tendency to knock is given an octane number of 100, and n-heptane, which knocks strongly has an octane number of zero. Fuel is tested for iso octane and n-heptane contents. The percentage of iso octane in the mixture gives the octane number of the fuel. Regular gasoline having an octane number about 80-90 is considered as normal petrol. Its performance is compared to that of iso-octane, once considered the perfect mixtures composed of 90- 95 parts of iso-octane and 10-5 parts of heptane (Bible *et al.*, 1949; Hopkin et al., 1949; Selwood, 1950; Karrer, 1950; Blucher *et al.*, 1954; Brewster and Ewen, 1968).

Aviation gasoline is superior pure iso octane. If gasoline is not refined perfectly, it contains other petroleum products which are undesirable.

Recently ethyl alcohol is mixed (20-30 %) with gasoline to produce a suitable motor fuel, as it burned clean and free from any deposits, it produced higher compression ratios inside the engines without knocking and produced more horse-power due to increase in the octane number. Addition of ethanol to gasoline would have reduced wehicle's use of gasoline by 20-30% (Nadim *et al.*, 2001).

In this paper is reported the water contamination in gasoline and analysis of hydrocarbon contents.

Material

The gasoline samples were taken from 3 stations (located in İstanbul) in 1998.

The analysis was made:

1 - Detection of water

100 ml samples were transfered into glass capped erlenmayer and a crystal of methylene blue was added and shaken.

2 – Hydrocarbon content was analysed by GC/MS HP 6890 capillary GC connected to a HP Mass selective Detector (MSD) controlled by a HP Chemstation. Operating conditions were:

Column 50 mx 0.25 x 0.25 mm HP PONA,

Temperature programme: 40°C, at 8 min, 40-280°C at 10°C/min, 280°C at 10 min.

Detector : 280 °C

Injector : 280 °C

Split: 20/1, flow 1.5 ml min.

Carrier gas: Helium 29.4 psi.

Results and Discussion

Blue water phase was observed within one of the gasoline samples, indicating water contamination.

The chromatograms of normal and super gasoline are shown in Fig. 1a-b and 2a-b respectively. Fig 3a-b shows the chromatogram superpose on normal and supper gasoline.

Hydrocarbon contents of examined gasoline samples are shown in Table 1. Butyl phthalate was identified only in the sample Nr. 1. The selected part of chromatogram of water contamined gasoline and its spectrum of phthalate and the spectrum taken from HP memory are in Fig. 4

Table 1 - The list of detected hydrocarbon compounds

1a- Compounds in normal gasoline:

1– Aliphatic

Heptane, Octane, Pentadecane, Hexadecane, Octadecane, Phytane, Heneicosane, Docasane, Tricosane, Tetracosane, Cyclohexane, Methyl cyclohexane.

2 - Aromatic

Toluene; m-Xylene; Benzene 1-ethyl 3-methyl; 1.2.4 Trimethyl benzene; 1.2.3 Trimethyl benzene; Benzene 4 ethyl 1.2 dimethyl; Benzene 1,3 dimethyl; 5 Isopropyl m- xylene; 1-H Indene 2.3 dihydro 4.7-di methyl; Naphthalene; 2-Methyl naphthalene; 1-Methyl naphthalene; Naphthalene 1 ethyl; Naphthalene 2.7 dimethyl; Naphthalene 1.5 dimethyl; Naphthalene 1.7 dimethyl; Phenol 2.6 bis (1.1 dimethyl ethyl) 4 ethyl; Naphthalene 1.4.6 trimethyl; Naphthalene 2.3.6 trimethyl; Naphthalene 1.6.7 trimethyl; Phenanthrene; 1H-Indene 2.3 dihydro-1-methyl.

1b– Super gasoline

1 - Aliphatic

Heptane; Octane; Eicosane; Pentadecane; Heptadecane; Octadecane; Phytane; Heneicosane; Tricosane.

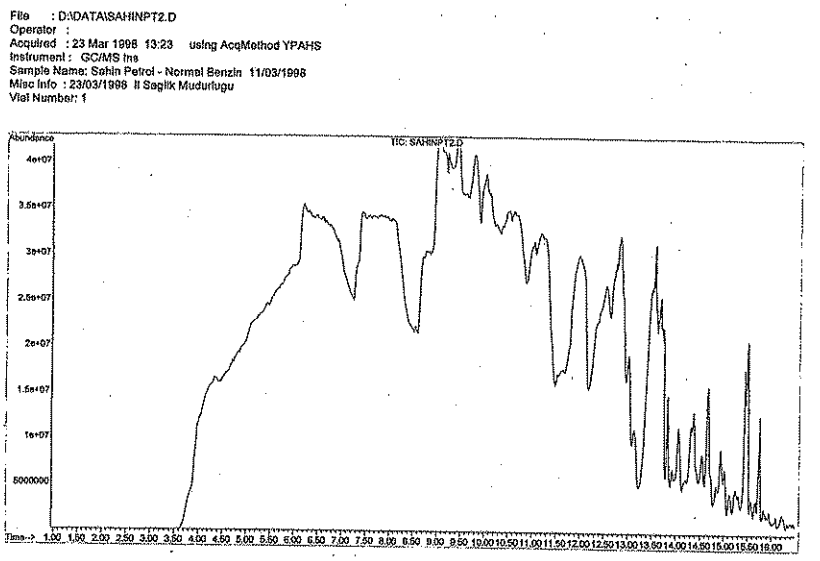
2 – Aromatic

Toluen; o-Xylene; m-Xylene; o-Ethyl toluene; 1.2.4 Trimethyl benzen; 1.2 Diethyl benzen; Benzen cyclopropyl; 1.2.4.5 Tetra methyl benzen; Naphthalene; Naphthalene 2 methyl; Naphthalene 1.2 dimethyl; Naphthalene 2.6 dimethyl; Naphthalene 2.3 dimethyl; Naphthalene 1.7 dimethyl; Naphthalene 1.4 dimethyl; Naphthalene 1.4.6 trimethyl; Naphthalene 1.6.7 trimethyl; Phenanthrene.

These compounds were usually detected in gasoline by GC/MS (Annon, 1990).

Tetra ethyl lead usually added into gasoline was also detected in tested samples.

Fig. 1. The chromatogram of normal gasoline.



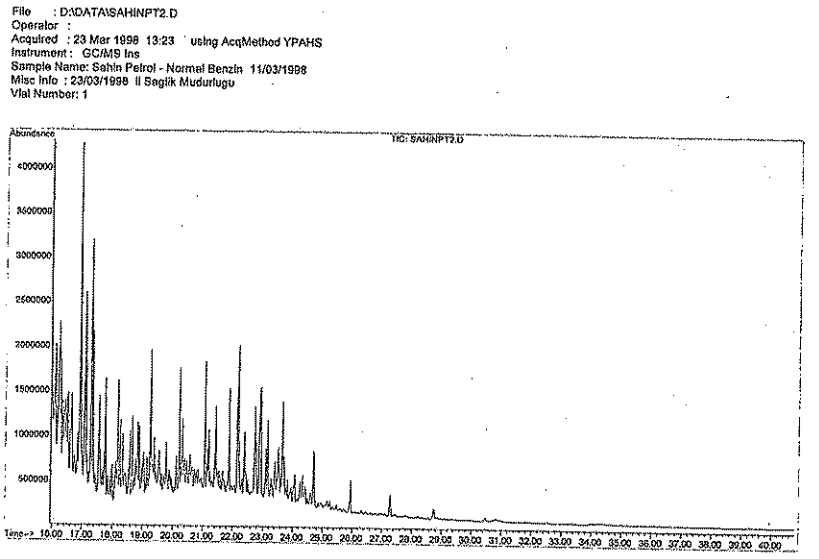
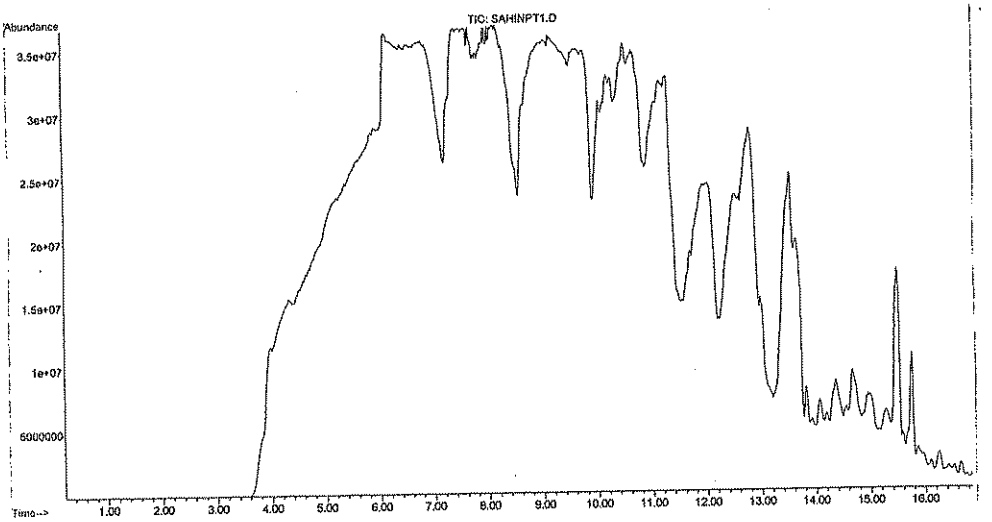


Fig. 2. The chromatogram of super gasoline.

File : D:\DATA\SAHINPT1.D
Operator :
Acquired : 23 Mar 1998 12:27 using AcqMethod YPAHS
Instrument : GC/MS Ins
Sample Name: Sahin Petrol - Super Benzin 11/03/1998
Misc Info : 23/03/1998 İl Saglik Mudurlugu
Vial Number: 1



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Acquired : 23 Mar 1998 12:27 using AcqMethod YPAHS
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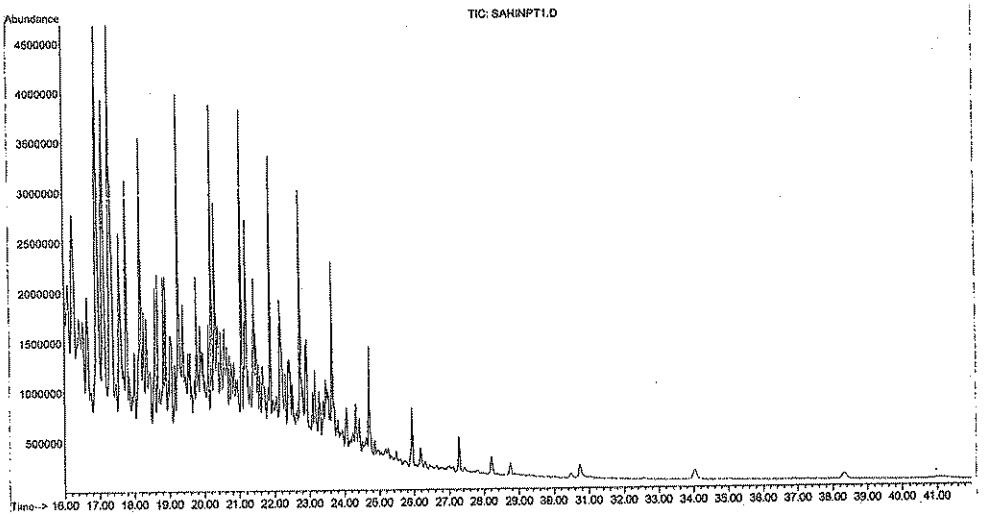


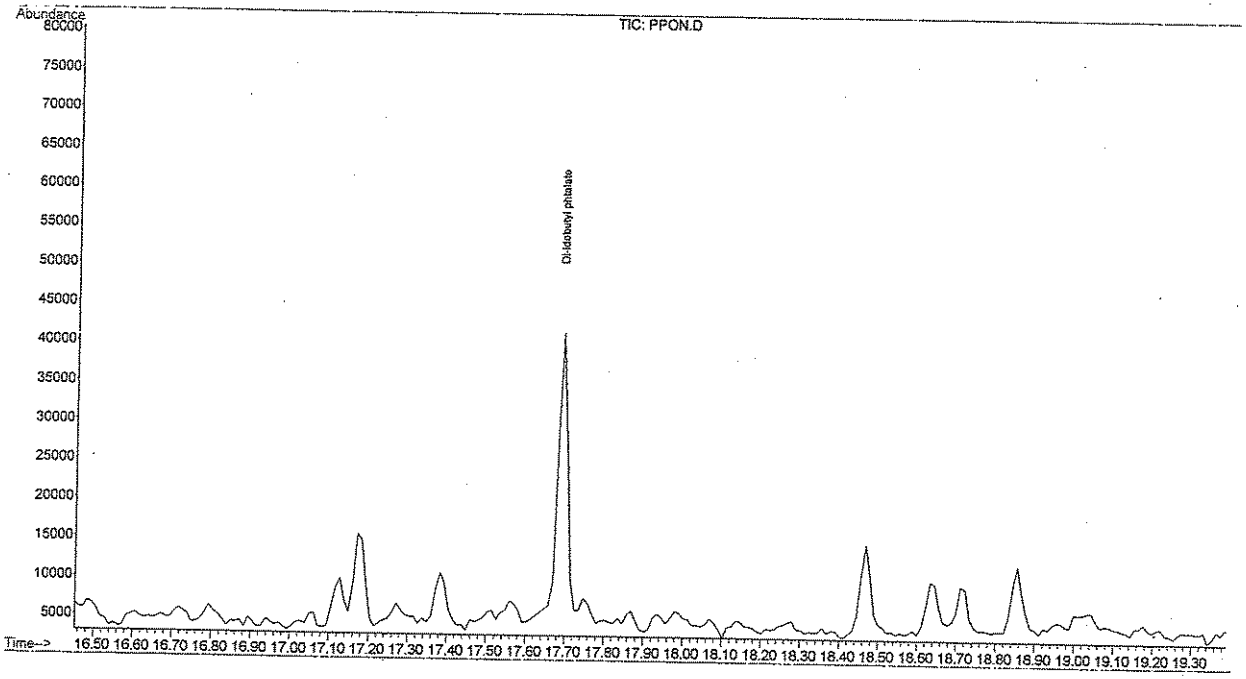
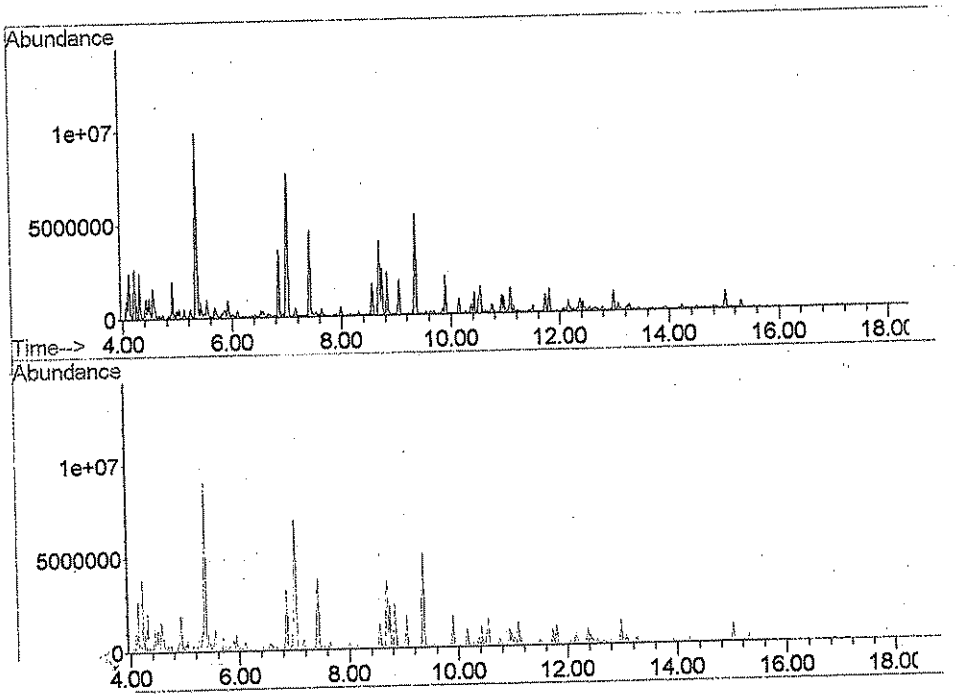


Fig. 3a) The selected part of chromatogram of the sample No:1.

DiBP- Diiso buthyl phthalate.

3b) 1- The spectrum of Di BP.
2- The spectrum taken from HP memory



It is concluded,

1 – That the contamination of gasoline with water can be identified simply and practically by this method proposed.

It was also found that contamined sample contained phthalate (DiBP). It is assumed that phthalate had been added into gasoline to facilitate water mixing.

2 – That aliphatic and aromatic compounds were detected in gasoline.

Özet

Bu çalışmada otomobil yakıtı petrole su ilavesinin teşhisi için kolay ve basit bir method önerilmiştir. Bunun için bir erlenmayer içinde petrole bir kaç kristal metilen mavisi ilave edilir ve çalkalanır. Petrol su içermesi halinde maviye boyanmış damlalar/faz görülür. Bu şekilde petrole su katılmış olduğu anlaşılır. İstanbul'da incelenen 3 petrol istasyonundan birinin petrole su kattığı tesbit edilmiştir. Bu su katılan petrol içinde ayrıca GC/MS analizinde ftalat (diisobutil ftalat) bulunmuştur. Bunun suyun petrolde dağılımını kolaylaştırmak için ilave edildiği düşünülmüştür. İncelenen bu petrollerin GC/MS analizinde normal benzinde 12 alifatik, 21 aromatik ve süper benzinde 9 alifatik, 19 aromatik madde saptanmıştır.

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