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GAS CHROMATOGRAPHIC ANALYSIS OF GASOLINE AND PURE NAPHTHA USING PACKED COLUMNS

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SUMMARY

Gas chromatographic analyses of samples of premium-grade gasoline and pure naphtha have been performed by the gas chromatography-mass spectrometry technique using 5-m columns packed with graphitized carbon black (Carbopack C) modified with 2,4,5,7-tetranitrofluorenone. 196 compounds were observed in the analysis of a premium-grade gasoline; 157 of them, with 18 overlappings, were identified.

Olefins and aromatics in distillate fractions of petroleum can be identified directly by the use of these packed columns.

INTRODUCTION

Graphitized carbon black (GCB) has been shown to be a highly selective adsorbent for hydrocarbons. Eggertsen *et al.*^{1,2} described the use of columns packed with carbon black modified with varying amounts of squalane for the fractionation of hydrocarbon mixtures. They were able to identify all but one of the 25 C₅-C₇ saturates.

Schneider *et al.*³ used a 10 m × 0.25 mm I.D. capillary column filled with squalane-modified GCB to separate a C₁-C₄ hydrocarbon mixture containing 20 components.

Bruner *et al.*⁴ tested the performance of a 1.5-m column packed with H₃PO₄-modified GCB by chromatographing a C₃-C₁₁ pure naphtha. They observed a number of peaks approximately equal to that found with a conventional 100-m capillary column, though resolution was poor.

Recently, a number of papers have appeared dealing with the separation of both unsaturated and saturated C₁-C₅ hydrocarbons⁵⁻⁸ and aromatics^{9,10} by the use of GCB modified with various Lewis-acid type molecules. The adsorption characteristics of the carbon surface are modified by strong lateral interactions through charge transfer between the π -acceptor and unsaturated or aromatic hydrocarbons. In addition, the extent of the modification is strictly dependent upon both the acid strength and the relative amount of the modifying agent deposited on the carbon surface.

In particular, it was found that by modifying the surface of Carbopack C, which

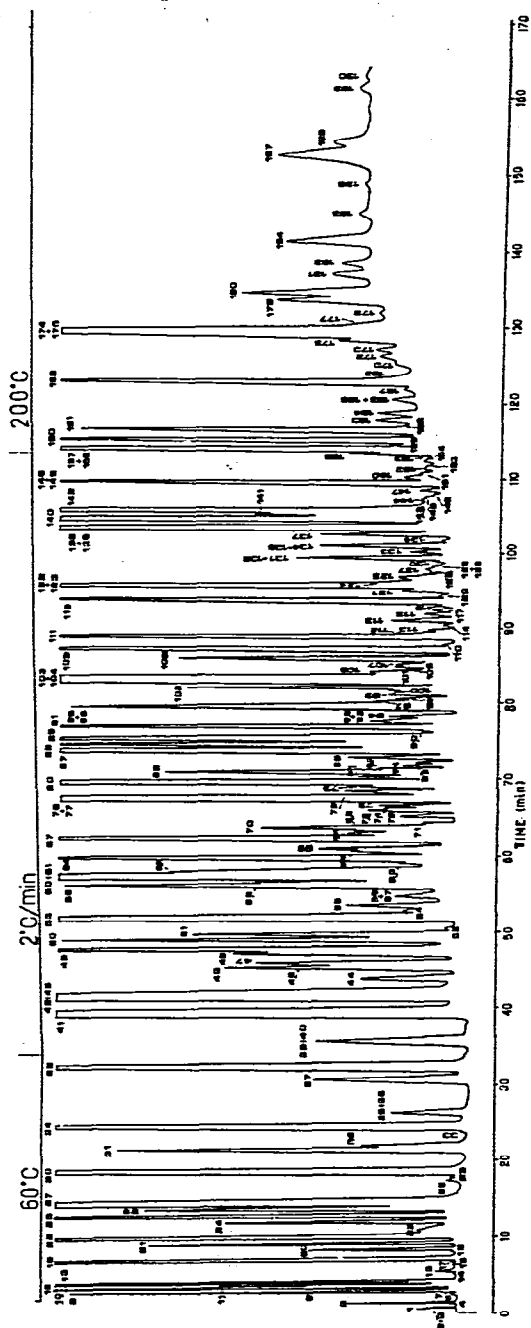


Fig. 1. Chromatogram of a premium-grade gasoline. Column, 5 m x 2 mm I.D.; packing, Carbo-pack C (100-120 mesh) + 0.28 TeNF; carrier gas, hydrogen; drop pressure, 6 kg/cm²; dead time, 43 sec.

is a type of GCB, with *ca.* 0.35% 2,4,5,7-tetranitrofluorenone (TeNF), the separation of 26 aromatics in the C_6 – C_{10} range with baseline separation of *meta*- and *para*-xylenes was accomplished in less than 45 min¹⁰.

The determination of the detailed composition of very complex hydrocarbon mixtures, such as full-range motor gasolines and petroleum fractions, is today achieved almost exclusively by using long capillary columns that provide a sufficiently high number of plates for the separation of close isomers. In the petroleum industry, the analysis of C_3 – C_{12} hydrocarbons is usually carried out by a method described in 1968 by Sanders and Maynard¹¹. The analysis of gasoline was accomplished on a 200-ft. squalane capillary column in less than 2 h using both temperature and flow programming; 240 peaks were observed in an average gasoline of which 180 were identified. To separate the light fraction of gasoline, a subambient starting column temperature was required and identification of peaks was carried out by using 230 standards.

The method described above has some drawbacks. One is that analysis of gasoline cannot be carried out by common gas chromatographic apparatus, because the starting temperature is -5° . A second is that the use of a complex temperature programme coupled with a flow programme may alter somewhat the actual elution time of a given peak from run to run. Another limitation is that the gas chromatography–mass spectrometry (GC–MS) technique cannot be used for the identification of all individual components of very complex mixtures because of the low loadability of a capillary column. Therefore, the identification procedure of an uncommon gasoline sample carried out by spiking with hydrocarbon standard becomes time-consuming and can be made difficult because of the difficulty of having more than 230 hydrocarbon standards.

The purpose of this paper is to show that the analysis of very complex hydrocarbon mixtures can be carried out on a 5-m column packed with Carbowack C modified with 0.28% TeNF in *ca.* 3 h. Approximately 172 chromatographic peaks were observed in the analysis of a premium-grade gasoline; 157 of them with 18 overlappings have been specifically identified by GC–MS.

To resolve peaks containing two or more components, another column packed with Carbowack C modified with 0.3% TeNF was also used.

The possibility of direct identification of olefins and aromatics contained in petroleum by the use of these packed columns was evaluated by chromatographing a blended mixture of light and medium pure naphtha.

EXPERIMENTAL

The graphitized carbon black (GCB) used, Carbowack C, was supplied by Supelco, Bellefonte, Pa., U.S.A. The particle size range was 60–80 mesh, which grinding reduced to 100–120 mesh.

The preparation of the packing materials and the packing method have been described elsewhere¹⁰.

The peaks were identified by GC–MS. An AEI MS₁₂ mass spectrometer coupled with a Carlo Erba (Milan, Italy) Model GI gas chromatograph was used¹². Spectra were taken for every significant peak when the intensity of the spectrum on the oscillograph was sufficient to ensure a clear recording.

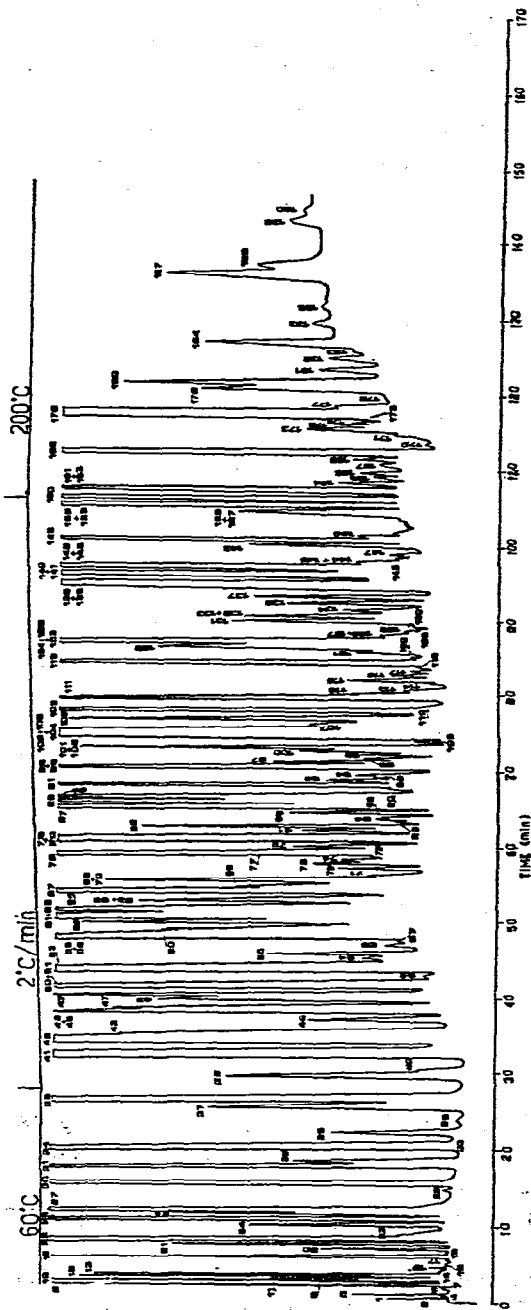


Fig. 2. Chromatogram of a premium-grade gasoline. Packing, Carbopack C + 0.30% TeNF. Other conditions as in Fig. 1.

TABLE I
HYDROCARBON COMPONENTS OF A PREMIUM-GRADE GASOLINE

1 Methane	53 Hexane
2 Ethane	54 2,2,3-Trimethylbutane
3 Ethylene	55 <i>cis</i> -1,3-Dimethylcyclopentane
4 Cyclopropane	56 Branched C ₇ -olefin
5 Propane + propene	57 Branched C ₇ -olefin
6 Propadiene	58 3,3-Dimethylpentane + 1,2- <i>trans</i> -dimethylcyclopentane
7 Methylcyclopropane	59 1,2- <i>cis</i> -Dimethylcyclopentane
8 Isobutane	60 Benzene
9 But-1-ene	61 2,2-Dimethylpentane
10 Butane	62 Methylcyclohexane
11 Isobutene	63 C ₇ -olefin
12 <i>cis</i> -But-2-ene	64 2,4-Dimethylpentane
13 <i>trans</i> -But-2-ene	65 C ₇ -olefin
14 Buta-1,3-diene	66 <i>trans</i> -1,3-Dimethylcyclopentane
15 Neopentane	67 2,3-Dimethylpentane
16 Unknown	68 C ₇ -olefin
17 Unknown	69 C ₇ -olefin
18 Cyclopentane	70 Ethylpentane
19 Unknown	71 C ₇ -olefin
20 3-Methylbut-1-ene	72 C ₇ -olefin
21 Cyclopentene	73 C ₇ -olefin
22 Isopentane	74 C ₇ -olefin
23 Unknown	75 C ₇ -olefin
24 Pent-1-ene	76 3-Methylhexane
25 2-Methylbut-1-ene	77 C ₇ -olefin
26 <i>cis</i> -Pent-2-ene	78 Ethylcyclopentane
27 Pentane + <i>trans</i> -pent-2-ene	79 C ₇ -olefin
28 Unknown	80 2-Methylhexane
29 Unknown	81 C ₇ -olefin
30 2-Methylbut-2-ene	82 2-Methyl-3-ethylpentane
31 Cyclohexane	83 C ₇ -olefin
32 2,2-Dimethylbutane	84 C ₇ -olefin
33 Unknown	85 C ₇ -olefin
34 Methylcyclopentane	86 2,2,3-Trimethylpentane
35 Methylcyclopentene	87 2,2,4-Trimethylpentane
36 Unknown	88 2,3,3-Trimethylpentane
37 4-Methyl- <i>cis</i> -pent-2-ene	89 Heptane + 1,3- <i>trans</i> -dimethylcyclohexane
38 2,3-Dimethylbutane	90 <i>cis</i> -1,2-Dimethylcyclohexane
39 4-Methyl- <i>trans</i> -pent-2-ene	91 2,3,4-Trimethylpentane
40 4-Methylpent-1-ene	92 3,3-Dimethylhexane
41 3-Methylpentane	93 C ₇ -alicyclic
42 2-Methylpentane	94 2,2-Dimethylhexane
43 C ₆ -olefin	95 2,5-Dimethylhexane
44 C ₆ -olefin	96 2,4-Dimethylhexane
45 2-Methylpent-1-ene	97 3,4-Dimethylhexane
46 1,1-Dimethylcyclopentane	98 1,2- <i>trans</i> -Dimethylcyclohexane
47 Hex-3-ene (<i>cis</i> or <i>trans</i>)	99 1,4- <i>cis</i> -Dimethylcyclohexane
48 <i>cis</i> -Hex-2-ene	100 Unknown
49 3-Methyl- <i>cis</i> -pent-2-ene + C ₅ -olefin	101 1,3- <i>cis</i> -Dimethylcyclohexane
50 3-Methyl- <i>trans</i> -pent-2-ene + 2-methylpent-2-ene	102 2,3-Dimethylhexane
51 <i>trans</i> -Hex-2-ene	103 1,4- <i>trans</i> -Dimethylcyclohexane
52 C ₆ -olefin	104 Toluene

(Continued on p. 152)

TABLE I (continued)

105 Ethylhexane	149 Propylbenzene
106 Unknown	150 C ₁₀ -isomer
107 Unknown	151 Unknown
108 4-Methylheptane	152 Unknown
109 3-Methylheptane	153 Unknown
110 Unknown	154 Unknown
111 2-Methylheptane	155 Unknown
112 C ₉ -isomer	156 Indane
113 C ₉ -isomer	157 C ₁₀ -isomer
114 C ₉ -isomer	158 <i>meta</i> -Ethyltoluene
115 Ethylcyclohexane	159 Unknown
116 C ₉ -isomer	160 <i>para</i> -Ethyltoluene
117 C ₉ -isomer	161 <i>ortho</i> -Ethyltoluene
118 Unknown	162 Unknown
119 Octane	163 C ₁₀ -isomer
120 Unknown	164 C ₁₀ -isomer
121 C ₉ -isomer	165 C ₁₀ -isomer
122 C ₉ -isomer	166 Isobutylbenzene
123 Ethylbenzene	167 C ₁₀ -isomer
124 C ₉ -isomer	168 1,3,5-Trimethylbenzene
125 C ₉ -isomer	169 C ₁₀ -isomer
126 Unknown	170 C ₁₀ -isomer
127 Unknown	171 C ₁₀ -isomer
128 Unknown	172 Butylbenzene
129 Unknown	173 C ₁₀ -isomer
130 Unknown	174 Decane
131 2,3-Dimethylheptane	175 C ₁₀ -aromatic
132 Unknown	176 1,2,4-Trimethylbenzene
133 4-Ethylheptane	177 <i>meta</i> -Diethylbenzene
134 3-Ethylheptane	178 Unknown
135 Isopropylbenzene	179 <i>meta</i> -Propyltoluene
136 Unknown	180 1,2,3-Trimethylbenzene
137 4-Methyloctane	181 <i>para</i> -Propyltoluene
138 <i>meta</i> -Xylene	182 <i>ortho</i> -Propyltoluene
139 3-Methyloctane	183 Unknown
140 <i>para</i> -Xylene	184 1,3-Dimethyl-5-ethylbenzene
141 2-Methyloctane	185 Unknown
142 <i>ortho</i> -Xylene	186 Unknown
143 Unknown	187 1,3-Dimethyl-4-ethylbenzene
144 Unknown	188 C ₁₀ -aromatic (tentatively: 1,2-dimethyl-4-ethylbenzene)
145 Unknown	189 1,3-Dimethyl-2-ethylbenzene
146 Unknown	190 Unknown
147 C ₁₀ -isomer	
148 Nonane	

Hydrogen containing less than 2 ppm of both oxygen and water was used as carrier gas, in order to avoid decomposition of TeNF, which occurs to a slight extent at high temperatures.

RESULTS AND DISCUSSION

Figs. 1 and 2 show chromatograms of a premium-grade gasoline obtained from a 5-m column packed with Carbo-pack C modified with 0.28 and 0.3% TeNF,

respectively. The hydrocarbon components found in the gasoline are listed by peak number in Table I. In analysing many gasoline samples over a period of 4 months, no significant variation was found in their composition. Thus the fuel under study can be considered representative of the fuels in use in Rome during 1977.

In the chromatographic profile of gasoline, noticeable changes can be observed by slightly varying the relative amount of TeNF adsorbed on the carbon surface. This effect is accounted for by considering that unlike paraffin, olefins and aromatics have specific interactions with a π -acceptor, which can provoke their retardation with respect to saturates. In many cases, therefore, it was possible to resolve components contained in a single peak by eluting gasoline on both 0.28 and 0.3% TeNF-modified Carbopack C, with the other experimental conditions unchanged.

Under the experimental conditions used, the GC-MS technique failed to identify components present in less than *ca.* 0.01% and whose peaks are too close to other components present in much greater amounts.

The mass spectra of many isomers are virtually identical. In these cases, therefore, we have reported only the molecular weights and pertaining classes.

In other cases, by the examination of mass spectra it was possible to identify two components contained in a single peak. In particular, we were able to identify *trans*-pent-2-ene, 3-methyloctane and 1,1-dimethylcyclopentane, which are eluted together with pentane, *meta*-xylene and *cis*(or *trans*)-hex-3-ene, respectively

Packed columns have the advantage over capillary columns that their loadability is much higher. This can be exploited in the direct analysis of the individual olefin and aromatic components contained in tiny amounts in pure naphthas and reformer feeds.

Fig. 3 shows a chromatogram of a blended mixture (1:1) of light and medium pure naphtha. As can be seen, except in cases where olefin and aromatic peaks are overlapped by saturate peaks, direct gas chromatographic quantitative determination of individual olefins and aromatics can be easily carried out.

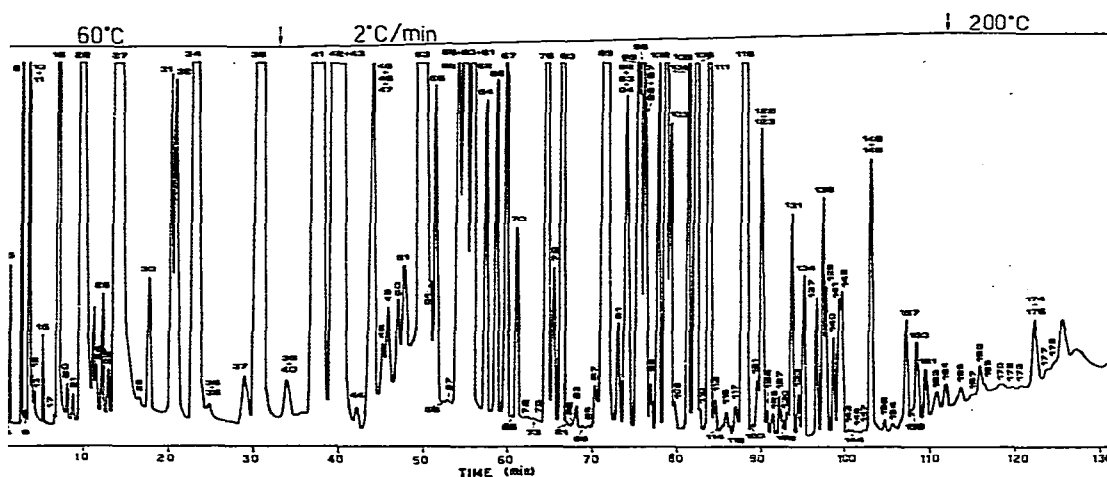


Fig. 3. Chromatogram of a blended mixture (1:1) of a light and a medium pure naphtha. Experimental conditions as in Fig. 1.

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