# QUANTITATIVE ANALYSIS OF HYDROCARBONS IN GASOLINES BY CAPILLARY GAS–LIQUID CHROMATOGRAPHY

## II. ISOTHERMAL AND TEMPERATURE-PROGRAMMED ANALYSES

E. MATISOVÁ* and J. KRUPČÍK

*Department of Analytical Chemistry, Faculty of Chemical Technology, Slovak Technical University, Jánska 1, 812 37 Bratislava (Czechoslovakia)*

P. ČELLÁR

*Slovnaft AV VVZ, Vlčie hrdlo, 824 12 Bratislava (Czechoslovakia)*

and

A. KOČAN

*Research Institute of Preventive Medicine, Department of Mass Spectrometry, Limbova 14, 833 01 Bratislava (Czechoslovakia)*

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SUMMARY

Quantitative analysis of the gasoline fraction of crude oil (paraffins, branched paraffins, aromatics and naphthenes) and structure group analysis has been performed by high resolution capillary gas chromatography using squalane columns with different film thicknesses under temperature-programmed conditions. The results obtained were compared with those from isothermal analysis. "The modified standard addition method" was used. The contents of aromatic hydrocarbons determined on a polar stationary phase, SP-2340, were in good agreement with those obtained on squalane.

INTRODUCTION

High resolution capillary gas chromatography (HRCGC) approaches the ultimate goal of a petroleum chemist, *i.e.*, complete component analysis, and provides the petrochemical engineer with the information and knowledge required to convert crude petroleum into profitable products. It is one of the few techniques capable of distinguishing between paraffins and naphthenes, thus providing a true PONA (paraffins, olefins, naphthenes and aromatics) analysis which is often required in the control of gasoline production. The disadvantage of this approach is that every peak must be identified in the chromatogram or at least classified according to the chemical group to which it belongs.

Though squalane has certain shortcomings as a liquid phase for capillary columns, *e.g.*, low maximum operating conditions and it is difficult to prepare a stable

column when using glass or fused-silica tubing[1,2], it has been used in the analysis of hydrocarbons because of its high selectivity towards hydrocarbons and the wealth of retention data already published. Most published data on the retention properties of hydrocarbons in the gasoline range have been obtained under isothermal conditions[3 8]. However, economics demands shorter analyses. Therefore, most practical analyses are temperature programmed[9-12]. Most hydrocarbons exhibit a change in retention relative to say, the normal hydrocarbons as the temperature is changed. The practical result is that the relative elution times and even the elution order can change with different chromatographic conditions[11].

Recently Johansen *et al.*[13] published a method of analysis of complex gasoline samples on an OV-101 capillary column under temperature-programmed conditions using modern sophisticated laboratory data systems. However, an identification based only on the so-called relative retention time obtained under the actual temperature-programmed conditions might be insufficient for a sample of unknown composition.

The combination of a gas chromatograph, a mass spectrometer and a computer is the premier technique for identifying or at least classifying unknown peaks in a chromatogram[11]. Some difficulties in the identification of hydrocarbons may arise from the similarity of the mass spectra of isomeric hydrocarbons.

In our previous paper[14] we elucidated further the composition of the gasoline fraction of crude oil using HRCGC and by carrying out the identification on the basis of retention data and gas chromatography–mass spectrometry (GC–MS). We pointed out the problems connected with generally acknowledged methods of quantitative analysis of gasolines. The aim of the present study was to compare the capillary GC analysis of the gasoline fraction of crude oil under isothermal and temperature-programmed conditions.

EXPERIMENTAL

Measurements were performed by two methods. In the first method a Hewlett-Packard 58 80 A gas chromatograph equipped with an integrator C R1 A (Shimadzu, Japan) and a metal capillary column (100 m × 0.25 mm I.D.) with a thick film of squalane (0.5 $\mu$m) was employed. Helium was the carrier gas. A temperature programme of 40–110°C with a gradient of 0.3°C/min was used. GC–MS measurements were performed using an HP 59 95 instrument under similar chromatographic conditions.

In the second method a Carlo Erba gas chromatograph equipped with an integrator Autolab 6 300 and a glass capillary column (98 m × 0.25 mm I.D.) with a thin film of squalane (0.1 $\mu$m) was employed. Hydrogen was the carrier gas. Both isothermal conditions (57.8°C) and temperature-programmed conditions (isothermal at 40°C up to the elution of *n*-heptane, then programmed to 80°C at a rate of 0.8°C/min, finally isothermal at 80°C) were used. A fused-silica capillary column (60 m × 0.25 mm I.D.) containing SP-2340 and nitrogen as carrier gas at 80°C was also employed.

Both chromatographs were equipped with a flame ionization detector and an inlet stream splitter.

A gasoline fraction of crude oil enriched with higher boiling hydrocarbons was analysed and was injected with a 1-$\mu$l Hamilton syringe.

Peak areas were measured as either the digital integration response, or the retention time, $t_R$ in mm, multiplied by the peak height, $h$ also in mm.

RESULTS AND DISCUSSION

In our previous paper we used "the modified standard addition method" for the isothermal quantitative analysis of hydrocarbons in gasolines and showed that this method gives more correct results than does "the area per cent technique". Both methods are based on the assumption that the relative weight responses (RWR) of hydrocarbons are nearly constant for the whole series of hydrocarbons[10,16–18]. "The modified standard addition method" does not require the elution of all components from the column and in contrast to "the standard addition method" does not require precise and reproducible injection. The sum of the determined contents of hydrocarbons in a gasoline sample may be far from 100%, as is always the case in "the area per cent technique", where there are large errors due to the presence of very small peaks below the flame ionization detection limit. Therefore, we have used "the modified standard addition method" for quantitative analysis of hydrocarbons also under temperature-programmed conditions.

*Quantitative analysis of hydrocarbons on squalane*
A temperature programme was used to shorten the analysis time for gasoline, and the results obtained were compared with those of isothermal analysis. Two methods were applied: a lower temperature gradient (0.3°C/min) and a column with a thick film of squalane; and a higher temperature gradient (0.8°C/min) and a column of comparable length but with a thin film of squalane. The starting temperature was 40°C. To avoid column bleeding in a glass capillary column with a thin film of squalane, the final temperature was 80°C. Therefore, a part of the analysis was performed under isothermal conditions. The number of unresolved peaks and the analysis time are highly dependent on the temperature gradient used. The $C_8$–$C_{10}$ *n*-alkanes were used as standards. To avoid peaks discrimination at the split injection compounds peak area was always related to the peak area of the near eluting standard.

The results of the temperature-programmed quantitative analysis of hydrocarbons are given in Table I, and chromatograms of the separation of gasoline constituents are given in Figs. 1, 2. The component numbering is as in Table I. The compound identification was performed by GC–MS with the help of GC and GC–MS under isothermal conditions. In Table I are included also the results of quantitative analysis under isothermal conditions (57.8°C) on a thin film column.

On the basis of these results the following conclusions can be drawn. The analysis time for gasoline up to the elution of *n*-decane on a metal capillary column with a thick film of squalane is relatively long, 173 min, and is similar to that for a published isothermal analysis of gasoline on a high resolution capillary column, 180 min[14]. However, the number of unresolved peaks is significantly increased using temperature programming. The analysis time was lower on the thin film column either under temperature-programmed (63 min) or isothermal conditions (68 min). The number of unresolved peaks under temperature-programmed conditions was even higher as on a thick film column of comparable length. Thus, the best peak resolution was obtained under isothermal conditions, though many peaks still re-

TABLE I

RESULTS OF THE QUANTITATIVE ANALYSIS OF GASOLINE ON SQUALANE BY THE MODIFIED STANDARD ADDITION METHOD

Temperature programmes: TP-1, 40–110°C, 0.3°C/min, TP-2, isothermally at 40°C up to $n$-C$_7$, then 40–80°C at 0.8°C/min, isothermally at 80°C; each using digital integration. Isothermal analyses at 57.8°C; peaks areas from $t_R \times h$.

| Peak No. | Component | Weight % | | |
|---|---|---|---|---|
| | | TP-1 | TP-2 | Isothermal |
| 2 | 2-Methylbutane | 0.035 | 0.033 | 0.038 |
| 3 | $n$-Pentane | 0.200 | 0.186 | 0.209 |
| 4 | 2,2-Dimethylbutane | 0.005 | 0.005 | – |
| 5 | Cyclopentane | 0.122 | 0.112 | 0.109 |
| 6 | 2,3-Dimethylbutane | 0.080 | 0.074 | } 0.998 |
| 7 | 2-Methylpentane | 0.809 | 0.834 | |
| 8 | 3-Methylpentane | 0.623 | 0.657 | 0.746 |
| 9 | $n$-Hexane | 2.059 | 2.122 | 2.433 |
| 10 | 2,2-Dimethylpentane | } 1.449 | } 1.395 | } 1.567 |
| 11 | Methylcyclopentane | | | |
| 12 | 2,4-Dimethylpentane | 0.106 | 0.095 | |
| 13 | Benzene | 0.113 | 0.111 | 0.121 |
| 14 | 3,3-Dimethylpentane | 0.012 | 0.014 | 0.015 |
| 15 | Cyclohexane | 1.043 | 0.965 | 1.054 |
| 16 | 2-Methylhexane | 1.180 | 1.238 | 1.396 |
| 17 | 2,3-Dimethylpentane | } 0.551 | } 0.578 | 0.550 |
| 18 | 1,1-Dimethylcyclopentane | | | 0.040 |
| 19 | 3-Methylhexane | 1.746 | 1.886 | 2.107 |
| 20 | 1(*cis*),3-Dimethylcyclopentane | 0.575 | 0.554 | 0.623 |
| 21 | 3-Ethylpentane | } 0.713 | } 0.707 | 0.227 |
| 22 | 1(*trans*),3-Dimethylcyclopentane | | | 0.608 |
| 23 | 1(*trans*),2-Dimethylcyclopentane | 1.213 | 1.206 | 1.372 |
| 24 | $n$-Heptane | 4.629 | 4.841 | 5.477 |
| 25 | 2,2-Dimethylhexane | } 0.248 | } 0.226 | 0.020 |
| 26 | 1(*cis*),2-Dimethylcyclopentane | | | 0.226 |
| 27 | 1,1,3-Trimethylcyclopentane | 0.150 | 0.155 | 0.149 |
| 28 | Methylcyclohexane | 3.295 | 3.346 | 3.781 |
| 29 | 2,5-Dimethylhexane | 0.290 | 0.281 | 0.325 |
| 30 | 2,4-Dimethylhexane | 0.335 | } 1.363 | 0.352 |
| 31 | Ethylcyclopentane | 1.052 | | 1.149 |
| 32 | 1(*trans*),2(*cis*),4-Trimethylcyclopentane | 0.535 | 0.520 | 0.575 |
| 33 | 3,3-Dimethylhexane | } 1.205 | 0.007 | 0.033 |
| 34 | Toluene | | 1.265 | 1.469 |
| 35 | 1(*trans*),2(*cis*),3-Trimethylcyclopentane | 0.746 | 0.730 | 0.820 |
| 36 | 2,3,4-Trimethylpentane | 0.090 | 0.085 | 0.092 |
| 37 | 2,3-Dimethylhexane | 0.295 | 0.340 | 0.307 |
| 38 | 2-Methyl-3-ethylpentane | 0.196 | 0.244 | 0.194 |
| 39 | 1,1,2-Trimethylcyclopentane | 0.106 | } 2.756 | } 3.046 |
| 40 | 2-Methylheptane | 2.629 | | |
| 41 | 4-Methylheptane | 0.778 | 0.766 | 0.872 |
| 42 | 3,4-Dimethylhexane | 0.175 | 0.168 | 0.153 |
| 43 | 3-Methylheptane | 1.780 | 1.855 | 1.794 |
| 44 | 3-Methyl-3-ethylpentane | } 0.049 | 0.029 | 0.052 |
| 45 | 1(*cis*),2(*trans*),4-Trimethylcyclopentane | | } 0.030 | 0.039 |
| 46 | Naphthene | 0.041 | | 0.026 |

TABLE I (*continued*)

| Peak No. | Component | Weight % | | |
|---|---|---|---|---|
| | | TP-1 | TP-2 | Isothermal |
| 47 | 1(*cis*),2(*trans*),3-Trimethylcyclopentane | 0.205 | 0.190 | 0.201 |
| 48 | 1(*cis*),3-Dimethylcyclohexane | 1.456 | 1.477 | } 1.212 |
| 49 | 1(*trans*),4-Dimethylcyclohexane | 0.164 | 0.121 | |
| 50 | 1,1-Dimethylcyclohexane | 0.512 | 0.467 | 0.665 |
| 51 | 1-Methyl-2(*trans*)-ethylcyclopentane | 0.413 | 0.470 | 0.517 |
| 52 | 1-Methyl-3(*cis*)-ethylcyclopentane | 1.157 | 1.049 | 1.270 |
| 53 | 1-Methyl-1-ethylcyclopentane | 0.137 | 0.113 | 0.103 |
| 54 | *n*-Octane | 5.771 | 6.132 | 6.164 |
| 55 | 1(*cis*),2(*cis*),3-Trimethylcyclopentane + 1(*trans*),2-dimethylcyclohexane | 1.003 | 0.749 | 1.053 |
| 56 | 1(*cis*),4-Dimethylcyclohexane + 1(*trans*),3-dimethylcyclohexane | 0.274 | } 0.244 | } 0.222 |
| 57 | Branched paraffin | | | |
| 58 | Branched paraffin | – | 0.017 | 0.016 |
| 59 | 2,3,5-Trimethylhexane | } 0.264 | } 0.170 | 0.082 |
| 60 | Isopropylcyclopentane | | | 0.174 |
| 61 | Branched paraffin | – | } 0.023 | – |
| 62 | Branched paraffin | – | | – |
| 63 | 2,2-Dimethylheptane | } 0.066 | 0.038 | 0.025 |
| 64 | Naphthene | | 0.063 | 0.034 |
| 65 | 2,4-Dimethylheptane | } 0.457 | 0.285 | 0.278 |
| 66 | 1-Methyl-2(*cis*)-ethylcyclopentane | | 0.135 | 0.158 |
| 67 | Branched paraffin | – | – | – |
| 68 | 2,2,3-Trimethylhexane | 0.033 | } 0.089 | 0.032 |
| 69 | Naphthene | 0.053 | | } 1.324 |
| 70 | 2,6-Dimethylheptane | } 1.249 | } 1.416 | |
| 71 | Naphthene | | | 0.027 |
| 72 | 1(*cis*),2-Dimethylcyclohexane | } 0.914 | } 0.707 | } 0.839 |
| 73 | *n*-Propylcyclopentane | | | |
| 74 | 2,5-Dimethylheptane | 0.470 | | 0.461 |
| 75 | 3,5-Dimethylheptane | 0.142 | | 0.133 |
| 76 | Ethylbenzene | } 2.399 | } 3.064 | } 2.266 |
| 77 | Ethylcyclohexane | | | |
| 78 | 3,3-Dimethylheptane | 0.026 | } 0.026 | 0.029 |
| 79 | Branched paraffin | 0.010 | | – |
| 80 | Naphthene | } 1.331 | | 0.190 |
| 81 | Naphthene | | } 1.457 | 1.288 |
| 82 | 1,1,3-Trimethylcyclohexane | 0.307 | | 0.274 |
| 83 | Branched paraffin | 0.116 | | 0.112 |
| 84 | 1(*cis*),3(*cis*),5-Trimethylcyclohexane | } 0.427 | 0.196 | } 0.310 |
| 85 | Branched paraffin | | 0.499 | |
| 86 | Branched paraffin | 0.030 | 0.032 | 0.010 |
| 87 | Cycloalkane + *p*-xylene | } 0.829 | } 0.793 | 0.465 |
| 88 | Branched paraffin | | | 0.382 |
| 89 | *m*-Xylene | 1.128 | 1.159 | 1.327 |
| 90 | Branched paraffin | – | – | – |
| 91 | Branched paraffin | 0.642 | } 0.690 | 0.640 |
| 92 | Branched paraffin | 0.010 | | 0.011 |
| 93 | Branched paraffin | } 0.493 | 0.113 | 0.203 |
| 94 | Naphthene | | 0.165 | 0.317 |
| 95 | 1(*trans*),2(*cis*),4-Trimethylcyclohexane | 0.212 | 0.268 | 0.172 |

TABLE I (*continued*)

| Peak No. | Component | Weight % | | |
|---|---|---|---|---|
| | | *TP-1* | *TP-2* | *Isothermal* |
| 96 | 1(*trans*),2(*trans*),4-Trimethylcyclohexane + 1(*trans*),3(*trans*),5-trimethylcyclohexane | 0.309 | 0.300 | 0.255 |
| 97 | 4-Methyloctane | 0.911 | 1.016 | 0.890 |
| 98 | 2-Methyloctane | 1.070 | 1.112 | 1.056 |
| 99 | Naphthene | 0.135 | ★ | 0.084 |
| 100 | Naphthene | } 0.310 | } 0.147 | 0.084 |
| 101 | Ethylheptane | | | 0.157 |
| 102 | o-Xylene | } 2.593 | 1.017 | } 2.551 |
| 103 | 3-Methyloctane | | } 1.606 | |
| 104 | Naphthene | | | 0.237 |
| 105 | Branched paraffin | 0.031 | — | 0.013 |
| 106 | Naphthene | 0.081 | 0.064 | 0.064 |
| 107 | Naphthene | 0.014 | 0.022 | 0.013 |
| 108 | Naphthene | } 0.103 | } 0.094 | } 0.079 |
| 109 | Naphthene | | | |
| 110 | Naphthene | 0.066 | 0.054 | 0.053 |
| 111 | 1(*trans*),2(*cis*),3-Trimethylcyclohexane | 0.107 | 0.095 | 0.094 |
| 112 | 1,1,2-Trimethylcyclohexane + 3,3-diethylpentane (5:1) | 0.542 | 0.627 | 0.492 |
| 113 | 1(*cis*),2(*trans*),4-Trimethylcyclohexane | } 0.400 | } 0.273 | } 0.290 |
| 114 | Branched paraffin | | | |
| 115 | 1(*cis*),2(*cis*),4-Trimethylcyclohexane + 1(*cis*),3(*cis*),4-trimethylcyclohexane | 0.266 | } 0.197 | 0.223 |
| 116 | Naphthene | 0.029 | | 0.028 |
| 117 | Naphthene | } 0.230 | } 0.217 | } 0.159 |
| 118 | Naphthene | | | |
| 119 | Methylethylcyclohexane | 0.510 | } 0.447 | 0.424 |
| 120 | Naphthene | 0.075 | | 0.029 |
| 121 | Naphthene | 0.081 | | 0.015 |
| 122 | Isopropylbenzene | } 0.739 | } 0.880 | } 0.583 |
| 123 | Naphthene | | | |
| 124 | Naphthene | — | 0.016 | — |
| 125 | Naphthene | } 5.470 | 0.089 | 0.046 |
| 126 | n-Nonane | | 5.455 | 5.068 |
| 127 | Naphthene | 0.170 | 0.116 | 0.110 |
| 128 | Naphthene | — | — | — |
| 129 | Naphthene + branched paraffin (1:1) | — | — | — |
| 130 | Naphthene | — | — | — |
| 131 | Naphthene | — | — | — |
| 132 | Naphthene | } 0.196 | | } 0.065 |
| 133 | Naphthene | | } 0.355 | |
| 134 | Branched paraffin | } 0.071 | | } 0.033 |
| 135 | Branched paraffin | | | |
| 136 | Naphthene | 0.258 | | 0.299 |
| 137 | Naphthene | — | — | — |
| 138 | Naphthene | } 0.349 | } 0.208 | } 0.067 |
| 139 | Naphthene | | | |
| 140 | Branched paraffin | | | 0.085 |
| 141 | Naphthene | } 0.532 | } 0.385 | } 0.461 |
| 142 | Naphthene | | | |

TABLE I (*continued*)

| Peak No. | Component | Weight % | | |
|---|---|---|---|---|
| | | TP-1 | TP-2 | Isothermal |
| 143 | Naphthene | — | } 0.200 | } 0.017 |
| 144 | Naphthene | — | | |
| 145 | Branched paraffin | 0.230 | | 0.141 |
| 146 | Naphthene | } 0.049 | } 0.063 | } 0.036 |
| 147 | Naphthene | | | |
| 148 | Naphthene | | 0.123 | } 0.255 |
| 149 | Branched paraffin | | 0.062 | |
| 150 | Naphthene | } 1.002 | 0.099 | |
| 151 | Naphthene | | 0.381 | 0.249 |
| 152 | Branched paraffin | | 0.078 | 0.178 |
| 153 | *n*-Propyl benzene | 0.924 | 0.986 | 0.731 |
| 154 | Naphthene | — | — | — |
| 155 | Branched paraffin | } 0.104 | 0.089 | } 0.076 |
| 156 | Branched paraffin | | 0.062 | |
| 157 | Naphthene | } 1.289 | } 0.714 | } 0.663 |
| 158 | C$_9$ naphthene | | | |
| 159 | C$_9$ naphthene | | 0.531 | 0.510 |
| 160 | Naphthene | } 1.482 | 0.094 | 0.040 |
| 161 | 2,6-Dimethyloctane | | 1.349 | 1.203 |
| 162 | Branched paraffin | — | — | — |
| 163 | Branched paraffin | } 0.324 | 0.088 | 0.020 |
| 164 | Branched paraffin | | 0.137 | 0.102 |
| 165 | Branched paraffin | | 0.101 | 0.041 |
| 166 | 2,5-Dimethyloctane | 0.610 | 0.588 | 0.375 |
| 167 | 1-Methyl-3-ethylbenzene | 0.713 | 0.670 | 0.673 |
| 168 | 1-Methyl-4-ethylbenzene | } 0.713 | 0.382 | 0.220 |
| 169 | Naphthene | | 0.132 | 0.100 |
| 170 | Naphthene | } 0.097 | 0.050 | 0.107 |
| 171 | C$_{10}$ branched paraffin | | } 0.093 | } 0.043 |
| 172 | Branched paraffin | | | |
| 173 | Branched paraffin | — | — | — |
| 174 | C$_{10}$ branched paraffin | 0.138 | 0.046 | 0.044 |
| 175 | Naphthene | } 0.087 | 0.046 | 0.044 |
| 176 | Branched paraffin | | 0.026 | 0.022 |
| 177 | Branched paraffin | — | 0.031 | — |
| 178 | Branched paraffin | — | — | — |
| 179 | Naphthene | — | — | — |
| 180 | Naphthene | } 0.095 | } 0.080 | } 0.060 |
| 181 | Naphthene | | | |
| 182 | Branched paraffin | 0.197 | 0.139 | 0.139 |
| 183 | Branched paraffin | — | — | — |
| 184 | Branched paraffin | — | — | — |
| 185 | 1-Methyl-2-ethylbenzene | 0.583 | 0.760 | 0.615 |
| 186 | Branched paraffin | 0.301 | 0.119 | } 0.190 |
| 187 | Branched paraffin | 0.049 | — | |
| 188 | Branched paraffin | — | — | — |
| 189 | Naphthene | } 0.257 | } 0.056 | } — |
| 190 | Naphthene | | | |
| 191 | 1,3,5-Trimethylbenzene | 0.193 | 0.203 | 0.173 |
| 192 | Branched paraffin | — | — | — |
| 193 | Branched paraffin | ★★ | 0.177 | 0.125 |
| 194 | Branched paraffin | — | — | — |

TABLE I *(continued)*

| Peak No. | Component | Weight % | | |
|---|---|---|---|---|
| | | *TP-1* | *TP-2* | *Isothermal* |
| 195 | Naphthene | } 0.736 | 0.316 | 0.252 |
| 196 | 4-Methylnonane | | } 0.739 | 0.637 |
| 197 | *tert.*-Butylbenzene | – | | } 0.077 |
| 198 | Naphthene | } 1.123 | } 0.106 | |
| 199 | Naphthene | | | – |
| 200 | 2-Methylnonane | | 0.738 | 0.579 |
| 201 | Naphthene | 0.104 | 0.133 | 0.132 |
| 202 | $C_{10}$ naphthene | } 0.060 | } 0.116 | } 0.053 |
| 203 | Naphthene | | | |
| 204 | Naphthene | } 0.056 | } 0.082 | } 0.040 |
| 205 | Naphthene | | | |
| 206 | Naphthene | – | – | – |
| 207 | 3-Methylnonane | 0.755 | 0.506 | 0.414 |
| 208 | Naphthene | 0.026 | } 0.164 | } 0.052 |
| 209 | Naphthene | 0.114 | | |
| 210 | 1,2,4-Trimethylbenzene | 0.770 | 0.734 | 0.679 |
| 211 | Branched paraffin | – | – | – |
| 212 | Naphthene | } 0.065 | 0.017 | – |
| 213 | Branched paraffin | | } 0.198 | – |
| 214 | *sec.*-Butylbenzene | 0.166 | | 0.146 |
| 215 | Branched paraffin | } 0.186 | – | – |
| 216 | Naphthene | | } 0.369 | 0.148 |
| 217 | Naphthene | 0.238 | | 0.208 |
| 218 | Naphthene | 0.165 | 0.160 | 0.120 |
| 219 | Branched paraffin | 0.087 | – | – |
| 220 | Naphthene | 0.101 | 0.098 | 0.031 |
| 221 | Branched paraffin | – | – | |
| 222 | Two naphthenes | 0.174 | } 0.304 | } 0.186 |
| 223 | Branched paraffin | – | | |
| 224 | Naphthene | 0.042 | | 0.033 |
| 225 | Naphthene | } 0.190 | } 0.091 | } 0.020 |
| 226 | Branched paraffin | | | |
| 227 | Branched paraffin | | | } 0.033 |
| 228 | Naphthene | | | |
| 229 | Naphthene | 0.108 | 0.067 | } 0.167 |
| 230 | Naphthene | } 0.147 | } 0.200 | |
| 231 | Branched paraffin | | | |
| 232 | Branched paraffin | | | |
| 233 | Naphthene | – | – | – |
| 234 | 1,2,3-Trimethylbenzene | 0.318 | 0.305 | 0.277 |
| 235 | Branched paraffin | – | 0.034 | – |
| 236 | 1-Methyl-4-isopropylbenzene | 0.092 | 0.069 | 0.065 |
| 237 | Branched paraffin | 0.048 | 0.049 | } 2.148 |
| 238 | *n*-Decane | 2.513 | 2.317 | |

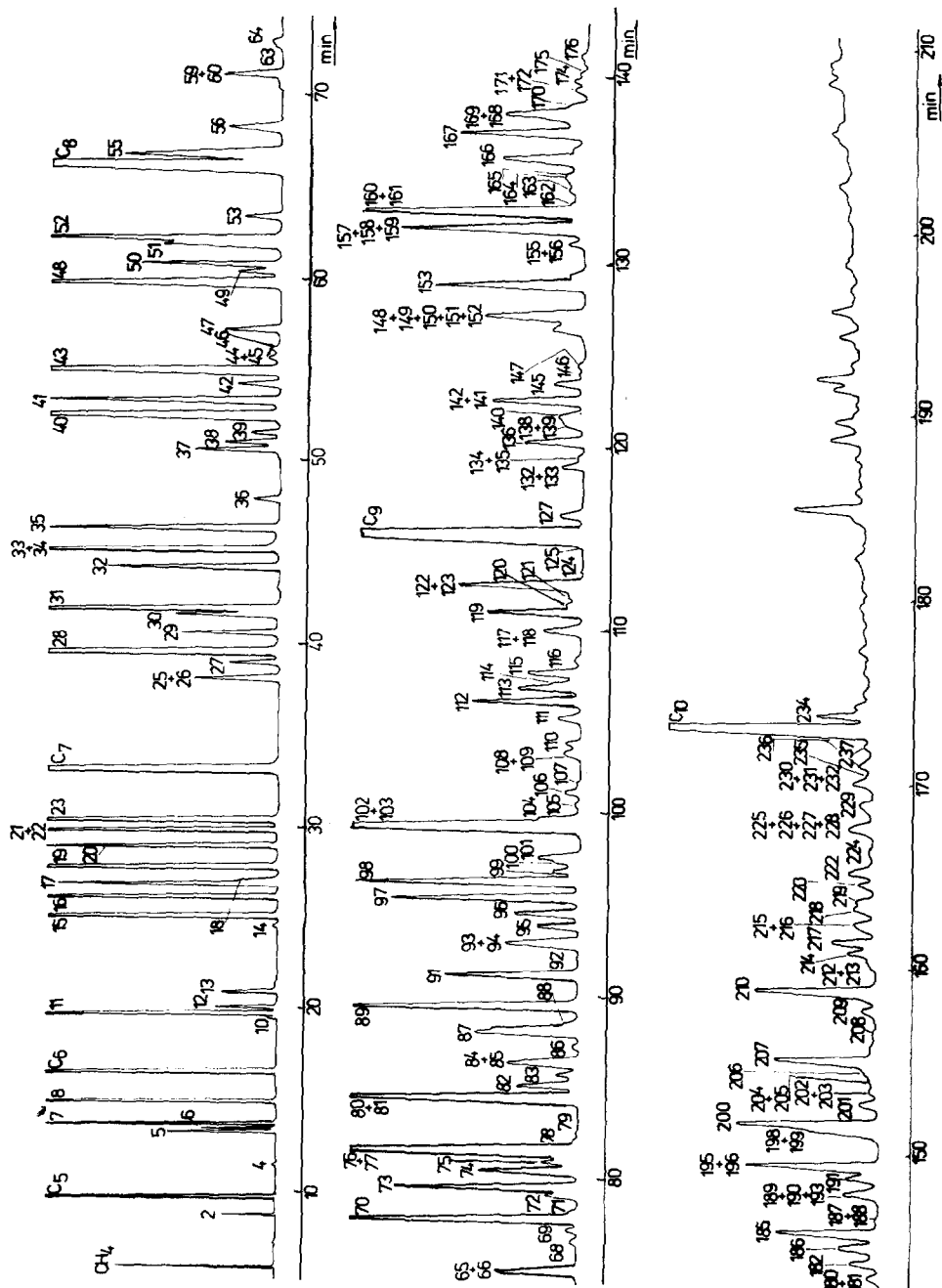    * Co-eluted with peak 97.
   ** Co-eluted with peaks 189, 190.

Fig. 1. Chromatogram of the separation of the hydrocarbon constituents of the gasoline fraction of crude oil on a metal capillary column containing a thick film of squalane under temperature-programmed conditions. For experimental details, see text.
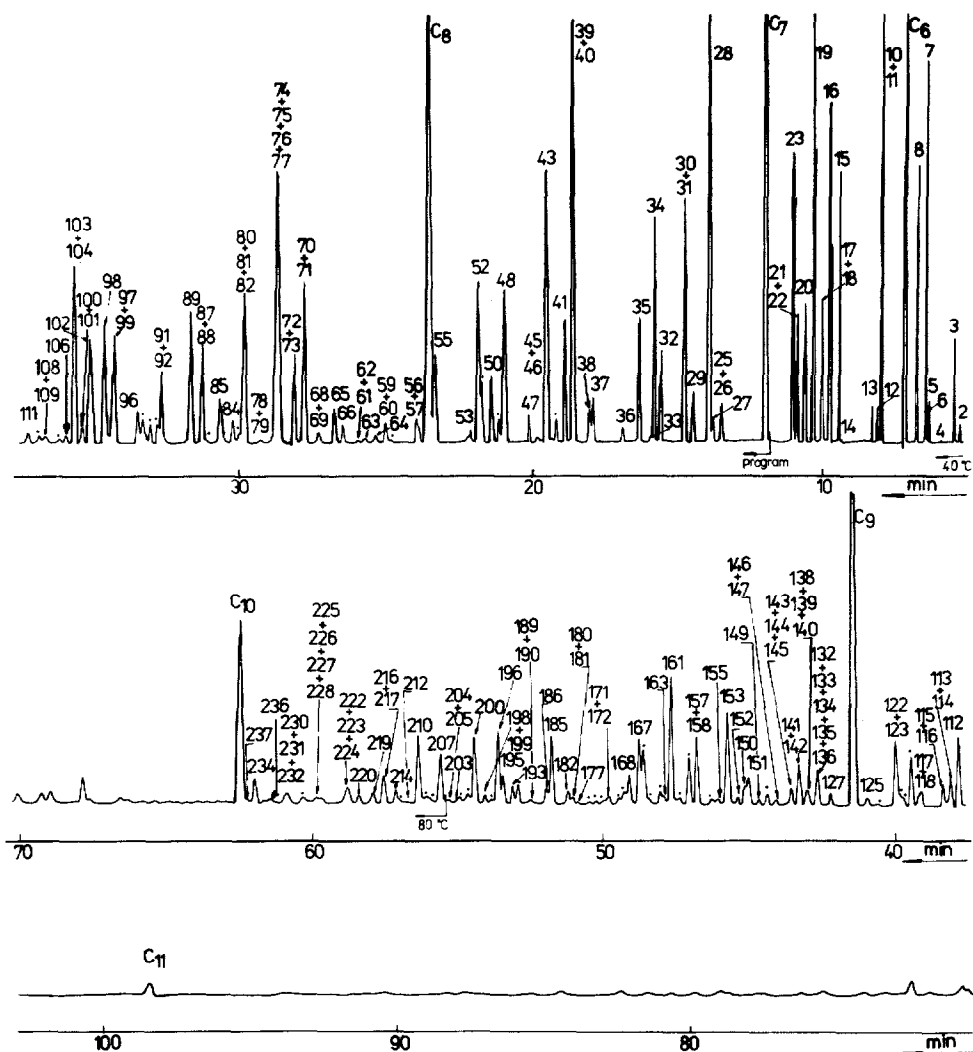
Fig. 2. Chromatogram of the separation of the hydrocarbon constituents of the gasoline fraction of crude oil on a glass capillary column containing a thin film of squalane under temperature-programmed conditions. For experimental details, see text.

TABLE II

GROUP ANALYSIS OF GASOLINE ON SQUALANE BY THE MODIFIED STANDARD ADDITION METHOD

Chromatographic conditions as in Table I.

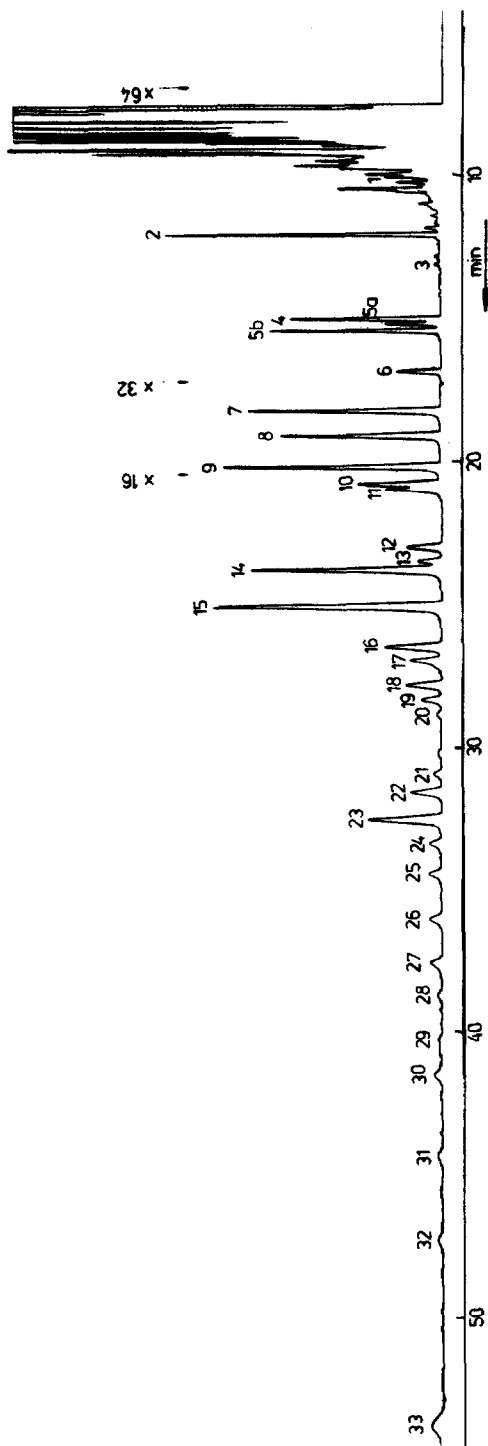| Compounds | Weight % | | |
|---|---|---|---|
| | TP-1 | TP-2 | Isothermal |
| *n*-Paraffins | 20.512 | 21.053 | 21.473 |
| Branched paraffins | 25.984 | 25.789 | 25.324 |
| Aromatics | 9.198 | 9.552 | 8.957 |
| Naphthenes | 31.733 | 29.260 | 30.148 |

Fig. 3. Chromatogram of the separation of the aromatics in the gasoline fraction of crude oil on SP-2340 in a fused-silica capillary column at 80°C and with a nitrogen pressure of 0.9 atm.

mained unresolved in comparison to published results[14]. The qualitative[19] and the preceding quantitative analysis in both isothermal and temperature programmed analysis was difficult when peaks overlapped, which was often the case. It is evident that for sufficient component separation and for the preceding group analysis it is necessary to optimize the experimental conditions, such as column length (efficiency), film thickness, temperature gradient, time of analysis, etc., with respect to the number of resolved peaks.

Comparing the weight per cent of the constituents determined under temperature-programmed conditions, where the peak areas were evaluated by digital integration, and the weight per cent under isothermal conditions, where the peak areas

TABLE III

RESULTS OF THE QUANTITATIVE ANALYSIS OF AROMATICS IN GASOLINE ON SP-2340 BY THE MODIFIED STANDARD ADDITION METHOD

| Peak No. | Compound | Weight % |
|---|---|---|
| 1 | Benzene | 0.177 |
| 2 | Toluene | 1.578 |
| 3 | Decahydronaphthalene | 0.035 |
| 4 | Ethylbenzene | 1.078 |
| 5a | p-Xylene | 0.383 |
| 5b | m-Xylene | 1.260 |
| 6 | Isopropylbenzene | 0.357 |
| 7 | o-Xylene | 0.841 |
| 8 | n-Propylbenzene | 0.729 |
| 9 | 1,3- + 1,4-Methylethylbenzene | 1.042 |
| 10 | 1,3,5-Trimethylbenzene | 0.204 |
| 11 | sec.-Butylbenzene | 0.135 |
| 12 | 1-Methyl-4-isopropylbenzene | 0.096 |
| 13 | Methylisopropylbenzene | 0.066 |
| 14 | 1-Methyl-2-ethylbenzene | 0.540 |
| 15 | 1,2,4-Trimethylbenzene | 0.686 |
| 16 | Methylpropylbenzene | 0.176 |
| 17 | Diethylbenzene | 0.094 |
| 18 | n-Butylbenzene | 0.119 |
| 19 | Diethylbenzene | 0.070 |
| 20 | Branched $C_{11}$ alkylbenzene | 0.016 |
| 21 | 1,2-Diethylbenzene | 0.028 |
| 22 | 1-Methyl-2-propylbenzene | 0.118 |
| 23 | 1,2,3-Trimethylbenzene | 0.286 |
| 24 | Dimethylethylbenzene | 0.045 |
| 25 | Dimethylethylbenzene | 0.051 |
| 26 | Tetramethylbenzene | 0.053 |
| 27 | Indane | 0.055 |
| 28 | Methylindane | 0.024 |
| 29 | Tetramethylbenzene | 0.018 |
| 30 | Methylindane | 0.040 |
| 31 | Dimethylethylbenzene | 0.030 |
| 32 | $C_{10}$ alkylbenzene | 0.032 |
| 33 | $C_{10}$ alkylbenzene | 0.073 |
| | $\Sigma$ Aromatics | 10.535 |

were evaluated by the $t_R \cdot h$ method, it is seen that the per cent of low boiling compounds determined by the latter method is slightly higher and of high boiling compounds lower than those determined with temperature programming and digital integration.

The components not given in Table I were either below the limit of detection under the given conditions or they were coeluted with other peaks, which was difficult to observe at their very low concentrations (less than 0.010%).

The results of the group analysis of hydrocarbons eluted up to $n$-decane on squalane are given in Table II. When peaks overlapped, their quantitative analysis was made according to the known proportion of constituents in peaks, determined either from isothermal analysis, when peaks were resolved, or from GC–MS measurements, when peaks were not due to isomers.

*Quantitative analysis of aromatic hydrocarbons on SP-2340*

The aromatic hydrocarbon content was determined also on the polar stationary phase SP-2340. Due to the high efficiency of the fused-silica column, it was possible to analyse also higher boiling aromatics with lower weights per cent than on the metal capillary column with 1,2,3-tris(cyanoethoxy)propane[14]. A chromatogram of the separation of hydrocarbons in gasoline on SP-2340 in a fused-silica capillary column at 80°C and with a nitrogen pressure of 0.9 atm is shown in Fig. 3. The component numbering is as in Table III; GC–MS was used for compound identification.

TABLE IV

RESULTS (WEIGHT %) OF THE QUANTITATIVE ANALYSIS OF AROMATICS IN GASOLINE ON SQUALANE AND SP-2340

Chromatographic conditions as in Table I; on SP 2340, peak areas were determined as $t_R \times h$.

| Compound | Squalane | | | SP 2340 |
|---|---|---|---|---|
| | TP-1 | TP-2 | Isothermal | |
| Benzene | 0.113 | 0.111 | 0.121 | 0.177 |
| Toluene | 1.154 | 1.265 | 1.469 | 1.578 |
| Ethylbenzene | 1.007 | 1.022 | 0.952 | 1.078 |
| *p*-Xylene | 0.307 | 0.293 | 0.289 | 0.383 |
| *m*-Xylene | 1.128 | 1.159 | 1.327 | 1.260 |
| *o*-Xylene | 0.838 | 1.017 | 0.886 | 0.841 |
| Isopropylbenzene | 0.402 | 0.401 | 0.317 | 0.357 |
| *n*-Propylbenzene | 0.924 | 0.986 | 0.731 | 0.729 |
| 1-Methyl-3-ethylbenzene | 0.713 | 0.670 | 0.673 | } 1.042 |
| 1-Methyl-4-ethylbenzene | 0.490 | 0.382 | 0.220 | |
| 1-Methyl-2-ethylbenzene | 0.583 | 0.760 | 0.615 | 0.540 |
| 1,3,5-Trimethylbenzene | 0.193 | 0.203 | 0.173 | 0.204 |
| *tert.*-Butylbenzene | – | 0.027 | 0.017 | – |
| 1,2,4-Trimethylbenzene | 0.770 | 0.734 | 0.679 | 0.686 |
| *sec.*-Butylbenzene | 0.166 | 0.148 | 0.146 | 0.135 |
| 1,2,3-Trimethylbenzene | 0.318 | 0.305 | 0.277 | 0.286 |
| 1-Methyl-4-isopropylbenzene | 0.092 | 0.069 | 0.065 | 0.096 |
| $\Sigma$ Aromatics | 9.198 | 9.552 | 8.957 | 9.392 |

The content of aromatics obtained on SP-2340 was calculated using the modified standard addition method[14] with ethylbenzene as the standard. The results of the quantitative analysis of individual aromatic hydrocarbons in gasoline are given in Table III.

In Table IV are summarized the results of quantitative analysis of aromatics in gasoline eluted up to *n*-decane on squalane (temperature-programmed and isothermal analysis) and on SP-2340. The results are in relatively good agreement.

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