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# QUANTITATIVE ANALYSIS OF HYDROCARBONS BY STRUCTURAL GROUP TYPE IN GASOLINES AND DISTILLATES

## III*. COMBINED USE OF LIQUID AND GAS CHROMATOGRAPHY

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SUMMARY

Liquid chromatography is combined with gas chromatography (GC) for the reliable determination of hydrocarbons in gasolines and similar products according to structural groups. The gasoline sample is pre-separated into three groups (saturates, olefins and aromatics) by liquid chromatography and aliquots of the individual fractions are analyzed by GC, resulting in a partial separation of the compounds present. The composition of the original gasoline sample is calculated from the GC results, utilizing the close uniformity of the flame ionization detector response for hydrocarbons. Possibilities for further improvements are outlined.

## INTRODUCTION

In three recent papers we have reported on our investigations related to the analysis of hydrocarbons by structural group type. In Part I[1] we dealt with the possibilities of carrying out group analysis by first achieving as complete a separation as possible and by utilizing the power of modern computerized data handling for the presentation and evaluation of the results. As shown, capillary gas chromatography (GC) is capable of achieving practically complete separation and the utilization of computerized data handling has the advantage of permitting to present the data according to different aspects. The only problem of this type of analysis is in the need to identify as many sample components as possible.

In connection with the study of capillary GC we have also separately reported the retention indices of a number of hydrocarbons on methylsilicone fluids at different temperatures[2].

* For Part II, see ref. 3.

In Part II[3] we dealt with the possibilities of carrying out group-type separation by liquid chromatography (LC). As shown there, one can achieve a true group fractionation and thus the need of properly identifying all components does not arise. However, the basic problem encountered is related to the significant differences in the response factors of the individual compounds forming a particular group, reducing the accuracy of quantitative analysis. Also, the proper establishment of the baseline under the peaks often requires the analyst's decision at each determination, a criterion undesirable in routine analytical work.

A third possibility for the analysis of gasoline-type samples according to structural groups is to utilize LC for class fractionation, with the subsequent GC analysis of each fraction representing a particular group, for quantitative determination. In this, last part, we discuss this possibility. In connection with this, we also investigated briefly the question of the response of the flame-ionization detector (FID).

## EXPERIMENTAL

The instrumentation and conditions of the LC analysis were identical with those detailed in Part II[3]. As indicated there, the mobile phase used was Fluorinert FC-72 (3M Company, St. Paul, MN, U.S.A.), a perfluorocarbon, with a boiling point of 50°C. The sample volume was always 10 $\mu$l (fixed loop). Fraction collection was performed manually, using appropriate small-volume vials. The exact volume of each fraction was established from the flow-rate and the time of collection.

GC analysis of the LC fractions was carried out on a Sigma 3B gas chromatograph (Perkin-Elmer, Norwalk, CT, U.S.A.). The chromatographic conditions are listed in Table I. A packed column was used because here, separation is not a crucial problem; the concentrations of the individual groups are calculated from the sum of the peak areas.

TABLE I

GAS CHROMATOGRAPHIC CONDITIONS USED FOR THE ANALYSIS OF LC FRACTIONS

| | |
|---|---|
| Column: | |
| Dimensions | 6 ft. (183 cm) × 1/8 in. O.D. (2.16 mm I.D.) |
| Material | Stainless steel |
| Stationary phase | Apiezon L grease |
| Support | Chromosorb W, 80–100 mesh |
| Stationary phase loading | 10% (w/w) |
| Column temperature: | |
| Initial isothermal temperature | 50°C |
| Initial isothermal period | 2.0 min |
| Program | 8°C/min to 200°C |
| Final isothermal temperature | 200°C |
| Final isothermal period | To the end of the analysis |
| Carrier gas | Helium |
| Carrier gas flow-rate | 35 ml/min |
| Injector temperature | 200°C |
| Sample volume injected | 10 $\mu$l |
| Detector | Flame ionization |
| Detector temperature | 250°C |

Data handling was performed using a Sigma 15 Chromatography Data System and a Model 3600 Data Station. For details see Parts I and II[1,3]. All these systems are available from Perkin-Elmer.

Samples were introduced with 1- and 10-$\mu$l microsyringes (Hamilton, Reno, NV, U.S.A.).

Standard hydrocarbons and other chemicals used were obtained from several commercial suppliers, and were of the highest purity available. Gasoline samples were obtained from various service stations during normal automobile servicing.

## RESULTS AND DISCUSSION

### *Relative response of the FID*

As already mentioned in Part I[1], quantitative evaluation of a gas chromatogram obtained when analyzing a hydrocarbon mixture is generally based on the assumption that the relative response of the individual hydrocarbons on an equal weight basis when using an FID is the same. Thus, area per cent values may be taken directly as concentration, in weight per cent.

In the early 1960s a number of researchers investigated the question of the response of the FID for hydrocarbons (see, *e.g.*, refs. 4–8). These studies have shown the general validity of this rule for the majority of compounds assuming that their carbon number does not vary greatly. For example, according to the data of Durrett *et al.*[6], if the response of *n*-heptane is taken as 1.00, then there is a $\pm 4\%$ variation in the $C_5$–$C_{10}$ range of paraffins and cycloparaffins. Generally, aromatics follow the same rule, being within $\pm 4\%$, except benzene and toluene; the relative response of these two compounds (*n*-heptane = 1.00) is given by Durrett *et al.*[6] as 1.12 and 1.07 respectively, while, according to Dietz[8], they are even higher [it should be noted that

TABLE II

TEST MIXTURE USED TO STUDY THE RELATIVE RESPONSE OF THE FLAME IONIZATION DETECTOR

Analytical conditions as in Table I except that sample volume was 1 $\mu$l.

| *Component* | *Density** (g/ml) | *Concentration* | | *Peak area*** | *Area* (%) | *Relative response factor**** |
|---|---|---|---|---|---|---|
| | | *Vol.%* | *Wt.%* | | | |
| *n*-Pentane | 0.6262 | 5 | 4.051 | 77.0375 | 3.766 | 0.976 |
| 2,2,4-Trimethylpentane | 0.6919 | 40 | 35.822 | 697.9775 | 34.124 | 1.000 |
| *n*-Dodecane | 0.7487 | 5 | 4.840 | 98.9183 | 4.836 | 1.049 |
| Dodecene-1 | 0.7584 | 5 | 4.905 | 97.5534 | 4.769 | 1.021 |
| Toluene | 0.8669 | 15 | 16.824 | 367.1391 | 17.949 | 1.120 |
| Ethylbenzene | 0.8670 | 15 | 16.837 | 354.3826 | 17.326 | 1.080 |
| *p*-Xylene | 0.8671 | 15 | 16.721 | 352.4255 | 17.230 | 1.082 |
| Total | | 100 | 100.000 | 2045.4339 | 100.000 | |

* From ref. 9.

** Average of four determinations.

*** Taking 2,2,4-trimethylpentane as 1.000.

Dietz is giving the response factor according to eqn. 2 (below); thus, the relative response factor comparable to the data of Durrett *et al.* will be equal to the reciprocal of eqn. 3 (below)].

As the quoted results were obtained nearly 20 years ago, we also wanted to check the relative response of the FID for some typical hydrocarbons. For this purpose we prepared a test mixture containing some paraffins, aromatics and an olefin; its composition is given in Table II together with the peak area recorded* when analyzing the sample by GC.

Detector response factors can be calculated in two different ways. In the first way, the response factor ($f_i$) is equal to the peak area for unit concentration (amount):

$$f_i = A_i/c_i \tag{1}$$

where $c_i$ is the concentration (amount) of the compound of interest in the sample and $A_i$ is the corresponding peak area. After obtaining these values, the concentration of an unknown mixture is calculated by *dividing* the individual peak area by the corresponding response factor, resulting in the corrected peak area. After normalization of these values, the obtained area percent values are taken as concentration by weight.

The second way to obtain detector response factors is to calculate the concentration for unit peak area, *i.e.*

$$f'_i = c_i/A_i \tag{2}$$

which is the reciprocal of eqn. 1. In this case, the corrected peak area (before normalization) are obtained by *multiplying* the original peak area by the response factor. While most data systems operate in this, second mode, most of the early work quoted utilized the first mode; therefore, we shall also use that here.

For studies of the relative response of a detector it is most convenient to express the *relative* response factor, by assigning an arbitrary value (usually 1.00 or 100.00) to the response factor of a selected compound. In this way the relative response factor [$f_{r(i)}$] of a compound on equal weight basis can be calculated as

$$f_{r(i)} = \frac{A_i}{c_i} \cdot \frac{c_{st}}{A_{st}} \tag{3}$$

where $A_{st}$ is the peak area and $c_{st}$ is the concentration (amount) of the compound selected as the standard. Table II also lists the relative response factors calculated from the peak area; 2,2,4-trimethylpentane was selected as the standard compound because in the literature[6,7] its value is also equal to 1.00.

Investigation of the results given in Table II shows that for paraffins and the olefin the previously mentioned rule (a variation of about $\pm 4\%$) is valid. However, the three aromatics now gave a higher response than found in the literature.

The conclusion of this brief study and the evaluation of literature data are that for the paraffins where the response factors are both lower and higher than unity, the

* In this and subsequent tables, peak area values are given to four places of decimals. This is due to the presentation of the data systems and, naturally, does not imply an accuracy to four significant decimals.

TABLE III

REPRODUCIBILITY OF ABSOLUTE PEAK AREA

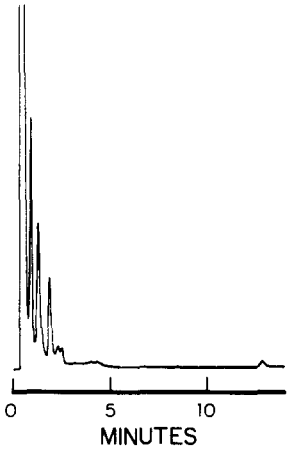
For sample composition, see Table II. Analytical conditions as in Table I except that the sample volume was 1 μl. Peak area in arbitrary units.

| | |
|---|---|
| Sum of peak area: | |
| First determination | 2041.8040 |
| Second determination | 2038.2615 |
| Third determination | 2035.0840 |
| Fourth determination | 2066.5860 |
| Mean | 2045.4339 |
| Standard deviation | 14.366 |
| Relative standard deviation (%) | 0.70 |

combined effect will most likely be negligible. However, in the case of aromatics where the relative response factors (using a paraffin as the standard) are consistently higher than unity, if area per cents are taken as weight per cents, the results obtained will be somewhat higher than the actual concentration. However, unless the gasoline contains an unusually high concentration of benzene and toluene, the difference will most likely be within the errors inherent to this type of determination and evaluation.

*Peak area reproducibility*

In our work samples were introduced manually into the chromatographs. Since the quantitative evaluation of the results assumes that the injected volume was always the same, it is important to check the validity of this assumption.



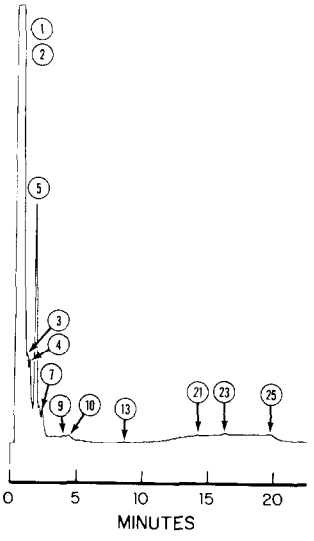




Fig. 1. Direct GC analysis of FC-72 perfluorocarbon. Column: as given in Table I. Column temperature: 30°C initial isothermal for 2 min, then programmed at 8°C/min to 150°C. Sample volume: 1 μl.

Fig. 2. GC analysis of FC-72 perfluorocarbon collected at the end of the LC column. For analytical conditions see Table I. Quantitative data are reported in Table IV. Some of the peaks are identified in the chromatogram.

TABLE IV

QUANTITATIVE EVALUATION OF THE GAS CHROMATOGRAM SHOWN IN FIG. 2

| *Peak No.* | *Retention time (min)* | *Area (%)* |
|---|---|---|
| 1 | 0.32 | 91.906 |
| 2 | 0.86 | 3.446 |
| 3 | 1.22 | 0.524 |
| 4 | 1.39 | 0.843 |
| 5 | 1.82 | 1.900 |
| 6 | 2.12 | 0.276 |
| 7 | 2.33 | 0.402 |
| 8 | 3.15 | 0.118 |
| 9 | 3.95 | 0.018 |
| 10 | 4.28 | 0.028 |
| 11 | 5.24 | 0.002 |
| 12 | 7.62 | 0.001 |
| 13 | 8.46 | 0.016 |
| 14 | 9.55 | 0.011 |
| 15 | 9.97 | 0.018 |
| 16 | 10.33 | 0.014 |
| 17 | 11.11 | 0.050 |
| 18 | 11.29 | 0.021 |
| 19 | 12.33 | 0.196 |
| 20 | 13.29 | 0.001 |
| 21 | 13.82 | 0.013 |
| 22 | 14.78 | 0.022 |
| 23 | 15.90 | 0.091 |
| 24 | 17.30 | 0.053 |
| 25 | 19.25 | 0.031 |
| Total | | 100.000 |

In the relative response studies we analyzed the same seven-component sample four times. The best way to evaluate the constancy of sample volume is to statistically evaluate the sum of the *absolute* peak area. This is given in Table III. We feel that the reproducibility is excellent.

*Influence of the LC mobile phase in the GC analysis*

One of the potential difficulties in multidimensional LC–GC is the interference of the LC mobile phase when analyzing the collected fractions by GC.

Fig. 1 shows the chromatogram obtained in the direct GC analysis of 1 $\mu$l of FC-72 perfluorocarbon. The printout of the data system corresponding to this chromatogram actually revealed the presence of over a dozen peaks up to a retention time of 13 min, including a split in the first peak (not seen in the chromatogram), indicating that the substance is not pure but contains a number of impurities; in fact, the main peak represented only about 70% of the total peak area.

Fig. 1 was obtained by the direct injection of the perfluorocarbon into the gas chromatograph and the initial temperature (30°C) was lower than that used in the actual analysis of the LC fractions (50°C). In order to see the interference of the

mobile phase under conditions identical with actual sample analysis, we collected the LC column effluent (without any sample) for 5 min (a total of 10 ml) and analyzed a 10-$\mu$l aliquot by GC under the conditions listed in Table I. The chromatogram obtained is shown in Fig. 2 and the corresponding quantitative data are listed in Table IV. Owing to the higher initial temperature we obtained a single peak at the beginning.

It should be mentioned that fluorocarbons have a poorer response on the FID than hydrocarbons and thus the relative interference when analyzing similar amounts would be less. Still, because peaks are distributed along the whole chromatogram and because in a sample fraction the fluorocarbon will be at least three orders of magnitude more abundant than the components of interest, the LC mobile phase will contribute heavily to the GC peak area. The interference will be most critical in the case of the saturates because these represent the first fraction in the LC analysis. This can be best seen in Fig. 3, which superimposes the gas chromatogram of the saturates LC fraction over the gas chromatogram of the mobile phase. Note that for the cleanness of presentation different attenuations were used for the two chromatograms: the full-scale response for the mobile phase chromatogram is 653.87 mV while it is 303.74 mV for the saturates chromatogram. If the two attenuations were the same the peaks on the shoulder of the first major peak in the mobile phase chromatogram would actually be of the size of the peaks in the saturates chromatogram.

The problem of interference by the mobile phase can be reduced by subtracting a blank from the chromatograms obtained in the GC analysis of the collected sample fractions. The subtraction is performed by the data system, data point by data point. As an illustration, Fig. 4 shows the chromatogram of the same saturates fraction as in

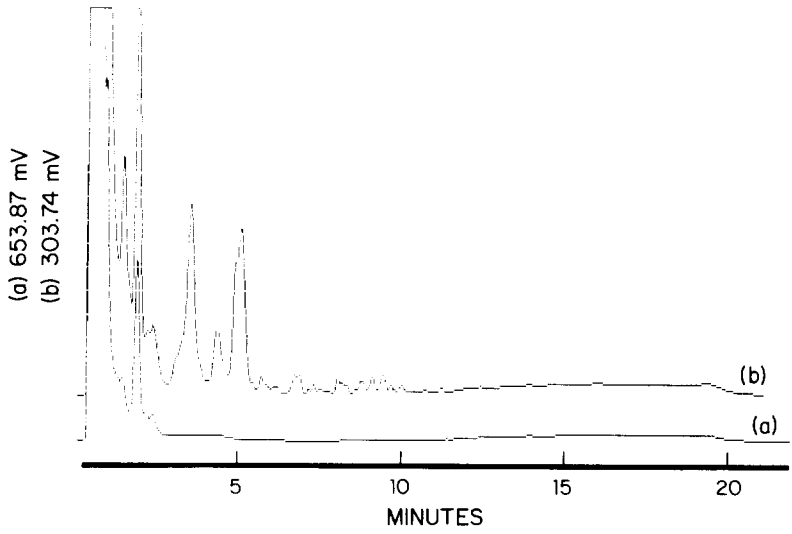



Fig. 3. Superimposed gas chromatograms of (a) pure mobile phase fraction, and (b) the saturates fraction of Brand D unleaded premium gasoline, both collected separately at the end of the LC column. The chromatograms were reconstructed on the video display unit of the chromatography data station. The values on the left-hand side give the full-scale response, in millivolts. For analytical conditions see Table I.

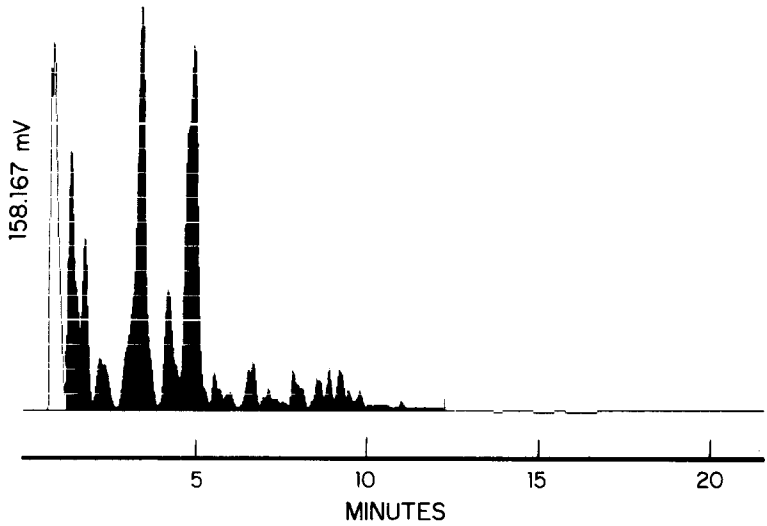



Fig. 4. Gas chromatogram of the saturates fraction of Brand D unleaded premium gasoline from which the blank has been subtracted. The chromatogram was reconstructed on the video display unit of the chromatography data station. Full-scale response: 158.167 mV. For analytical conditions see Table I.

Fig. 3 but with the blank subtracted from it. Note that the second and third peaks which were located on the tail of the solvent peak in the raw chromatogram (b in Fig. 3) are now well resolved.

However, even in the most careful analysis, with injection of the same sample

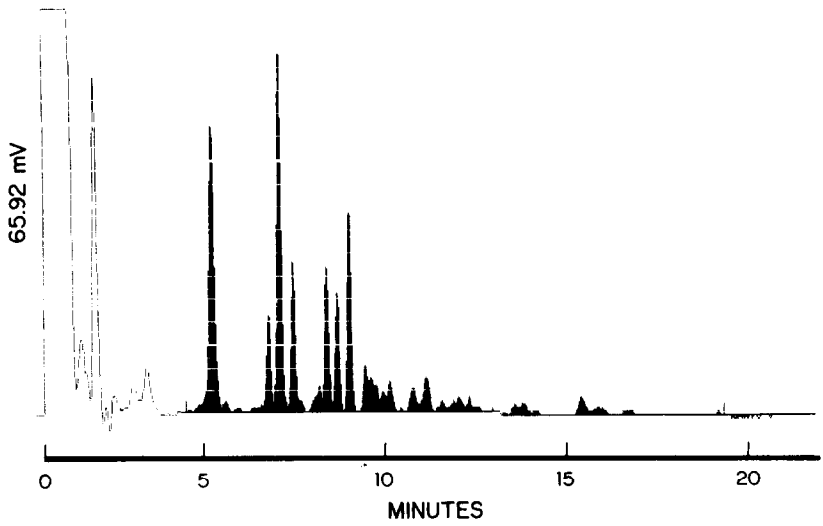



Fig. 5. Gas chromatogram of the aromatics fraction of Brand D unleaded premium gasoline from which the blank has been subtracted. The chromatogram was reconstructed on the video display unit of the chromatography data station. Full-scale response: 65.32 mV. For analytical conditions see Table I.

volumes, exact matching cannot be achieved. For example, in Fig. 4 the first (unshaded) peak corresponds to mobile phase only and not to any sample components. Therefore, for the quantitative evaluation of the analysis, the area of this peak is not considered and quantitation starts at the end of this peak. A similar case is shown in Fig. 5, illustrating the gas chromatogram of the aromatics fraction of the same gasoline. Here, again, the unshaded part is discarded and quantitation starts at the small vertical line (at 4.48 min).

In the previous two cases the blank had a lower value than the corresponding peaks of the actual sample. In some cases the blank might be higher at a particular point creating a negative peak. This is illustrated in Fig. 6, which presents the subtracted gas chromatogram of the olefin fraction of the same gasoline sample. Here, actual quantitation starts at 3.53 min (indicated on the chromatogram).

The chromatogram in Fig. 6 also emphasizes the problem of accurate detection of fractions present in low concentrations: there are 19 very small peaks present corresponding to various olefins, some of which correspond to very low concentrations.

This discussion and the representative chromatograms shown illustrate the difficulties in the elimination of mobile phase interference in the GC analysis of the LC fractions. Even with exact matching of the sample volumes and carrying out blank measurements during the same set-up, collecting the mobile phase prior to sample introduction, individual evaluation of each gas chromatogram is necessary. The chromatograms in Figs. 4–6 also show the other problem which we have already discussed in connection with the quantitative evaluation of the liquid chromatograms[3]: it is often difficult to establish accurately the individual peak area. This is particularly critical in the case of small peaks.

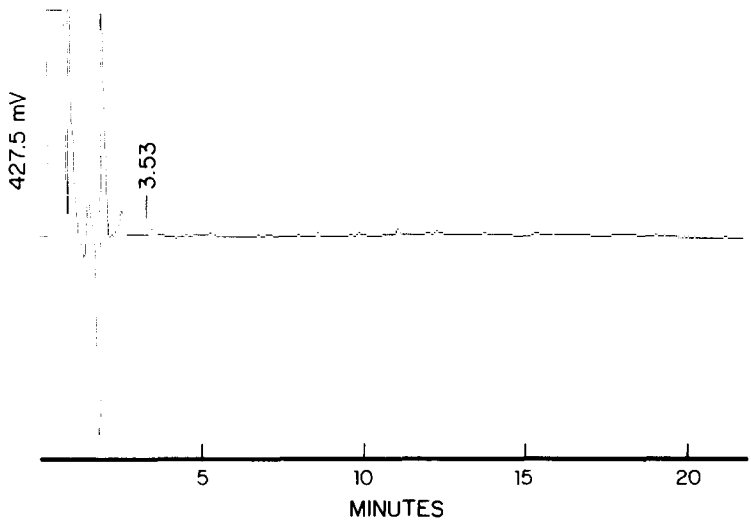



Fig. 6. Gas chromatogram of the olefins fraction of Brand D unleaded premium gasoline from which the blank has been subtracted. The chromatogram was reconstructed on the video display unit of the chromatography data station. Full-scale response: 427.54 mV. For analytical conditions see Table I.

TABLE V

EVALUATION OF THE GC ANALYSIS OF THE COLLECTED LC FRACTIONS FROM A STANDARD SAMPLE

| *Component* | *Density* (g/ml)* | *Concentration* | | *Collected volume (ml)* | *Peak area*** | *Peak area proportional to the collected volume* | *Area (%)* | *Relative deviation from actual concentration (in wt.%) (%)* |
|---|---|---|---|---|---|---|---|---|
| | | *Vol.%* | *Wt.%* | | | | | |
| 2,2,4-Trimethylpentane | 0.6919 | 40 | 34.92 | 4.0 | 770.0350 | 770.0350 | 34.70 | −0.63 |
| Cyclooctene | 0.8452 | 20 | 21.33 | 7.6 | 244.9340 | 465.3746 | 20.97 | −1.69 |
| Ethylbenzene | 0.8670 | 40 | 43.75 | 17.4 | 226.1805 | 983.8852 | 44.33 | +1.33 |
| Total | | 100 | 100.00 | | | 2219.2948 | 100.00 | |

* From ref. 9; cyclooctene measured.

** Obtained by injecting 10-$\mu$l aliquots of the individual fractions. Peak area in arbitrary units.

TABLE VI

ANALYSIS OF A STANDARD MIXTURE BY THE COMBINATION OF LC AND GC

| *Component* | *Concentration (wt.%)* | *Normalized area per cent values** | | | | *Average relative deviation from actual concentration (%)* | *Relative deviation of mean from actual concentration (%)* |
|---|---|---|---|---|---|---|---|
| | | *No. 1* | *No. 2* | *No. 3* | *Mean* | | |
| 2,2,4-Trimethylpentane | 34.92 | 34.70 | 35.82 | 36.57 | 35.697 | 2.87 | 2.22 |
| Cyclooctene | 21.33 | 20.97 | 21.11 | 21.38 | 21.153 | 0.78 | 0.83 |
| Ethylbenzene | 43.75 | 44.33 | 43.07 | 42.05 | 43.150 | 2.76 | 1.37 |
| Total | 100.00 | 100.00 | 100.00 | 100.00 | 100.00 | | |

* Normalization after correcting the peak area for the collected volumes.

TABLE VII

ANALYSIS OF GASOLINE SAMPLES

| *Type* | *Brand* | *Group* | *Collected volume (ml)* | *Total peak area** | *Corrected peak area*** | *Normalized peak area (%)* |
|---|---|---|---|---|---|---|
| Leaded regular gasolines | A | Saturates | 5.4 | 774.2905 | 774.2905 | 50.36 |
| | | Olefins | 6.2 | 43.8720 | 50.3716 | 3.28 |
| | | Aromatics | 17.0 | 226.3765 | 712.6668 | 46.36 |
| | | Total | | | 1537.3289 | 100.00 |
| | B | Saturates | 4.0 | 834.8830 | 834.8830 | 53.80 |
| | | Olefins | 6.4 | 46.8955 | 75.0328 | 4.84 |
| | | Aromatics | 12.4 | 207.0115 | 641.7357 | 41.36 |
| | | Total | | | 1551.6515 | 100.00 |
| | D | Saturates | 5.6 | 629.4965 | 629.4965 | 38.79 |
| | | Olefins | 6.0 | 113.7580 | 121.8836 | 7.51 |
| | | Aromatics | 15.8 | 308.9420 | 871.6578 | 53.70 |
| | | Total | | | 1623.0379 | 100.00 |
| Unleaded regular gasolines | A | Saturates | 5.6 | 674.8730 | 674.8730 | 42.02 |
| | | Olefins | 6.0 | 215.9555 | 231.3809 | 14.41 |
| | | Aromatics | 15.8 | 248.0350 | 699.8130 | 43.57 |
| | | Total | | | 1606.0669 | 100.00 |
| | B | Saturates | 4.2 | 643.8660 | 643.8660 | 43.10 |
| | | Olefins | 7.2 | 145.1360 | 248.8046 | 16.65 |
| | | Aromatics | 15.2 | 166.1410 | 601.2721 | 40.25 |
| | | Total | | | 1493.9427 | 100.00 |
| | C | Saturates | 4.0 | 537.9955 | 537.9955 | 21.42 |
| | | Olefins | 7.4 | 144.5030 | 267.3306 | 10.64 |
| | | Aromatics | 17.2 | 396.9530 | 1706.8979 | 67.94 |
| | | Total | | | 2512.2240 | 100.00 |
| | D | Saturates | 5.4 | 716.5075 | 716.5075 | 44.67 |
| | | Olefins | 6.2 | 125.8975 | 144.5490 | 9.01 |
| | | Aromatics | 16.2 | 247.6420 | 742.9260 | 46.32 |
| | | Total | | | 1603.9825 | 100.00 |
| Unleaded premium gasolines | A | Saturates | 4.6 | 643.2790 | 643.2790 | 32.69 |
| | | Olefins | 7.0 | 50.6800 | 77.1217 | 2.92 |
| | | Aromatics | 17.0 | 337.4805 | 1247.2105 | 63.39 |
| | | Total | | | 1967.6112 | 100.00 |
| | B | Saturates | 4.2 | 681.8065 | 681.8065 | 39.04 |
| | | Olefins | 7.0 | 89.4850 | 149.1417 | 8.54 |
| | | Aromatics | 14.8 | 259.8365 | 915.6143 | 52.42 |
| | | Total | | | 1746.5625 | 100.00 |
| | C | Saturates | 4.6 | 581.5530 | 581.5530 | 37.61 |
| | | Olefins | 6.4 | 37.4515 | 52.1064 | 3.37 |
| | | Aromatics | 16.0 | 262.3375 | 912.4783 | 59.02 |
| | | Total | | | 1546.1377 | 100.00 |
| | D | Saturates | 4.4 | 868.2260 | 868.2260 | 43.70 |
| | | Olefins | 7.2 | 94.5100 | 154.6527 | 7.78 |
| | | Aromatics | 17.2 | 246.5770 | 963.8919 | 48.52 |
| | | Total | | | 1986.7706 | 100.00 |

* Obtained by analyzing a 10-$\mu$l aliquot of the collected volume. Peak area in arbitrary units.

** Corrected to reflect the ratio of the collected volumes.

TABLE VIII

ANALYSIS OF GASOLINE SAMPLES BY THE COMBINATION OF LC AND GC

| *Type* | *Brand* | *Concentration (wt.%)* | | |
|---|---|---|---|---|
| | | *Saturates* | *Olefins* | *Aromatics* |
| Leaded regular | A | 50.3 | 3.3 | 46.4 |
| | B | 53.8 | 4.8 | 41.4 |
| | D | 38.8 | 7.5 | 53.7 |
| Unleaded regular | A | 42.0 | 14.4 | 43.6 |
| | B | 43.1 | 16.6 | 40.3 |
| | C | 21.4 | 10.7 | 67.9 |
| | D | 44.7 | 9.0 | 46.3 |
| Unleaded premium | A | 32.7 | 3.9 | 63.4* |
| | B | 39.1 | 8.5 | 52.4* |
| | C | 37.6 | 3.4 | 59.0 |
| | D | 43.7 | 7.8 | 48.5 |

* Contain about 4% of MTBE.

*Quantitative evaluation of the GC analyses*

Since we were using an FID in the GC analysis and assumed an equal response factor for the individual sample components, no response factors were utilized. Thus, the concentration of the gasoline samples can be calculated directly from the peak area. However, the cumulative peak area obtained in the separate analyses of the collected fractions are not additive. The reason for this is that while the collected volumes are different we always injected the same volume aliquot (10 $\mu$l) into the gas chromatograph. Thus, before normalization, the cumulative peak areas obtained for the individual fractions have to be corrected for the differences in the volumes of the fractions. This method of calculation is illustrated in Table V, giving the results of the analysis of a standard sample which was first separated by LC in the usual way and then 10-$\mu$l aliquots of each collected fraction were analyzed by GC. The raw area of cyclooctene is multiplied by 7.6/4.0 and the raw area of ethylbenzene by 17.4/4.0 to obtain the corrected peak area, which can then be normalized in the usual way. Table V also compares the results obtained with the actual sample composition.

We carried out the analysis of this standard mixture in triplicate on different days, and the results are summarized in Table VI (No. 1 is identical with the data in Table V), giving also the average relative deviations from the actual concentration. In our opinion, these data show the reliability of this type of calculation.

*Comparative measurements on gasoline samples*

Again, we analyzed eleven gasoline samples using the described combination of LC and GC. Table VII summarizes the analytical results and the steps of calculation. In order to permit a better survey of the data Table VIII summarizes the final results: the given concentration data are identical with the normalized peak area values given in Table VII. As already indicated in Part II[3], the additive methyl *tert.*-butyl ether (MTBE) will now elute together with the aromatics.

It is difficult to compare the results obtained here with those of the LC measurements[3] mainly because, owing to the calculation method used there, a sizeable portion of the compounds is unaccounted in the LC analysis. Also, one should not forget the uncertainty in the establishment of the calibration factors in the LC analysis utilizing refractive index detectors, a problem which is much less significant here.

## CRITIQUE OF THE METHODS

In our opinion, there is no question that the capillary GC method as outlined in Part I[1] may give the most accurate results, and the possibility of presenting the data according to various aspects is a special advantage of that method. However, the essential problem encountered is that for accurate data presentation, the identity of practically every peak must be known. Identification may be facilitated by combining capillary GC with LC: carrying out a preseparation by LC and analyzing the individual fractions by capillary GC under conditions identical with those used in the direct capillary GC of the gasoline samples. In this way one may establish the group to which certain unknown peaks belong.

As expressed at the end of Part II[3], we are skeptical about the use of LC for the routine determination of hydrocarbons in gasolines and similar products according to structural groups. However, we believe that the combination of LC with GC as outlined here offers an attractive possibility for such determinations, particularly if the method is further improved.

### *Possible improvements to the method*

Below we list the questions in which improvement of the method is desired and possible:

(a) The most serious shortcoming of the method is related to the interference of the mobile phase. It is highly desirable that a chemically purer substance with as low a solvent strength as possible be utilized.

(b) In addition to the interference of the impurities in the mobile phase the separation of the major mobile phase component from the early emerging saturates also represented a problem. Therefore, it is desirable to use a stationary phase in the GC column which retards the hydrocarbons a little longer relative to the mobile phase peak. Column efficiency and separation of paraffins from aromatics is not critical: after all, the sample is pre-separated by LC and the peak areas within one fraction are summed anyway.

(c) The accuracy of the method of calculation depends significantly on the exact reproducibility of the aliquot volumes injected into the gas chromatograph. In our opinion the reproducibility we could achieve with manual injection (*cf.*, Table VI) is remarkable. Still, this can be further improved by using autosampling devices.

(d) It is also very important to know exactly the volume of the collected fractions. Modern liquid chromatographs have very reliable flow control and there is no problem in measuring the time of collection; thus, the collected volumes can be readily calculated. For even higher accuracy one may want to check whether there is any deviation of the nominal flow-rates indicated by the control device of the instrument and the actual flow-rates.

(e) We have discussed the question of the response of the FID. As shown,

while in the case of paraffins and olefins slight differences in the response factors most likely will compensate, aromatics and particularly benzene and toluene have a higher response than the paraffins and this may present an unacceptable deviation, particularly for gasolines with very high aromatics contents. In this respect we would like to refer to Table V in Part I[1], which showed that Brand A leaded regular and Brands A and B unleaded regular gasolines contained as much as 20% of toluene, representing 40–60% of the total aromatics present. This problem, however, could be overcome fairly easily. Since when analyzing the collected aromatics fraction by GC (*cf.*, Fig. 5) some separation is obtained, there is no difficulty in correcting the individual peak area by a response factor prior to normalization.

## CONCLUSIONS

To conclude, we believe that the combination of LC and GC presents good possibilities for the accurate determination of hydrocarbons in gasolines and similar products according to structural group.

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