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

I. GAS CHROMATOGRAPHY

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SUMMARY

The questions related to the analysis of complex gasoline samples are outlined and the criteria of both detailed analysis and data presentation according to structural group types are discussed. Conditions for optimum separation using open-tubular (capillary) columns are given. Retention data for a large number of hydrocarbons are listed. Analysis of eleven gasoline samples is presented and the reproducibility of peak identification is demonstrated.

INTRODUCTION

The ever-increasing cost and diminishing supply of petroleum raw materials imposes a growing burden upon the industrial analyst. Production facilities require better, more detailed, information regarding feedstocks and products to realize optimum operational economics. Feedstock material is becoming more variable, and may eventually become a mixture of hydrocarbons of natural and synthetic origin, or even totally synthetic.

The purpose of the evaluation of complex hydrocarbon mixtures, *i.e.*, naphtha, reformates, gasolines and light gas liquids*, is to provide the petrochemical engineer with the information required for process control, operation and product quality

* These petroleum products have definite specifications in each country. In general a *naphtha* corresponds to a certain cut of a distillate (generally from crude oil), usually containing hydrocarbons in the carbon range of C_3–C_{15}; *reformates* are products obtained from naphthas by changing their composition over catalysts, *e.g.*, by increasing the aromatics content; *gasolines* refer to fuels for internal combustion engines and their composition varies from state to state depending on the altitude and atmospheric temperature; and *light gas liquids* refer to liquids condensed from natural gases.

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assurance. This may involve determination of individual mixture components or may only require chemical group-type composition or physical properties, such as boiling range, volatility or fuel ignition characteristics. The major analytical technique utilized for petroleum hydrocarbon characterization is chromatography. A number of approaches have been utilized to fulfil the various requirements.

Total analysis

The ultimate goal in the evaluation of the complex hydrocarbon mixtures is the identification of each component present and the determination of their relative amounts. Such activities have been carried out extensively in the past. One need only to refer to Research Project No. 6 of the American Petroleum Institute (API). Between 1927 and 1967, well over 500 man-years of work have been utilized to identify the components of the crude of Brett No. 6 well in the Ponca City field of Oklahoma. Until 1960, the isolation of 175 individual hydrocarbons from their crude was accomplished primarily utilizing liquid-adsorption chromatography[1–6].

The introduction of gas–liquid partition chromatography by Martin and James in 1952[7] opened new possibilities to the petroleum chemists. Early work on packed columns[8–12] already illustrated the potential of the new technique for the separation of the complex hydrocarbon mixtures. The introduction of open-tubular (capillary) columns by Golay[13], in 1957, was immediately followed by their utilization in hydrocarbon analysis. The literature of the last 25 years abounds in papers describing methods for the analysis of various petroleum fractions illustrating the separation of hundreds of compounds in such mixtures; here we only quote a few key papers from the first decade[14–17]. Probably the ultimate chromatogram published is by Whittemore[18] showing the analysis of a gasoline sample on a 300 m (1000 ft.) × 0.50 mm I.D. open-tubular column coated with squalane; a total of 378 peaks were separated in just over 4 h, leaving only 17 unclassified.

Group analysis

While the knowledge of the ultimate composition of petroleum feedstocks and gasolines is of great importance, it is more of academic interest. In practice, such samples are usually characterized in two ways: by their boiling-point range determined either by distillation[19–21] or by a gas chromatographic technique called simulated distillation[22,23], and by giving the relative amounts of hydrocarbons present corresponding to structural groups such as paraffins, olefins, naphthenes (cycloparaffins) and aromatics. A number of approaches are available to obtain such information utilizing both gas and liquid chromatography. We shall discuss the methods involving liquid chromatography in Part II of our report; here we deal only with the utilization of gas chromatography (GC) to obtain information on composition according to hydrocarbon groups.

A particular advantage of GC analysis is that the quantitative response of the flame-ionization detector is approximately the same for equal weights of any hydrocarbon so that, in first approximation, relative peak areas can directly be used for weight percent values[24–28]. Thus, even unknown components from a mixture can be quantitated with reasonable accuracy. This becomes a distinct advantage over spectroscopic or other detection methods used in liquid chromatography.

A large number of GC methods are described in the literature, most employing

multiple column systems with valving configurations [*e.g.*, refs. 29–38]. Packed columns have been commonly used although open-tubular columns are becoming more popular. In some cases, packed and open-tubular columns can be combined to employ their respective advantages, as demonstrated by Johansen[39] for the analysis of natural gas and light petroleum samples. The analytical schemes may also employ chemical means of separation in combination with gas chromatography. A typical example is the classical work of Martin[40], first separating the aromatics from saturates and olefins, and then eliminating the olefins by absorption in mercury(II) perchlorate.

Most of the GC methods for group analysis also provide some separation within a group and thus peak areas have to be summed up to obtain the relative concentrations of paraffins, olefins, naphthenes and aromatics on any other groups of interest. It also follows from this that peak identification is important, at least knowing to which group the particular compound belong. Originally, the complex calculation involved in this type of analysis was time consuming; however, the proliferation of modern computers and data systems simplified this problem.

Combination of total and group analysis

The availability of modern data systems and computers makes one desire a practical reality: to combine the ultimate goal of a petroleum chemist with the need of a simplified presentation of data according to functional group types. This can be approached by using very-high-resolution open-tubular columns, obtaining as many peaks as possible, providing the computer system with the proper retention data so that the peaks can be identified and also feeding in the proper instructions how the individual data should be combined. A particular advantage of such an approach is that 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 while also having the possibility of establishing the concentration of individual components or special compound groups. In fact, a study group of Committee D-2 of ASTM is currently investigating the possibility of such an approach as a standard method.

Disadvantages of this approach are that every peak must be identified in the chromatogram, at least according to the chemical group to which it belongs, and the relatively long time necessary for the analysis and data presentation. However, with modern instrumentation and data systems, this time only involves very little actual labor: most of the functions are performed automatically.

The scope of this paper

This paper summarizes our detailed investigation on the use of high-resolution capillary gas chromatography for the group-type analysis of hydrocarbons in light petroleum products, by first achieving as complete a separation as possible and then combining the results obtained using up-to-date laboratory data systems. Our studies were limited to materials with an upper boiling point of 230–250°C.

Since the reliability of the calculation depends on the degree of separation, we discuss in detail the selection of the analytical conditions required. Further subjects of our investigations were the reliability of peak identification and the reproducibility of the capillary column analysis. Finally, possibilities of how the results can be combined are demonstrated.

The second and third parts of our report will discuss the use of high-performance liquid elution chromatography (HPLC) and the combination of GC and HPLC.

EXPERIMENTAL

The GC analyses were performed on Sigma 1 and 2 gas chromatographs (Perkin-Elmer, Norwalk, CT, U.S.A.), equipped with flame-ionization detectors and all-glass split-type injectors. Open-tubular (capillary) columns were made of soda-lime glass (Perkin-Elmer) with an I.D. of 0.27 mm. OV-101 methylsilicone fluid liquid phase was used, coated in two different film thicknesses (d_f), approximately 0.2 and 0.9 μm. Helium was used as the carrier gas. The instrumental conditions are reported in Table I.

Data handling was carried out by Sigma 15 chromatography data systems which provided raw data integration, component identification, normalization and group-type summations using BASIC programming. These were also connected via an RS-232C Communication Interface to a Model 3600 Data Station having chromatography data handling software with extended capabilities (*e.g.*, replot, reintegrate and printer graphics). The Model 3600 was equipped with a video display unit, dual microfloppy disk drive and a Model 660 printer. All these systems are available from Perkin-Elmer.

Standard hydrocarbons and known mixtures of naphtha and reformates used in this project were obtained from several commercial petroleum laboratories. Gasoline samples were obtained from various gasoline service stations during normal automobile servicing.

TABLE I

GAS CHROMATOGRAPHIC CONDITIONS USED FOR THE ANALYSIS OF GASOLINE SAMPLES

Column:	
Dimensions	55 m × 0.27 mm I.D.
Material	Soda-lime glass
Liquid phase	OV-101 methylsilicone fluid
Film thickness	0.9 μm
Column temperature:	
Initial isothermal temperature	35°C
Initial isothermal period	8.0 min
First program	1.4°C/min to 60°C
Middle isothermal temperature	60°C
Middle isothermal period	15.0 min
Second program	2.1°C/min to 180°C
Final isothermal temperature	180°C
Final isothermal period	To the end of the analysis
Carrier gas	Helium
Carrier gas flow-rate	1.2 ml/min
Injector temperature	200°C
Sample volume injected	0.3–0.5 μl
Split ratio	1:80–100
Detector	Flame ionization
Detector temperature	250°C

RESULTS AND DISCUSSION

Selection of the liquid phase and its film thickness

A petrolcum or gasoline sample represents a very complex mixture containing many hundreds of components. Thus, in its analysis, two basic problems are encountered: it is difficult to separate every sample component or most of these and to identify them. Separation depends on the selection of column parameters, the liquid phase and on column efficiency while identification assumes that retention data are accurately reproduced.

Much of the early development in capillary analysis of petroleum hydrocarbons was accomplished through the use of metal (stainless steel) open-tubular columns, using squalane as the liquid phase. Squalane, however, has certain shortcomings as a liquid phase for capillary columns: its maximum operating temperature is inconveniently low[41,42] (about 100°C) and it is difficult to prepare a stable column with it when using glass or fused-silica tubing. In the last decade squalane has been largely replaced by the various polydimethylsiloxanes (methylsilicones) as liquid phases in capillary gas chromatography with glass or fused-silica columns. These fluids have more favorable characteristics providing a low bleed rate from sub-ambient temperature to 300°C and result in high-efficiency stable columns. In our work we have selected OV-101 methylsilicone fluid as the liquid phase for the columns used.

A particular advantage of methylsilicone phases and glass and fused-silica tubing is the flexibility of selecting the proper liquid phase film thickness. Columns used in general applications have a coating of about 0.1–0.2 μm; however, it has been shown by Johansen[43] that in the analysis of wide boiling range mixtures starting at low-boiling compounds, columns with a thicker film have special merits such as better resolution for earlier peaks (up to about *n*-octane) and the possibility of carrying out the analysis without the need of sub-ambient initial column temperatures. In fact, a shorter thick-film column may provide a better overall result than a longer column with a thin film. For this reason, while our initial work was carried out using 100-m long capillary columns with a 0.2-μm film of OV-101, we have selected a 55 m long column with an average liquid phase film thickness of 0.9 μm for the systematic investigation of the gasoline samples. In a separate paper[44] we have shown that the retention characteristics of hydrocarbons are independent of the film thickness of the liquid phase.

Influence of temperature on the elution sequence

The most difficult and time-consuming aspect of developing a method for such complex analyses is the optimization of the separation in respect to column temperature. In 1967, Ettre and Billeb[45] showed the effect of column temperature on the retention indices of various homologous series of hydrocarbons when using squalane as the liquid phase. Their data indicates a linear relationship between column temperature and retention index according to the equation

$$I = aT + b \tag{1}$$

where I is the retention index, T is the column temperature (°C) and a and b are specific homolog constants. Particularly highly branched paraffins, naphthenes and

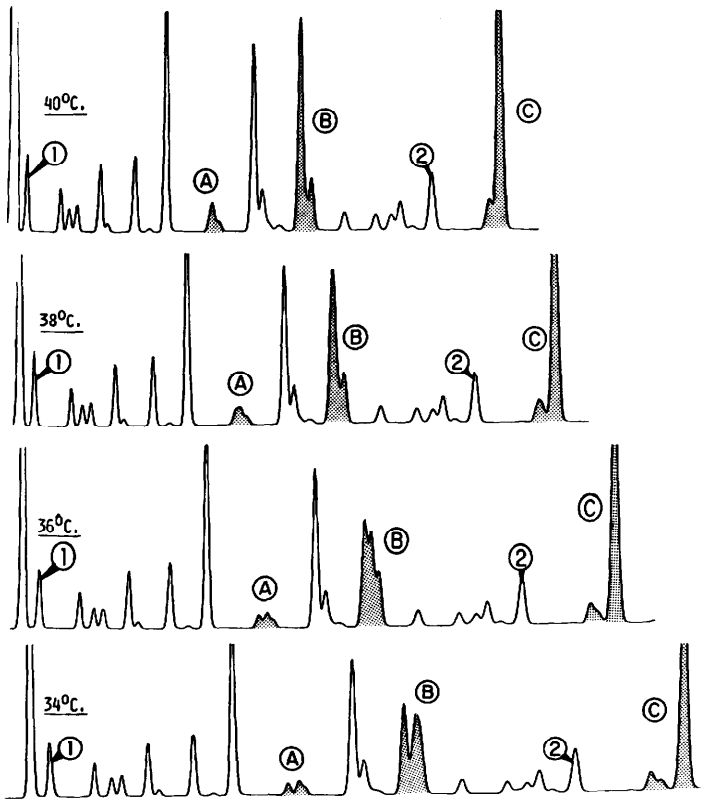

Fig. 1. Part of the chromatogram of a naphtha sample. Column: 55 m × 0.27 mm I.D., glass capillary column coated with OV-101 methylsilicone fluid liquid phase (d_f = 0.9 μm). Isothermal operation at the temperatures given. Substances representing the shaded groups of peaks are: (A) 1,1,2-trimethylcyclopentane, 2,3-dimethylhexane and 2-ethyl-3-methylpentane; (B) 1(*cis*),2(*trans*),3-trimethylcyclopentane, 3-methylheptane and 1(*trans*),4-dimethylcyclohexane; (C) 1(*cis*),4-dimethylcyclohexane, 1(*trans*),3-dimethylcyclohexane and *n*-octane. The retention times of the numbered peaks are: (1) 30.11 min (34°C), 28.14 min (36°C), 26.29 min (38°C), 24.65 min (40°C); (2) 54.89 min (34°C), 50.81 min (36°C), 47.03 min (38°C), 43.65 min (40°C).

aromatics show a significant temperature dependence (high value of a) while the retention index of paraffins with only a few side chains is very little affected by the column temperature. In a recent paper[44] we have confirmed the validity of eqn. 1 and that the relationship is similar for methylsilicone phases.

The result of this observation is that at higher temperatures the highly branched paraffins, naphthenes and aromatics will be retained longer relative to the *n*-paraffins or paraffins with little substitution and in some cases their relative position in the chromatogram will even change.

The sensitivity of the elution sequence (and hence, the degree of separation) to column temperature is shown in Fig. 1. Here, segments of the chromatograms of a naphtha sample are shown at column temperatures differing by only 2°C. The three sets of peaks indicated (A, B and C) represent a paraffin eluting in the proximity of naphthenes. When considering set A, the 1,1,2-trimethylcyclopentane peak appears to move into the 2,3-dimethylhexane peak as the temperature is raised. Set C shows

that as the temperature increases, the two dimethylcyclohexanes are covered by the *n*-octane peak. Set B presented a special challenge for the method optimization. When using the 100-m column (d_f = 0.2 μm), the temperature profile was established, resulting in the elution of 3-methylheptane between 1(*cis*),2(*trans*),3-trimethylcyclopentane and 1(*trans*),4-dimethylcyclohexane. However, the 55-m (d_f = 0.9 μm) column lacked sufficient efficiency to resolve the three peaks. Thus, a different (higher) temperature was necessary here to cause 3-methylheptane to elute prior to the naphthenes.

Optimization of the temperature program

In the analysis of such complex samples as naphthas or gasolines, one should not work under isothermal conditions but rather utilize temperature programming; if necessary, a combination of isothermal and programmed-temperature steps with different program rates may also be applied.

If column temperature programming is used instead of isothermal analysis one adds to the complexity of the retention characteristics of multicomponent mixtures. As solutes are partitioned within the column, their relative positions will approximate the average temperature of the column during their residence. One may then make adjustments in the initial temperature, program rate and final temperature in order to exactly position particular peaks. As sample complexity increases, so does the probability of co-eluting components, and the necessity for making additional temperature profile adjustments to achieve separation optimization. It will likely become necessary to sacrifice resolution between some minor components in order to achieve adequate separation of the more important components. In the case cited above, regarding the use of the 55-m column, it was necessary to sacrifice the separation of 1,1,2-trimethylcyclopentane from 2,3-dimethylhexane to achieve the separation of 3-methylheptane and 1,2,3-trimethylcyclopentane, which are usually present in higher concentrations in most petroleum naphthas. This compromise was not necessary when using the 100-m column.

Table I lists the complex temperature program we found as the optimum with the particular column used for the analysis of the gasoline samples. While these conditions can certainly serve as a guideline for other chromatographers desiring to analyze similar samples, a caution is necessary against copying these, or other, conditions without any adjustment. The reason for this is that columns obtained from different sources tend to vary in dimension, material and liquid phase coating. These variations result in columns having differences in their retention capacity and, thus, cause different elution patterns if identical operating conditions are employed. For this reason we point out the specific segments in the chromatogram where resolution is most critical. The actual resolution of these peak pairs can be improved, if necessary, by column temperature adjustments.

Our experience has shown that there are five sets of closely eluting components in petroleum samples that may be used to optimize the analytical conditions using OV-101 capillary columns:

Cyclopentane–2,3-dimethylbutane. Here one may adjust the initial isothermal temperature and time.

3-Ethylpentane–1(trans),2-dimethylcyclopentane. These are not separated on the 100-m (d_f = 0.2 μm) column without affecting other more significant separations.

Adjustment of the initial isothermal time and the rate of the first temperature program can achieve this separation on the 55-m (d_f = 0.9 μm) column.

3-Methylheptane–1,2,3-trimethylpentane. This is a critical separation influenced by the initial program rate and, to some extent, by the initial isothermal time.

n-Propylcyclopentane–2,3-dimethylheptane. This pair can be used to set the mid-program isothermal temperature.

m-Xylene–3,4-dimethylheptane. This separation depends on the length of the mid-program isothermal period and on the mid-program temperature.

These critical separations can be seen in Fig. 2 corresponding to the peak nos. 22–23, 57–58, 88–89 and 111–112. 3,4-Dimethylheptane was not separated from *m*-xylene (no. 123) due to the relatively high concentration of the latter in these gasolines.

Relative retention times

Although retention indices are the most universal way to express retention for identification, their use is restricted to isothermal operation. It is true that retention indices can also be calculated for a programmed temperature operation; however these will differ somewhat from the isothermal values and, in the case of a multistep program incorporating both isothermal and programmed-temperature periods, the retention index is meaningless. Therefore, one should rather rely on relative retention data. These are, however, different from those used in isothermal analysis.

Under isothermal conditions the relative retention (r or α) values are independent on the analytical conditions (except the stationary phase and the column temperature) and represent the basis of peak identification:

$$r = t'_{R(i)}/t'_{R(st)} \tag{2}$$

where t'_R represents the *adjusted* retention time (corrected for the gas holdup time) and subscripts i and st refer to the peak of interest and the standard peak respectively.

Eqn. 2 is valid only for isothermal analysis. Therefore, a different expression is used here for peak identification: the so-called relative retention time (RRT). This is calculated similarly to eqn. 2 except that now the actual retention time (measured from sample introduction), obtained under the actual temperature-programmed conditions (t_R^T) are used:

$$RRT = t^T_{R(i)}/t^T_{R(st)} \tag{3}$$

As discussed elsewhere[46] this usage is common in the computer evaluation of chromatographic data and, *within one system*, these values are just as reproducible as the true relative retention values.

In addition to the way expressed in eqn. 3 RRT values can also be calculated by assigning a different value to the standard. If this is RRT_{st}, then the relative retention time of a particular peak can be calculated as:

$$RRT_i = [t^T_{R(i)}/t^T_{R(st)}]RRT_{st} \tag{4}$$

This equation is particularly convenient if the standard peak has a relatively long retention time, in which case, the RRT values of early peaks would not have enough

significant figures if eqn. 3 is used. The method of eqn. 4 is used below, assigning an *RRT* value of 15.000 to *o*-xylene (t_R^T = 62.01 min). As seen later, in Table II, methane will have an *RRT* value of 0.844. Using eqn. 3 (*i.e.*, having an *RRT* value of 1.000 for *o*-xylene), the *RRT* value of methane would be only 0.056.

Investigation of gasoline samples

By analyzing standard mixtures we first established the optimum conditions for gasoline samples and determined the *RRT* values for as many compounds as

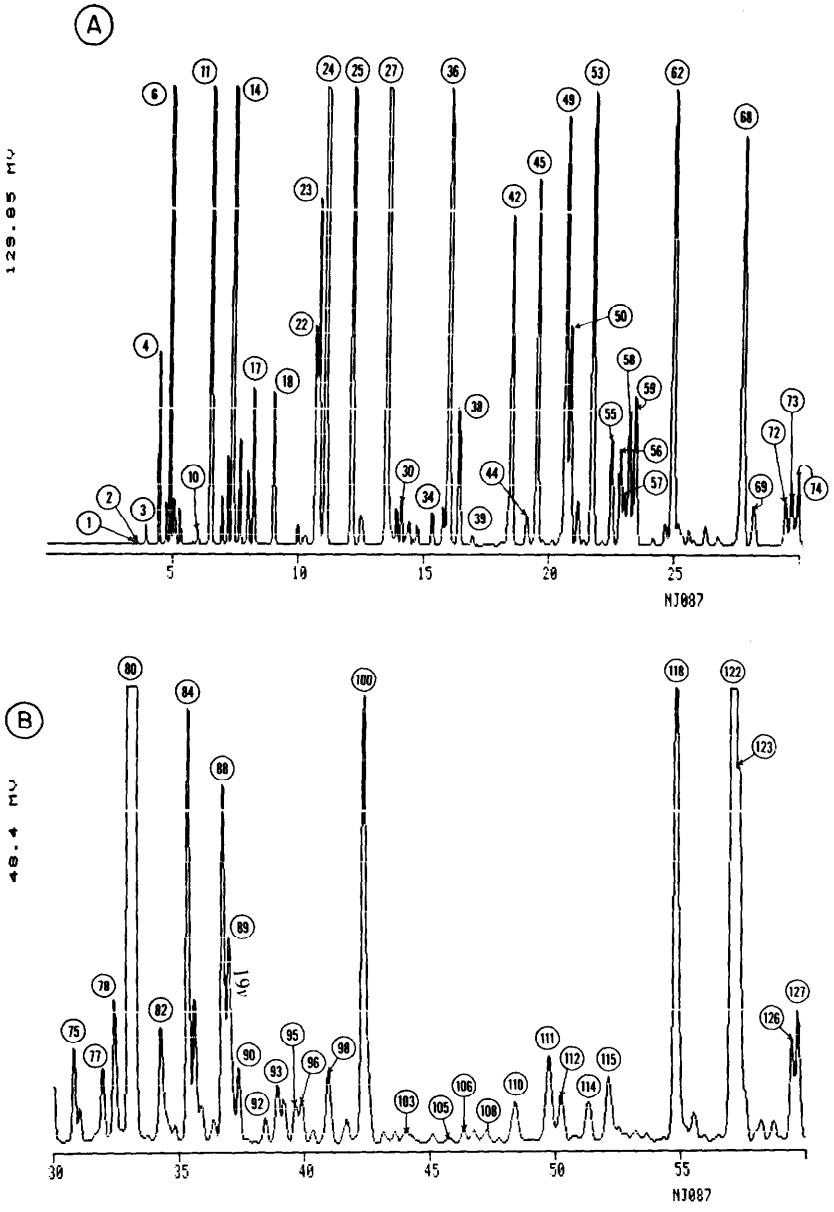

Fig. 2

(Continued on p. 402)

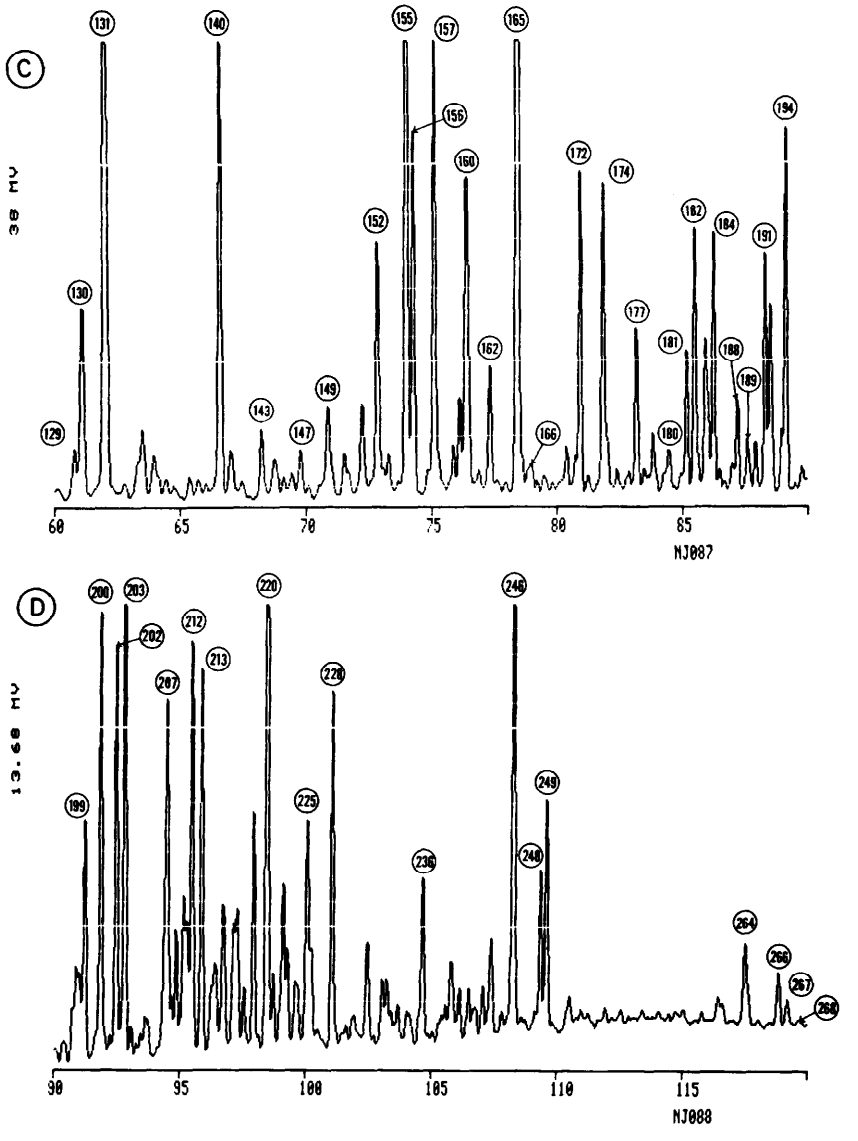

Fig. 2. Chromatogram of a typical gasoline sample. Column and conditions as listed in Table I. The chromatogram was reconstituted in 30-min segments on the video display unit of the chromatography data station. The values on the left-hand side of each segment give the full-scale response, in millivolts. The scale at the bottom of each segment represents time, in minutes. The numbers identifying the individual peaks correspond to the peak numbers in Table II. The most important peaks: (6) *n*-butane, (11) 2-methylbutane, (14) *n*-pentane, (22) cyclopentane, (23) 2,3-dimethylbutane, (24) 2-methylpentane, (25) 3-methylpentane, (27) *n*-hexane, (36) methylcyclopentane, (42) benzene, (45) cyclohexane, (49) 2-methylhexane, (58) 1(*trans*),2-dimethylcyclopentane, (59) 2,2,4-trimethylpentane, (62) *n*-heptane, (68) methylcyclohexane, (80) toluene, (84) 2-methylheptane, (88) 3-methylheptane, (89) 1(*cis*),2(*trans*),3-trimethylcyclopentane, (100), *n*-octane, (111) *n*-propylcyclopentane, (118) ethylbenzene, (122) *p*-xylene, (123) *m*-xylene, (130) 3-methyloctane, (131) *o*-xylene, (140) *n*-nonane, (143) isopropylbenzene, (152) *n*-propylbenzene, (155) 1-methyl-3-ethylbenzene, (157) 1,3,5-trimethylbenzene, (165) 1,2,4-trimethylbenzene, (172) *n*-decane, (174) 1,2,3-trimethylbenzene, (188) 1-methyl-2-*n*-propylbenzene, (194) 1,3-dimethyl-4-ethylbenzene, (200) *n*-undecane, (203) 1,2,3,5-tetramethylbenzene, (236) *n*-dodecane, (248) *n*-tridecane, (264) *n*-tetradecane.

possible. Then we analyzed eleven samples of various gasolines and utilized the data obtained to evaluate the reproducibility of capillary gas chromatography under routine laboratory conditions. The possibilities of combining the data to obtain composition according to structural groups and the various other ways of data presentation were als investigated.

Chromatographic analysis and data presentation. As mentioned earlier, the OV-101 coated capillary column with an average liquid film thickness of 0.9 μm was found best suited for the analysis of gasoline samples representing a boiling-point range of -164°C (methane) to about 250°C (tetradecane: 253.7°C), using a 55-m long column with a multistage program. Table I lists the analytical conditions used.

Fig. 2 shows the chromatogram of a typical gasoline sample. This chromatogram was obtained by displaying the original chromatogram stored in the memory of the data system in 30-min segments and selecting the optimum attenuation of the particular segment before printing. The attenuations are indicated by a value on the left-hand side giving the full-scale detector response in millivolts. If desired, the retention times and/or peak identification may also be displayed over the peaks. For clarity of presentation, this information was deleted in Fig. 2; instead, the peaks are numbered consecutively. The numbers of the most important peaks are given in Fig. 2. The full numbering is included in Table II representing the simplified form of the full analytical report corresponding to this chromatogram. In the full report, which is the result of a BASIC program, additional information is also given, *e.g.*, the way the baseline of the individual peaks is established and incompletely resolved peaks split, and listing of the response factors used in calculating the concentration from the relative peak area. In the present work a response factor of 1.000 was used for every compound, *i.e.*, it was assumed that peak area values are equal to concentration in weight percent.

In the chromatogram shown in Fig. 2 a total of 268 peaks are indicated and from these 123 are identified. Inevitably some of these peaks might also contain additional compound(s) present in trace quantities; also one may be able to identify more peaks, thus reducing the number of unknowns. It should, however, be emphasized that out of the 145 "unknowns" none is present in a concentration higher than 0.30% and only 15 have a concentration between 0.10 and 0.30%.

It is very intuitive to investigate the breakdown of the composition of this (and similar) samples according to functional groups and, within each group, the most dominant compounds. Table III presents the data of Table II in this way. The lower concentration limit for the individually listed compounds was 0.50% for the paraffins and aromatics, 0.30% for the naphthenes and 0.10% for the olefins and unknowns. As seen, it is easy to select the most prominent paraffins, naphthenes and aromatics; however, this is practically impossible for the olefins and unknowns where a large number of compounds are present in very small concentrations. This observation will have an important implication later when discussing the possibility of group analysis by HPLC (see Part II of our report[49]).

The main purpose of this investigation was to examine the possibility of utilizing the detailed capillary GC analysis data for structural-group type analysis. The data system can combine the data, providing this information: Fig. 3 presents such a printout for the data detailed in Table II. Here, cycloolefins are included in the group of olefins but, naturally, different grouping is also possible.

TABLE II

FULL ANALYTICAL REPORT CORRESPONDING TO THE CHROMATOGRAM IN FIG. 2

Peak No.	*Retention time (min)*	*RRT*	*Peak area (%)*	*Compound*
1	3.49	0.844	0.0008	Methane
2	3.62	0.876	0.0013	Ethane
3	3.94	0.953	0.0288	Propane
4	4.44	1.074	0.3758	2-Methylpropane
5	4.74	1.147	0.0602	Butene-1
6	4.88	1.181	3.5613	*n*-Butane
7	5.03	1.217	0.0596	Butene-2, *trans*
8	5.10	1.234	0.0428	2,2-Dimethylpropane
9	5.28	1.277	0.0621	Butene-2, *cis*
10	5.99	1.449	0.0245	3-Methylbutene-1
11	6.39	1.546	10.6459	2-Methylbutane
12	6.95	1.681	0.0811	Pentene-1
13	7.19	1.739	0.1414	2-Methylbutene-1
14	7.38	1.785	8.3147	*n*-Pentane
15	7.66	1.853	0.1921	Pentene-2, *trans*
16	7.99	1.933	0.1416	Pentene-2, *cis*
17	8.22	1.988	0.2760	2-Methylbutene-2
18	9.02	2.182	0.3269	2,2-Dimethylbutane
19	9.98	2.414	0.0447	3-Methylpentene-1
20	10.20	2.467	0.0181	4-Methylpentene-2
21	10.30	2.492	0.0264	2,3-Dimethylbutene-1
22	10.68	2.584	0.5105	Cyclopentane
23	10.80	2.613	0.8624	2,3-Dimethylbutane
24	11.09	2.683	4.5346	2-Methylpentane
25	12.12	2.932	2.6143	3-Methylpentane
26	12.48	3.019	0.1253	Hexene-1
27	13.52	3.271	4.5171	*n*-Hexane
28	13.67	3.307	0.0075	Hexene-3
29	13.90	3.362	0.0888	Hexene-2, *trans*
30	14.11	3.413	0.0993	2-Methylpentene-2
31	14.40	3.483	0.0844	3-Methylpentene-2
32	14.58	3.527	0.0140	4-Methylcyclopentene-1
33	14.74	3.566	0.0566	Cyclohexene-2
34	15.33	3.708	0.0998	3,3-Dimethylpentene-1
35	15.77	3.815	0.1175	2,2-Dimethylpentane
36	15.98	3.866	1.9575	Methylcyclopentane
37	16.17	3.912	0.0017	Unknown
38	16.39	2.965	0.4215	2,4-Dimethylpentane
39	16.93	4.095	0.0302	2,2,3-Trimethylbutane
40	17.74	4.291	0.0067	Unknown
41	18.12	4.383	0.0125	Unknown
42	18.48	4.470	1.0322	Benzene
43	18.77	4.541	0.0017	Unknown
44	19.11	4.623	0.1074	3,3-Dimethylpentane
45	19.51	4.720	1.1368	Cyclohexane
46	19.75	4.778	0.0097	Unknown
47	20.15	4.874	0.0137	Unknown
48	20.45	4.947	0.0343	Unknown
49	20.65	4.995	1.4532	2-Methylhexane

TABLE II *(continued)*

Peak No.	*Retention time (min)*	*RRT*	*Peak area (%)*	*Compound*
50	20.84	5.041	0.7023	2,3-Dimethylpentane
51	21.14	5.114	0.1591	1,1-Dimethylcyclopentane
52	21.39	5.174	0.0117	Unknown
53	21.74	5.252	1.5467	3-Methylhexane
54	22.13	5.353	0.0161	Unknown
55	22.49	5.440	0.3619	1(*cis*),3-Dimethylcyclopentane
56	22.85	5.527	0.3356	1(*trans*),3-Dimethylcyclopentane
57	23.01	5.566	0.1313	3-Ethylpentane
58	23.20	5.612	0.4681	1(*trans*),2-Dimethylcyclopentane
59	23.44	5.670	0.5744	2,2,4-Trimethylpentane
60	24.16	5.844	0.0292	Unknown
61	24.66	5.965	0.0837	Unknown
62	24.94	6.033	2.0107	*n*-Heptane
63	25.18	6.091	0.0363	Unknown
64	25.58	6.188	0.0433	Unknown
65	25.79	6.239	0.0164	Unknown
66	26.24	6.347	0.0716	Unknown
67	26.73	6.466	0.0450	Unknown
68	27.72	6.705	1.6595	Methylcyclohexane
69	28.17	6.814	0.1641	1,1,3-Trimethylcyclopentane + 2,2-dimethylhexane*
70	28.67	6.933	0.0100	Unknown
71	28.99	7.013	0.0083	Unknown
72	29.42	7.117	0.1724	Ethylcyclopentane
73	29.66	7.175	0.2121	2.5-Dimethylhexane
74	29.95	7.245	0.3072	2,4-Dimethylhexane
75	30.80	7.451	0.1506	1(*trans*),2(*cis*),4-Trimethylcyclopentane
76	31.02	7.504	0.0562	3,3-Dimethylhexane
77	31.94	7.726	0.1597	1(*trans*),2(*cis*),3-Trimethylcyclopentane
78	32.42	7.842	0.2822	2,3,4-Trimethylpentane
79	32.70	7.910	0.0024	Unknown
80	33.20	8.031	20.0394	Toluene
81	33.74	8.162	0.0076	Unknown
82	34.26	8.287	0.3166	2,3-Dimethylhexane + 1,1,2-trimethylcyclopentane**
83	34.82	8.423	0.0132	Unknown
84	35.34	8.549	0.6915	2-Methylheptane
85	35.60	8.612	0.2468	4-Methylheptane
86	35.86	8.675	0.0779	3,4-Dimethylhexane
87	36.34	8.791	0.0532	Unknown
88	36.73	8.885	0.6131	3-Methylheptane
89	36.97	8.943	0.4540	1(*cis*),2(*trans*),3-Trimethylcyclopentane
90	37.35	0.035	0.1431	1(*trans*),4-Dimethylcyclohexane
91	37.67	9.112	0.0037	Unknown
92	38.41	9.291	0.0439	1,1-Dimethylcyclohexane
93	38.90	9.410	0.1222	2,2,5-Trimethylhexane
94	39.15	9.470	0.0878	1-Methyl-3(*cis*)-ethylcyclopentane
95	39.61	9.582	0.0799	1-Methyl-3(*trans*)-ethylcyclopentane
96	39.87	9.645	0.0921	1-Methyl-2(*trans*)-ethylcyclopentane
97	40.30	9.749	0.0240	2,2,4-Trimethylhexane

(Continued on p. 406)

TABLE II *(continued)*

Peak No.	*Retention time (min)*	*RRT*	*Peak area (%)*	*Compound*
98	40.91	9.896	0.1685	1(*trans*),2-Dimethylcyclohexane
99	41.67	10.080	0.0524	Unknown
100	42.34	10.242	1.0119	*n*-Octane
101	43.13	10.433	0.0263	Unknown
102	43.58	10.542	0.0240	Unknown
103	43.98	10.639	0.0491	Isopropylcyclopentane
104	45.10	10.910	0.0184	Unknown
105	45.77	11.072	0.0141	2,3,5-Trimethylhexane
106	46.31	11.024	0.0287	2,2,3,4-Tetramethylpentane
107	46.74	11.306	0.0298	2,2,4-Trimethylhexane
108	47.25	11.548	0.0056	2,2-Dimethylheptane
109	47.74	11.548	0.0056	2,2-Dimethylheptane
110	48.35	11.696	0.1164	2,2,3-Trimethylhexane
111	49.70	12.022	0.2445	*n*-Propylcyclopentane
112	50.21	12.146	0.1194	2,4-Dimethylheptane
113	50.73	12.272	0.0159	Unknown
114	51.29	12.407	0.1095	Ethylcyclohexane
115	52.08	12.598	0.2306	2,6-Dimethylheptane
116	53.16	12.859	0.0290	Unknown
117	53.62	12.971	0.0210	Unknown
118	54.80	13.256	1.2591	Ethylbenzene
119	55.49	13.423	0.0453	Unknown
120	55.92	13.527	0.0081	Unknown
121	56.48	13.663	0.0177	Unknown
122	57.08	13.808	2.7960	*p*-Xylene
123	57.24	13.846	0.1196	*m*-Xylene
124	58.17	14.071	0.0637	Unknown
125	58.68	14.195	0.0487	Unknown
126	59.39	14.366	0.1900	4-Methyloctane
127	59.64	14.427	0.2494	2-Methyloctane
128	60.12	14.543	0.0195	Unknown
129	60.78	14.703	0.0762	3-Ethylheptane
130	61.08	14.775	0.3107	3-Methyloctane
131	62.01	15.000	1.1369	*o*-Xylene
132	62.79	15.189	0.0185	Unknown
133	63.46	15.351	0.1516	Unknown
134	63.92	15.462	0.0927	Unknown
135	64.42	15.583	0.0314	Unknown
136	64.72	15.656	0.0243	Unknown
137	65.36	15.811	0.0293	Unknown
138	65.71	15.895	0.0303	Unknown
139	66.01	15.968	0.0198	Unknown
140	66.56	16.101	0.5833	*n*-Nonane
141	66.98	16.202	0.0766	Unknown
142	67.45	16.316	0.0213	Unknown
143	68.21	16.500	0.0956	Isopropylbenzene
144	68.72	16.623	0.0783	Unknown
145	69.09	16.713	0.0269	Unknown
146	69.42	16.793	0.0409	Unknown
147	69.76	16.875	0.0702	Unknown

TABLE II *(continued)*

Peak No.	*Retention time (min)*	*RRT*	*Peak area (%)*	*Compound*
148	70.08	16.952	0.0185	Unknown
149	70.83	17.134	0.1809	Unknown
150	71.47	17.289	0.0913	Unknown
151	72.20	17.465	0.1413	Unknown
152	72.81	17.613	0.3641	*n*-Propylbenzene
153	73.24	17.717	0.0637	Unknown
154	73.63	17.811	0.0176	Unknown
155	73.95	17.889	0.9476	1-Methyl-3-ethylbenzene
156	74.23	17.956	0.3945	1-Methyl-4-ethylbenzene
157	75.07	18.159	0.5618	1,3,5-Trimethylbenzene
158	75.83	18.343	0.0495	Unknown
159	76.07	18.401	0.1026	Unknown
160	76.34	18.467	0.4965	1-Methyl-2-ethylbenzene
161	76.86	18.592	0.0187	Unknown
162	77.29	18.696	0.1596	Unknown
163	77.60	18.771	0.0076	Unknown
164	77.93	18.851	0.0117	Unknown
165	78.39	18.963	1.5832	1,2,4-Trimethylbenzene
166	78.93	19.093	0.0408	Isobutylbenzene
167	79.19	19.156	0.0066	Unknown
168	79.45	19.219	0.0227	Unknown
169	79.81	19.306	0.0089	Unknown
170	80.35	19.437	0.0667	Unknown
171	80.69	19.519	0.0378	Unknown
172	80.88	19.565	0.3199	*n*-Decane
173	81.21	19.645	0.0180	Unknown
174	81.80	19.787	0.4121	1,2,3-Trimethylbenzene
175	82.36	19.923	0.0196	Unknown
176	82.83	20.037	0.0237	Unknown
177	83.12	20.107	0.1853	1-Methyl-2-isopropylbenzene
178	83.44	20.184	0.0390	Unknown
179	83.78	20.266	0.0716	Unknown
180	84.43	20.424	0.0834	Unknown
181	85.12	20.591	0.1645	1,3-Diethylbenzene
182	85.43	20.666	0.2944	Unknown
183	85.86	20.770	0.2272	Unknown
184	86.18	20.847	0.2703	1,4-Diethylbenzene + 1-methyl-3-*n*-propylbenzene
185	86.44	20.910	0.0125	Unknown
186	86.65	20.961	0.0050	*n*-Butylbenzene
187	86.94	21.031	0.0275	1,2-Diethylbenzene
188	87.13	21.877	0.1033	1-Methyl-2-*n*-propylbenzene
189	87.53	21.174	0.0668	Unknown
190	87.85	21.251	0.0507	1,3-Dimethyl-5-ethylbenzene
191	88.24	21.345	0.2318	1,4-Dimethyl-2-ethylbenzene
192	88.45	21.396	0.2111	Unknown
193	88.90	21.505	0.0470	1-Methyl-3-*tert.*-butylbenzene
194	89.07	21.546	0.3766	1,3-Dimethyl-4-ethylbenzene
195	89.47	21.643	0.0054	Unknown
196	89.72	21.703	0.0412	1,3-Dimethyl-2-ethylbenzene

(Continued on p. 408)

TABLE II *(continued)*

Peak No.	*Retention time (min)*	*RRT*	*Peak area (%)*	*Compound*
197	90.40	21.868	0.0115	Unknown
198	90.84	21.974	0.0855	Unknown
199	91.17	22.054	0.1026	Unknown
200	91.80	22.206	0.1794	*n*-Undecane
201	92.20	22.303	0.0049	Unknown
202	92.42	22.356	0.1512	1,2,4,5-Tetramethylbenzene
203	92.77	22.441	0.2159	1,2,3,5-Tetramethylbenzene
204	93.02	22.502	0.0083	Unknown
205	93.40	22.593	0.0108	Unknown
206	93.60	22.642	0.0236	Unknown
207	94.45	22.848	0.1982	Unknown
208	94.63	22.891	0.0041	Unknown
209	94.81	22.935	0.0487	Unknown
210	95.10	23.005	0.0662	Unknown
211	95.23	23.036	0.0429	Unknown
212	95.43	23.085	0.1582	Unknown
213	95.82	23.179	0.1411	Unknown
214	96.37	23.312	0.0739	Unknown
215	96.68	23.387	0.0742	Unknown
216	97.09	23.486	0.0588	Unknown
217	97.24	23.522	0.0729	Unknown
218	97.50	23.585	0.0265	Unknown
219	97.88	23.677	0.0927	Unknown
220	98.40	23.803	0.2686	Unknown
221	98.67	23.868	0.0147	Unknown
222	99.06	23.963	0.0807	Unknown
223	99.23	24.004	0.0441	Unknown
224	99.56	24.084	0.0469	Unknown
225	100.01	24.192	0.1055	Unknown
226	100.18	24.234	0.0546	Unknown
227	100.44	24.296	0.0059	Unknown
228	100.99	24.429	0.1313	Unknown
229	101.57	24.570	0.0105	Unknown
230	101.87	24.642	0.0226	Unknown
231	102.41	24.773	0.0550	Unknown
232	103.00	24.916	0.0288	Unknown
233	103.19	24.962	0.0509	Unknown
234	103.63	25.068	0.0210	Unknown
235	103.97	25.150	0.0250	Unknown
236	104.59	25.300	0.0790	*n*-Dodecane
237	105.01	25.402	0.0024	Unknown
238	105.51	25.523	0.0292	Unknown
239	105.75	25.581	0.0472	Unknown
240	106.07	25.658	0.0219	Unknown
241	106.44	25.748	0.0224	Unknown
242	106.73	25.818	0.0210	Unknown
243	107.01	25.886	0.0223	Unknown
244	107.33	25.963	0.0507	Unknown
245	107.77	26.070	0.0140	Unknown
246	108.20	26.174	0.2356	Unknown

TABLE II *(continued)*

Peak No.	*Retention time (min)*	*RRT*	*Peak area (%)*	*Compound*
247	108.55	26.258	0.0058	Unknown
248	109.29	26.437	0.0701	*n*-Tridecane
249	109.53	26.495	0.1012	Unknown
250	110.45	26.718	0.0250	Unknown
251	110.91	26.829	0.0195	Unknown
252	111.19	26.897	0.0138	Unknown
253	111.90	27.069	0.0214	Unknown
254	112.50	27.214	0.0233	Unknown
255	112.83	27.294	0.0170	Unknown
256	113.36	27.422	0.0266	Unknown
257	113.99	27.574	0.0173	Unknown
258	114.39	27.671	0.0073	Unknown
259	114.67	27.739	0.0149	Unknown
260	114.97	27.811	0.0150	Unknown
261	115.71	27.990	0.0217	Unknown
262	116.35	28.145	0.0331	Unknown
263	116.94	28.288	0.0076	Unknown
264	117.42	28.404	0.0541	*n*-Tetradecane
265	117.98	28.539	0.0035	Unknown
266	118.76	28.728	0.0276	Unknown
267	119.11	28.813	0.0121	Unknown
268	119.62	28.936	0.0004	Unknown

* In the quantitative evaluation, taken as naphthene.
** In the quantitative evaluation, taken as paraffin.

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              PETROLEUM PONA ANALYSIS
      SIGMA BASIC - GAS CHROMATOGRAPHIC SYSTEM
      55M OV-101(4X) GLASS OPEN TUBULAR COLUMN

              BRAND X LEADED REGULAR
      ----------------------------------------


       THE TOTAL PARAFFIN WT % =  49.5403

       THE TOTAL NAPHTHENE WT % =  8.7393

       THE TOTAL AROMATICS WT % =  33.1497

       THE TOTAL OLEFINS WT % =  1.7235

       THE TOTAL UNKNOWN AREA % =  6.8650

END OF PONA REPORT:  BRAND X LEADED REGULAR
                     RUN DATE:  5 / 27 / 81   @ 6 : 16.7
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Fig. 3. Simplified PONA analysis report.

TABLE III

SOME OF THE MORE PROMINENT COMPONENTS OF THE GASOLINE SAMPLE ANALYZED IN FIG. 2

Cycloolefins are considered as olefins in the evaluation.

Group	*Peak No.*	*Compound*	*Weight-%*	*Normalized % of the group*
Paraffins	6	*n*-Butane	3.56	7.19
	11	2-Methylbutane	10.65	21.50
	14	*n*-Pentane	8.32	16.79
	23	2,3-Dimethylbutane	0.86	1.74
	24	2-Methylpentane	4.54	9.16
	25	3-Methylpentane	2.62	5.29
	27	*n*-Hexane	4.52	9.12
	49	2-Methylhexane	1.45	2.93
	50	2,3-Dimethylpentane	0.70	1.41
	53	3-Methylhexane	1.55	3.13
	59	2,2,4-Trimethylpentane	0.57	1.15
	62	*n*-Heptane	2.01	4.06
	84	2-Methylheptane	0.69	1.39
	88	3-Methylheptane	0.61	1.23
	100	*n*-Octane	1.01	2.04
	140	*n*-Nonane	0.58	1.17
		16 compounds having a concentration of 0.50% or more each	44.24	89.30
		Rest (36 compounds), each less than 0.50% in the sample	5.30	10.70
		Total paraffins (52 compounds)	49.54	100.00
Olefins	13	2-Methylbutene-1	0.14	8.14
	15	Pentene-2, *trans*	0.19	11.04
	16	Pentene-2, *cis*	0.14	8.14
	17	2-Methylbutene-2	0.28	16.28
	26	Hexene-1	0.13	7.56
		5 compounds having a concentration of 0.10% or more each	0.88	51.16
		Rest (15 compounds), each less than 0.10% in the sample	0.84	48.84
		Total olefins (20 compounds)	1.72	100.00
Naphthenes	22	Cyclopentane	0.51	5.83
	36	Methylcyclopentane	1.96	22.43
	45	Cyclohexane	1.14	13.04
	55	1(*cis*),3-Dimethylcyclopentane	0.36	4.12
	56	1(*trans*),3-Dimethylcyclopentane	0.33	3.78
	58	1(*trans*),2-Dimethylcyclopentane	0.47	5.38
	68	Methylcyclohexane	1.66	18.99
	89	1,2,3-Trimethylcyclopentane	0.45	5.15
		8 compounds having a concentration of 0.30% or more each	6.88	78.72

TABLE III *(continued)*

Group	*Peak No.*	*Compound*	*Weight-%*	*Normalized % of the group*
		Rest (15 compounds), each less than 0.30% in the sample	1.86	21.28
		Total naphthenes (23 compounds)	8.74	100.00
Aromatics	42	Benzene	1.03	3.11
	80	Toluene	20.04	60.45
	118	Ethylbenzene	1.26	3.80
	122	*p*-Xylene	2.79	8.42
	131	*o*-Xylene	1.14	3.44
	155	1-Methyl-3-ethylbenzene	0.95	2.87
	157	1,3,5-Trimethylbenzene	0.56	1.69
	160	1-Methyl-2-ethylbenzene	0.50	1.51
	165	1,2,4-Trimethylbenzene	1.58	4.77
		9 compounds having a concentration of 0.50% or more each	29.85	90.06
		Rest (19 compounds), each less than 0.50% in the sample	3.30	9.94
		Total aromatics (28 compounds)	33.15	100.00
Unknowns	133		0.15	2.20
	149		0.18	2.64
	151		0.14	2.05
	159		0.10	1.46
	162		0.16	2.34
	182		0.29	4.25
	183		0.23	3.37
	192		0.21	3.08
	199		0.10	1.46
	207		0.20	2.93
	220		0.27	3.95
	225		0.11	1.61
	228		0.13	1.90
	246		0.24	3.51
	249		0.10	1.46
		15 compounds having a concentration of 0.10% or more each	2.61	38.21
		Rest (130 compounds), each less than 0.10% in the sample	4.25	61.79
		Total unknowns (145 compounds)	6.86	100.00

The primary advantage of a detailed GC analysis on a capillary column as a source of structural group data is that it permits the separate evaluation of the relative amount of naphthenes present. In addition, if a high-power data system is used, the data can be examined in a number of ways. Table II shows one way of data presentation, by listing individually the most prominent compounds and summing up the rest. Another possibility is to list all the individual compounds separately, according to their structural groups. It is also possible to further subdivide the data, *e.g.*, by

TABLE IV

ANALYSIS OF GASOLINE SAMPLES BY OPEN-TUBULAR COLUMN GAS CHROMATOGRAPHY

For analytical conditions see Table I. Cycloolefins are grouped as olefins.

Sample	*Weight-% (area-%)*				
	Paraffins	*Naphthenes*	*Olefins*	*Aromatics*	*Unknowns*
Leaded regular:					
Brand A	49.4	8.7	1.7	32.5	7.7
Brand B	49.1	8.6	4.1	25.7	12.5
Brand D	41.4	6.6	5.9	25.5	20.6
Unleaded regular:					
Brand A	43.7	5.6	6.8	29.6	14.3
Brand B	44.7	5.4	6.7	27.5	15.7
Brand C	38.5	4.4	4.6	43.0	9.5
Brand D	45.7	4.9	4.3	32.9	12.2
Unleaded premium:					
Brand A	32.1	4.1	4.7	44.3	14.8*
Brand B	38.1	4.3	3.9	42.0	11.7*
Brand C	46.4	5.3	3.0	36.8	8.5
Brand D	47.6	3.2	4.8	37.3	7.1

* Includes about 4% methyl *tert.*-butyl ether.

grouping the unknowns according to boiling point range (see below), converting the weight percent values to volume percents, calculating the specific gravity or provide any other type of data presentations as may be required.

Comparative measurements. Eleven samples of various gasolines were analyzed over a period of one week. The samples were obtained from four different manufacturers (listed as Brands A, B, C and D) and consisted of leaded regular, unleaded regular and unleaded premium grades. Table IV summarizes the PONA-type analytical results.

Two of the unleaded premium grades (Brands A and B) appeared to have unusually high concentrations of cyclopentane. Upon further investigation it was found that this is due to the presence of methyl *tert.*-butyl ether (MTBE) which elutes with cyclopentane under the conditions which we employed. The concentration of MTBE was estimated at 4% in both cases by separate analysis. The PONA data were corrected for this by subtracting that amount from the naphthene content and adding it to the unknown content. If necessary, MTBE can be separated from cyclopentane with this column, by lowering the initial temperature to 25°C or less.

It is well known that in general, higher aromatics content provides a higher performance for a gasoline. Therefore one may want to investigate the relative abundance of aromatics present. This is illustrated in Table V giving both the absolute values and normalized data. In this table, the individual aromatics are grouped according to carbon number thus presenting a condensed picture of the individual compounds present. With the proper software, laboratory data systems can combine the individual values in such a way providing such data presentation.

The shortcoming of any analysis based on the identification of the individual

TABLE V

AROMATICS CONTENT OF THE GASOLINES INVESTIGATED

	Regular							*Premium*			
	Leaded			*Unleaded*				*Unleaded*			
	A	*B*	*D*	*A*	*B*	*C*	*D*	*A*	*B*	*C*	*D*
	Weight-% (area-%)										
Benzene	1.03	1.72	0.98	1.82	1.83	1.35	1.82	1.04	1.25	1.28	0.93
Toluene	20.04	6.04	4.11	7.50	7.32	11.01	7.98	18.98	20.06	5.93	12.09
C_8 aromatics*	5.32	7.81	8.18	8.20	7.63	14.39	11.16	10.92	10.88	14.36	12.07
C_9 aromatics**	4.86	8.43	9.83	10.05	8.89	14.76	10.55	11.26	8.35	13.10	10.82
C_{10} aromatics***	1.26	1.74	2.42	1.99	1.82	1.46	1.42	2.13	1.42	2.10	1.37
Total aromatics	*32.51*	*25.74*	*25.52*	*29.56*	*27.49*	*42.57*	*32.93*	*44.33*	*41.96*	*36.77*	*37.28*
	Normalized peak area (%)										
Benzene	3.17	6.68	3.84	6.16	6.66	3.14	5.53	2.35	2.98	3.48	2.50
Toluene	61.64	23.47	16.11	25.37	26.63	25.62	24.23	42.82	47.81	16.13	32.43
C_8 aromatics*	16.36	30.34	32.05	27.74	27.75	33.49	33.89	24.63	25.93	39.05	32.38
C_9 aromatics**	14.95	32.75	38.52	34.00	32.34	34.35	32.04	25.40	19.90	35.63	29.02
C_{10} aromatics***	3.88	6.76	9.48	6.73	6.62	3.40	4.31	4.80	3.38	5.71	3.67
Total aromatics	*100.00*	*100.00*	*100.00*	*100.00*	*100.00*	*100.00*	*100.00*	*100.00*	*100.00*	*100.00*	*100.00*

* Ethylbenzene and the xylenes.

** Propyl, methylethyl and trimethylbenzenes.

*** Butyl, methylpropyl, diethyl, tetramethyl, dimethylethyl and higher benzenes.

TABLE VI

EVALUATION OF THE UNKNOWNS ACCORDING TO THEIR BOILING POINT RANGE

Boiling point data from ref. 47.

Unknowns	*Leaded regular gasoline*			
	Brand A		*Brand D*	
	Weight-%	*Normalized % of the group*	*Weight-%*	*Normalized % of the group*
Eluting before:				
n-heptane (b.p. 98.4°C)	0.22	2.87	0.51	2.48
n-octane (b.p. 125.7°C)	0.45	5.87	1.51	7.35
n-nonane (b.p. 150.8°C)	0.78	10.17	0.38	1.85
n-decane (b.p. 174.1°C)	1.33	17.34	1.74	8.47
n-undecane (b.p. 195.9°C)	1.93	25.16	4.61	22.43
Eluting after *n*-undecane	2.96	38.59	11.80	57.42
Total unknowns	7.67	100.00	20.55	100.00

peaks is that there will always be unknowns which cannot be included in the individual groups. Thus, additional information about these compounds is useful. For example, one may investigate them according to their boiling-point range. This is possible because on a methylsilicone liquid phase, the order of elution essentially corresponds to the boiling points; this fact is the basis of the so-called simulated distillation[22,23]. Again, laboratory data systems can subdivide the data according to this principle. Table VI compares the composition of the unknowns in two regular leaded gasolines, Brands A and D, which had the highest amount of unknowns. As seen, the major difference is in the heavier ends: Brand D has 11.8% boiling above 196°C while the corresponding amount in Brand A is only 2.96%.

Retention time reproducibility. In the analysis of such complex mixtures, with up to 270 peaks, and particularly when using a multistep temperature program, it is very important that the retention times, both absolute and relative, are reproduced

TABLE VII

RELATIVE STANDARD DEVIATION RANGE OF ABSOLUTE RETENTION TIMES IN FIVE TIME SEGMENTS

The values listed represent the smallest and largest relative standard deviation values of the individual compounds eluting within the time segment indicated, for the eleven gasoline analyses.

Time segment (min)	*Relative standard deviation (%)*
0–8	0.115–0.192
8–24	0.168–0.282
24–40	0.166–0.241
40–60	0.098–0.248
>60	0.056–0.145

TABLE VIII

REPRODUCIBILITY OF ABSOLUTE RETENTION TIMES OF SELECTED COMPOUNDS

Calculated for the eleven determinations summarized in Table IV; for analytical conditions see Table I.

*Peak No.**	*Compound*	*Average retention time (min)*	*Standard deviation (min)*	*Relative standard deviation (%)*	*95% confidence limit (min)*
6	*n*-Butane	4.878	0.0075	0.1537	4.861– 4.895
36	Methylcyclopentane	15.941	0.0302	0.1891	15.872– 16.010
74	2,4-Dimethylhexane	29.894	0.0497	0.1661	29.781– 30.007
80	Toluene	33.055	0.0762	0.2305	32.881– 33.229
118	Ethylbenzene	54.682	0.1150	0.2102	54.420– 54.944
131	*o*-Xylene	61.934	0.0897	0.1448	61.729– 62.139
140	*n*-Nonane	66.478	0.0721	0.1084	66.314 66.642
172	*n*-Decane	80.836	0.0578	0.0716	80.704– 80.968
200	*n*-Undecane	91.764	0.0518	0.0565	91.646 91.882
236	*n*-Dodecane	104.533	0.0717	0.0686	104.372–104.694

* See Table II.

accurately; otherwise, peak identification would be impossible. We have evaluated the results of the eleven analyses from this aspect, from the points of both the absolute and relative retention times.

Table VII and VIII present the statistical evaluation of the reproducibility of absolute retention times. Table VII gives the relative standard deviation range of the absolute retention times for five time segments within the chromatogram. The values listed represent the smallest and largest relative standard deviations within that range. Table VIII provides data for selected compounds giving the mean values of the

TABLE IX

REPRODUCIBILITY OF RELATIVE RETENTION TIMES OF SELECTED COMPOUNDS

Calculated for the eleven determinations summarized in Table IV; for analytical conditions see Table I. *o*-Xylene is used as the standard with an *RRT* value of 15.000.

*Peak No.**	*Compound*	*Average RRT*	*Standard deviation*	*Relative standard deviation (%)*	*95% confidence limit (RRT)*
6	*n*-Butane	1.181	0.00117	0.0989	1.178– 1.184
36	Methylcyclopentane	3.861	0.00397	0.1028	3.852– 3.840
74	2,4-Dimethylhexane	7.240	0.00308	0.0436	7.233– 7.247
80	Toluene	8.006	0.01538	0.1920	7.971– 8.041
118	Ethylbenzene	13.244	0.01049	0.0792	13.220–13.268
140	*n*-Nonane	16.101	0.00770	0.0478	16.083–16.118
172	*n*-Decane	19.578	0.01581	0.0807	19.542–19.609
200	*n*-Undecane	22.225	0.02100	0.0945	22.177–22.273
236	*n*-Dodecane	25.317	0.02760	0.1090	25.254–25.380

* See Table II.

retention times, the corresponding standard deviations and relative standard deviations and the 95% confidence limits*. As shown the reproducibility of the data is excellent.

As seen in Table VIII, the highest relative standard deviation was found for toluene. This is related to the fact that this compound is present in high concentration and its concentration varies widely (*cf.*, Table V). It is known that the maximum of a peak will shift in case of high concentrations of the corresponding compound and hence its retention time will also vary[48].

As already mentioned earlier, we have used the relative retention times for peak identification taking *o*-xylene as the standard with an *RRT* of 15.000. Table IX presents the evaluation of the reproducibility of the *RRT* values for the compounds listed in Table VIII. Again, the data demonstrate the high precision of the measurements.

CONCLUSIONS

The data shown here demonstrate that open-tubular column gas chromatography is an excellent way to analyze complex gasoline samples and similar petroleum products. With the help of modern sophisticated laboratory data systems the primary analytical results can be re-evaluated and presented in a number of ways, including a PONA-type report.

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* For eleven determinations (degrees of freedom: 10),

$$95\%\ C.L. = \bar{X} \pm 2.28(S.D.)$$

where *C.L.* refers to the confidence limits, $\bar{X}$ is the mean value of the determinations and *S.D.* is the standard deviation.

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