

CHROM. 4714

THE USE OF A GAS CHROMATOGRAPH-MASS SPECTROMETER FOR THE ANALYSIS OF COMPLEX HYDROCARBON MIXTURES

M. KURAŠ AND S. HÁLA

Laboratory of Synthetic Fuel and Petroleum, Institute of Chemical Technology, Prague (Czechoslovakia)

SUMMARY

In the present article several examples are given of the analysis of complex hydrocarbon mixtures by means of the combined gas chromatograph-mass spectrometer LKB-9000. Several methods, published in the literature or recommended as ASTM methods, were verified for group-type analysis on the mass spectrometric part of the apparatus. With fractions which can be divided into individual components by gas chromatography, the gas chromatograph-mass spectrometer enables the mass spectra of all the components to be determined without the necessity of isolating them from the mixture. The identification of seventeen individual hydrocarbons by one analysis of the fraction of aromatic hydrocarbons which have been isolated from a petroleum fraction boiling up to 200° was shown as an example. The high sensitivity of the LKB-9000 apparatus has also been utilized to obtain mass spectra of several hydrocarbons which have been unknown up to now and which have been prepared for this purpose in very low concentration by means of the methylene insertion reaction.

INTRODUCTION

The present development of the technology of petroleum processing makes demands upon the analytical control of processes which are well fulfilled by the modern methods of chromatography and spectrometry. The advantages of these methods consist in the minute sample amounts, relatively accurate results, elimination of subjective errors, and especially in a very short time of analysis.

While gas chromatographic methods are mainly applied to the analysis of substances in the light petroleum fractions at the present time mass spectrometry methods are chiefly used for group-type analyses which may be used equally for the light and heavy petroleum fractions. The direct linking of a mass spectrometer with a gas chromatograph (there has already been one on the market for several years) to give a single instrument represents one of the most perfect analytical possibilities, especially in the field of analysis of petroleum, petrochemical raw materials and products. This combination allows one to obtain mass spectra of all the components — and, hence, their identification in most cases — which the chromatographic column is able to separate, without their preliminary isolation from the mixture. With regard to the

possibility of using a capillary column with an order of resolving efficiency of about 100000 theoretical plates, the apparatus just mentioned surpasses all kinds of analysis of complicated fractions used until now.

In the present paper we are presenting several examples of analyses of petroleum fractions and products, carried out on a Swedish gas chromatograph-mass-spectrometer LKB 9000, installed in the Technical University, Institute of Chemical Technology in Prague. These examples are selected in such a way as to demonstrate, as completely as possible, the wide applicability of the said instrument for analysis of complicated hydrocarbon mixtures.

APPARATUS

The apparatus consists of the gas chromatography part and of the mass spectrometer which is a single-focus Nier type apparatus with a 20 cm ion trajectory radius. Helium is used as carrier gas. The eluent from the chromatographic column is introduced into a separator where helium is separated from the components of the analyzed mixture; the latter enter directly to the ion source where they are ionized by an electron current. The ions so created pass through a magnetic field where their trajectories are bent in agreement with their dependence upon the m/e of the ion; they then pass through an amplifier to a recording system. The mass spectra are recorded on an oscillograph for a few seconds which even permits the scanning of the spectra of components eluted close together from the chromatographic column.

Of all the analytical problems we have solved by using the instrument described above, the first to be mentioned should be the group-type analysis of petroleum fractions. The published methods of mass spectrometry whereby the amounts of individual structural types of hydrocarbons are determined by means of their mass spectrum, were sequentially verified, using only the mass spectrometer part of the LKB-9000 apparatus. For these analyses, the samples of the fractions were dosed directly into the reservoir of the mass spectrometer without using the chromatographic column. First of all, the applicability of coefficients and the calculation methods derived for other types of instruments, and stated in the literature, was established for their application to the LKB-9000. The reproducibility for individual fractions was determined and the exactness of the results of the group-type analysis was further verified.

GROUP-TYPE ANALYSIS OF HYDROCARBON MIXTURES

The group-type analysis of complex hydrocarbon mixtures may be carried out practically in two ways: the fragment-peak method and the low-voltage method.

The fragment-peak method

This method utilizes the stable fragments with a mass lower than that of the primary molecule, and is based mainly upon the fact that the spectra of each structural group include some dominant fragment-peaks characteristic for each group which are not present, or in little amounts, in other groups.

The mass spectra of a petrol obtained by thermal cracking, and containing mainly paraffins and olefins, and those of the concentrate of aromatic hydrocarbons isolated from a petroleum fraction, are compared in Fig. 1. In the first spectrum the

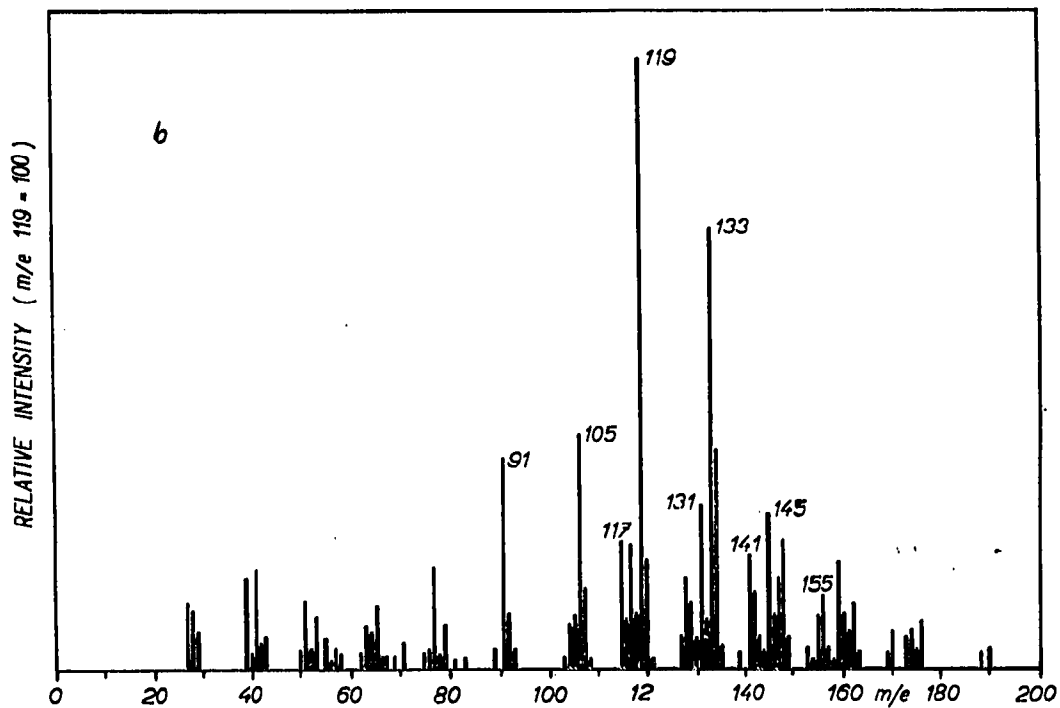
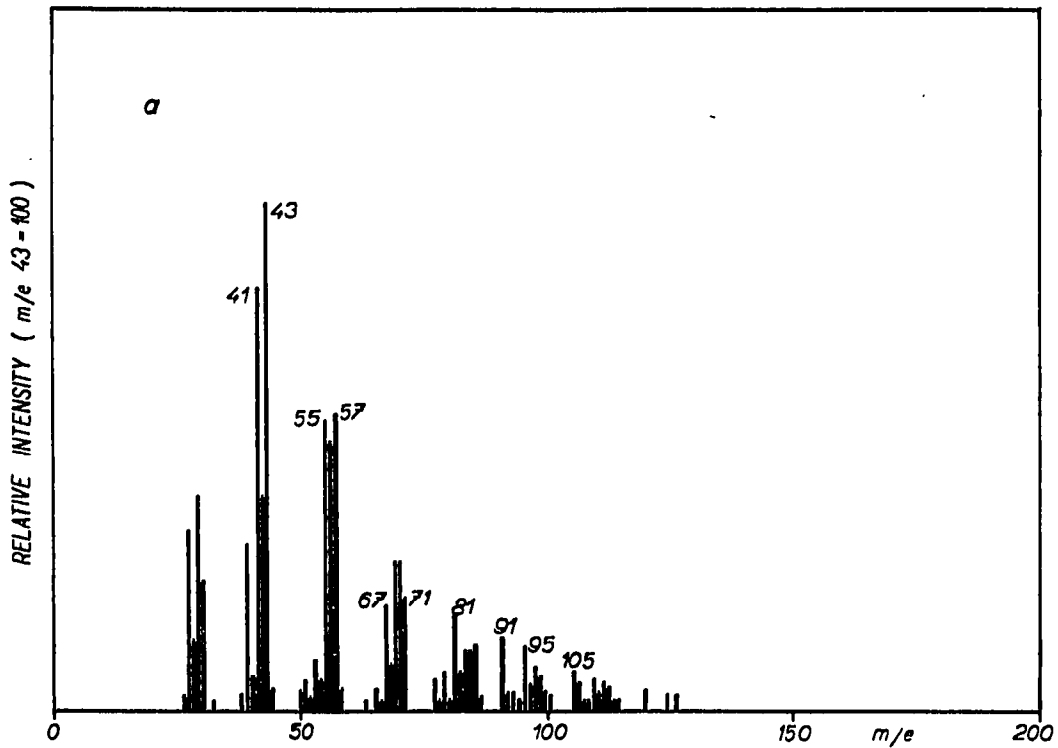


Fig. 1. Comparison of the mass spectra of petrol from thermal cracking (a) and aromatic concentrate (200–270°) from the kerosene fraction, obtained at 70 eV (b).

ions found at m/e 43, 57, 71, 85, belonging to the paraffins, the ions at m/e 41, 55, 69, 83, belonging to the monocycloparaffins and monoolefins, and the ions at m/e 67, 68, 81, 82, 95, 96, belonging to the dicycloparaffins, or diolefins, ultimately cycloolefins, are the dominant ones. In the spectrum of the aromatic hydrocarbon concentrate, the ions found at m/e 91, 105, 119, 133, belonging to the alkylbenzenes, the ions at m/e 117, 131, 145, 159, belonging to the indanes or tetralins ultimately, and the ions at m/e 128, 141, 155, 169, 183, belonging to the alkylnaphthalenes, are the most significant ones.

Each group of hydrocarbons in the mixture is then characterized by a summary of these dominant ions, and considered as a homogeneous component of the mixture, its content being calculated by solving a system of linear equations. It is necessary to know the calibration coefficients derived from the spectra of pure hydrocarbons for the purposes of calculation. These coefficients express the average values for isomers with a given molecular weight and depend upon the number of carbons in the molecule, and partly also upon the type of instrument used. Therefore, the application of this method requires a preliminary calibration of the apparatus to be used.

When using the usual mass spectrometers, possessing a resolution ability of about 1000, this method may be applied practically to any petroleum fraction, with the exception of the heavy residues. At the present time, we have already verified this method for the LKB-9000 instrument, for the fractions shown in Table I.

TABLE I

PETROLEUM FRACTIONS ANALYZED ON THE GAS CHROMATOGRAPH-MASS SPECTROMETER LKB-9000

<i>Fractions</i>	<i>Distillation limits</i>	<i>Number of hydrocarbon groups determined</i>
Petrol, low olefinic	95% distill. point 210°	7
Olefinic petrol	95% distill. point 210°	10
Kerosene	200-300°	8 + benzothiophenes
Middle distillates	200-350°	11
Heavy oils	average carbon number	8
(saturated hydrocarbons)	16-32	
Heavy aromatic concentrates	320-530°	9 + 3 thiophenic groups

TABLE II

COMPOSITION OF AN AROMATIC CONCENTRATE (200-270°) ISOLATED FROM THE KEROSENE FRACTION OF ROMASHKINO PETROLEUM

(Fragment-peak method¹ - 70 eV)

<i>Hydrocarbon group</i>	<i>Concentration in weight per cent</i>
Paraffins	0
Cycloparaffins non cond.	0.5
Cycloparaffins cond.	0.4
Alkylbenzenes	52.1
Indanes + tetralins	29.7
Alkylnaphthalenes	16.2
Acenaphthenes + diphenyls	1.1

When this method is used, the following hydrocarbon groups of light and middle petroleum fractions may be determined: paraffins; monocycloparaffins; dicycloparaffins; tricycloparaffins; alkylbenzenes; indanes + tetralins; indenenes; alkylnaphthalenes; monoolefins; diolefins + cycloolefins + acetylenes; triolefins + cyclodiolefins; acenaphthenes + diphenyls; acenaphthylenes + fluorenes; triaromatic hydrocarbons.

As for the heavy petroleum distillates (oil fractions, high-boiling aromatic concentrates), in addition to some of the above groups, it is possible to determine other groups as well as follows: tetracycloparaffins; pentacycloparaffins; hexacycloparaffins; dinaphthenebenzenes; pyrenes; chrysenes; benzothiophenes; dibenzothiophenes; naphthobenzothiophenes.

As an example, the result of an analysis of an aromatic concentrate (boiling within the range of 200–270°) isolated from the kerosene fraction of Romashkino petroleum is shown in Table II.

The low-voltage method

This method is associated with the parent peaks obtained at a low energy of ionizing electrons. The method is used for analyses of mixtures containing hydrocarbon groups with characteristic parent ions (aromatics, olefins). Due to the absence of fragment ions, the spectrum is not so complicated, and for the computation of the composition itself, the system of linear equations is not used, which simplifies the calculation, especially in the case of narrow fractions. The simplification of the spectrum is apparent in Fig. 2, where the spectra of the liquid part obtained by petrol pyrolysis³, and taken at 70 eV and 10 eV, are compared.

For application of this method, it is necessary to find out the coefficient of proportionality between the spectral image representing the parent ions and the concentration of each component in the analyzed mixture (so-called coefficients of sensitivity of the parent ions).

With respect to some hydrocarbon structures yielding parent ions with equal nominal values of m/e , and overlapping in the spectra, group-type analysis on the basis of parent peaks is limited to only seven hydrocarbon groups. The parent ions of the hydrocarbon type C_nH_{2n+z} have the same nominal value of m/e as the parent ions of the type $C_{n+1}H_{2(n+1)+(z-14)}$ — for example, indanes and pyrenes, or indenenes and chrysenes. The differentiation of such couples is, therefore, possible only after an accurate determination of the m/e by a high resolution mass spectrometer.

The low-voltage method provides more data than the fragment-peak method, because it even permits the determination of the spectrum representing the individual components in their groups, in accordance with their molecular weights, in addition to the composition of each hydrocarbon group. The results of an analysis of the same aromatic concentrate obtained by the low-voltage method, are shown in Table III, as a comparison with the results shown in Table II.

The coefficients used for the calculation of the compositions of the fractions in both the fragment-peak and low-voltage method, depend upon a number of factors, and even upon the type of apparatus used. As we have not found in the accessible literature any statements about using the gas chromatograph-mass spectrometer LKB-9000 for group-type analysis of petroleum fractions and similar hydrocarbon mixtures, we have verified the feasibility of using the LKB-9000 for these analyses by various means, using the coefficients obtained with other instruments.

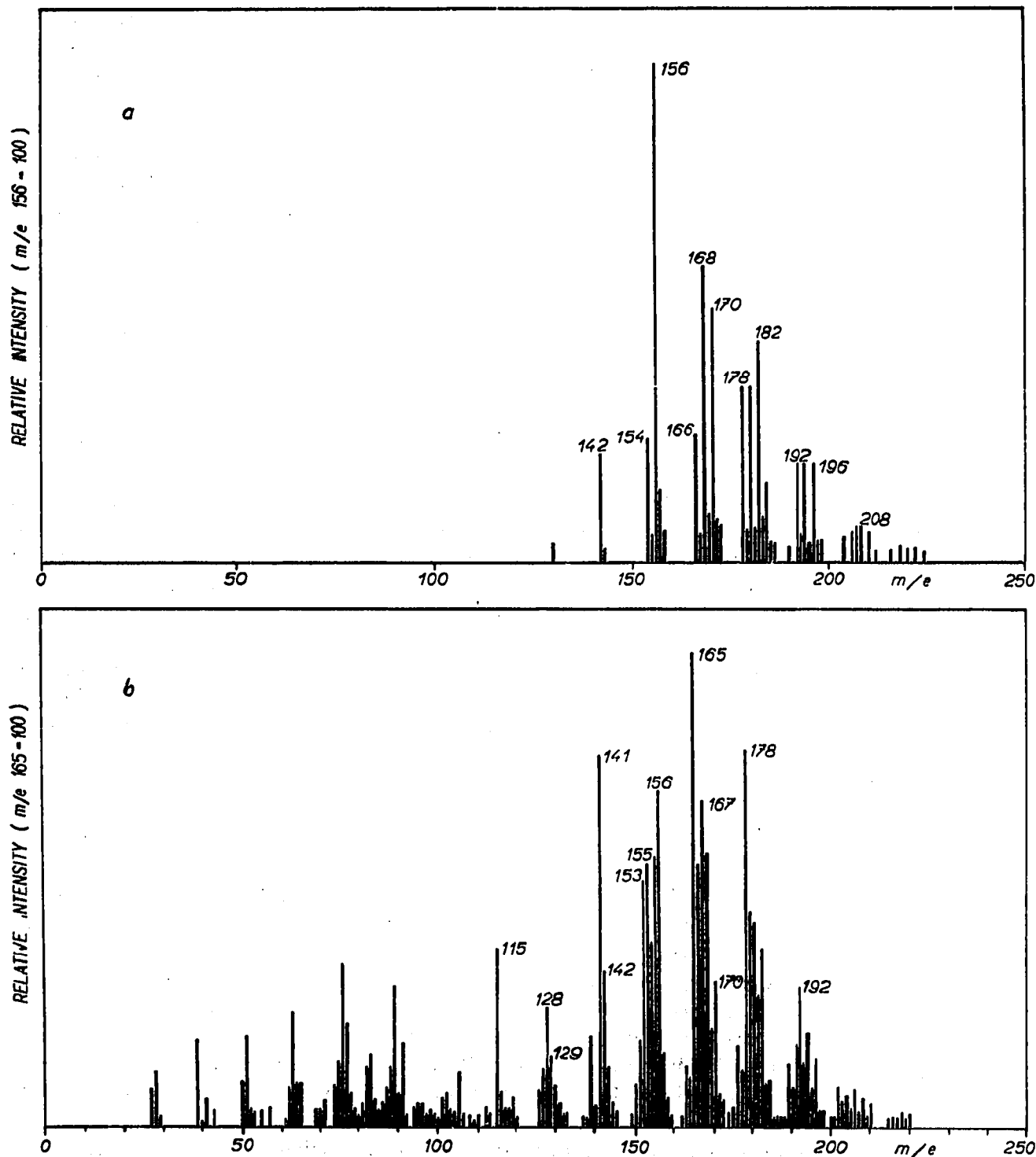


Fig. 2. Comparison of mass spectra of pyrolysis oil (250–350°) obtained at 10 eV (a) and 70 eV (b). (a) Parent ions of the dominant components (m/e): 142 = methylnaphthalenes; 154 = acenaphthene + diphenyl; 156 = alkylnaphthalenes C_{12} ; 166 = fluorene + methylacenaphthylene; 168 = methylacenaphthenes + methyldiphenyls; 170 = alkylnaphthalenes C_{13} ; 178 = anthracene + phenanthrene; 182 = alkylacenaphthenes + alkyldiphenyls C_{14} ; 192 = methylanthracenes + methylphenanthrenes; 196 = alkylacenaphthenes + alkyldiphenyls C_{16} ; 208 = alkylfluorenes + alkylacenaphthylenes C_{16} . (b) Characteristic ions for hydrocarbon groups (m/e): 91, 105, 119, 133 etc. = alkybenzenes; 103, 117, 131 etc. = indanes + tetralins; 115, 129, 143 etc. = indenenes + dihydronaphthalenes; 128 = naphthalene; 141, 142, 155, 156 etc. = alkylnaphthalenes; 153, 154, 167, 168 etc. = acenaphthenes + diphenyls; 151, 152, 165, 166 etc. = fluorenes + acenaphthylenes; 177, 178, 191, 192 etc. = anthracenes + phenanthrenes.

TABLE III

COMPOSITION OF AROMATIC CONCENTRATE (200–270°) ISOLATED FROM THE KEROSENE FRACTION OF ROMASHKINO PETROLEUM
(Low-voltage method² — 10 eV)

Number of carbons	Concentration in weight per cent				
	Alkylbenzenes	Indanes + tetralins	Indenes + dihydro-naphthalenes	Alkyl-naphthalenes	Acenaphthenes + diphenyls
10	17.1	3.3	0.5	1.7	
11	13.7	7.0	0.4	4.4	
12	7.8	8.1	0.4	6.3	0.2
13	7.0	6.4	0.4	3.5	0.4
14	3.8	3.1	0.5	0.8	0.1
15	1.3	1.2	0.3	0.3	0
Total	50.7	29.1	2.5	17.0	0.7

TABLE IV

BLEND OF KEROSENE FRACTION AND AROMATIC CONCENTRATE

Hydrocarbon group	Concentration in weight per cent			
	Kerosene	Aromatic concentrate	Blend of both	
			Calculated	Measured
Paraffins	52.2	0	39.3	40.8
Cycloparaffins non cond.	23.1	0.5	17.4	16.4
Cycloparaffins cond.	9.9	0.4	7.4	7.8
Alkylbenzenes	11.3	52.1	21.5	21.5
Indanes + tetralins	3.4	29.7	9.7	9.6
Alkyl-naphthalenes	0.1	16.2	4.0	3.6
Acenaphthenes + diphenyls	0	1.1	0.7	0.3

The repeatability of the results and the reproducibility of the measurements on the same sample upon two different instruments was established. The repeatability of four measurements on a petrol sample, independent of the time, was good, the average difference being not higher than 3 %, relatively. The reproducibility of the results for samples measured independently on two different apparatus, *e.g.* the LKB-9000 and the AEI type MS-2 at the Institut Français du Pétrole*, was also satisfactory, the differences of single measurements being not higher than 5 % rel.

The method was also tested for the correct indication of changes in the composition of the fraction analyzed caused by the addition of a defined amount of another fraction which had previously been analyzed by the same method. In some cases, the results obtained by mass spectrometry were also compared with those of the gas chromatographic analysis. The results are shown in Tables IV and V.

* This measurement was made by the courtesy of Dr. BUZON.

The good results of the check tests enable us to use almost solely these mass spectrometric methods instead of the previously used methods of group-type and type analyses. For most of them we have already worked out a program for the

TABLE V

CONTENT OF SOME AROMATIC HYDROCARBONS IN PYROLYSIS OIL DETERMINED BY GAS CHROMATOGRAPHY AND MASS SPECTROMETRY (LOW VOLTAGE)

<i>Hydrocarbons</i>	<i>Concentration in weight per cent determined by</i>	
	<i>Gas chromatography CHROM II</i>	<i>Mass spectrometry LKB-9000</i>
Methylindenes	5.5	5.8
Naphthalene	24.4	22.8
Methylnaphthalenes	21.2	22.7
Acenaphthene + diphenyl	3.1	2.9
Fluorene	1.5	2.3
Anthracene + phenanthrene	2.0	1.7

required calculations on an automatic computer, so that the time needed for carrying out an analysis of a certain fraction is very much shorter compared with the previous methods. In addition, this method provides substantially more reliable information.

IDENTIFICATION OF INDIVIDUAL HYDROCARBONS IN MIXTURES

A further example of the usefulness of the gas chromatograph-mass spectrometer LKB-9000 is the identification of the main components in a fraction of aromatic hydrocarbons, boiling within the range of 135–200°, which was isolated from a kerosene fraction of the Romashkino petroleum by means of silica gel chromatography and reported earlier⁴. At that time, we had analyzed the aromatic fraction by gas chromatography only. In order to identify the main components, it was necessary to determine and compare the retention times of eighteen synthetic standard aromatic hydrocarbons in the range from C₈ to C₁₀, including all kinds of aromatics with a boiling point from 136 to 173°. When Apiezon L was used, some of the hydrocarbons had the same retention times, and in order to differentiate between them it was necessary to determine the retention times of the standards once again on a second column having a polar stationary phase (Bentone-34). Only after comparing the retention times of the main components of the fractions analyzed with those of standards on two stationary phases, was it possible to identify most of the components. However, we did not succeed in identifying some components with a higher boiling point (above 173°), as we did not possess all the standards needed in this range.

This time, during the testing of the gas chromatograph-mass spectrometer LKB-9000 apparatus, for the control and supplementation, we repeated the analysis of this fraction with a combined apparatus for gas chromatography and mass spectrometry. The chromatogram of the fraction analyzed, boiling within the range of 135–

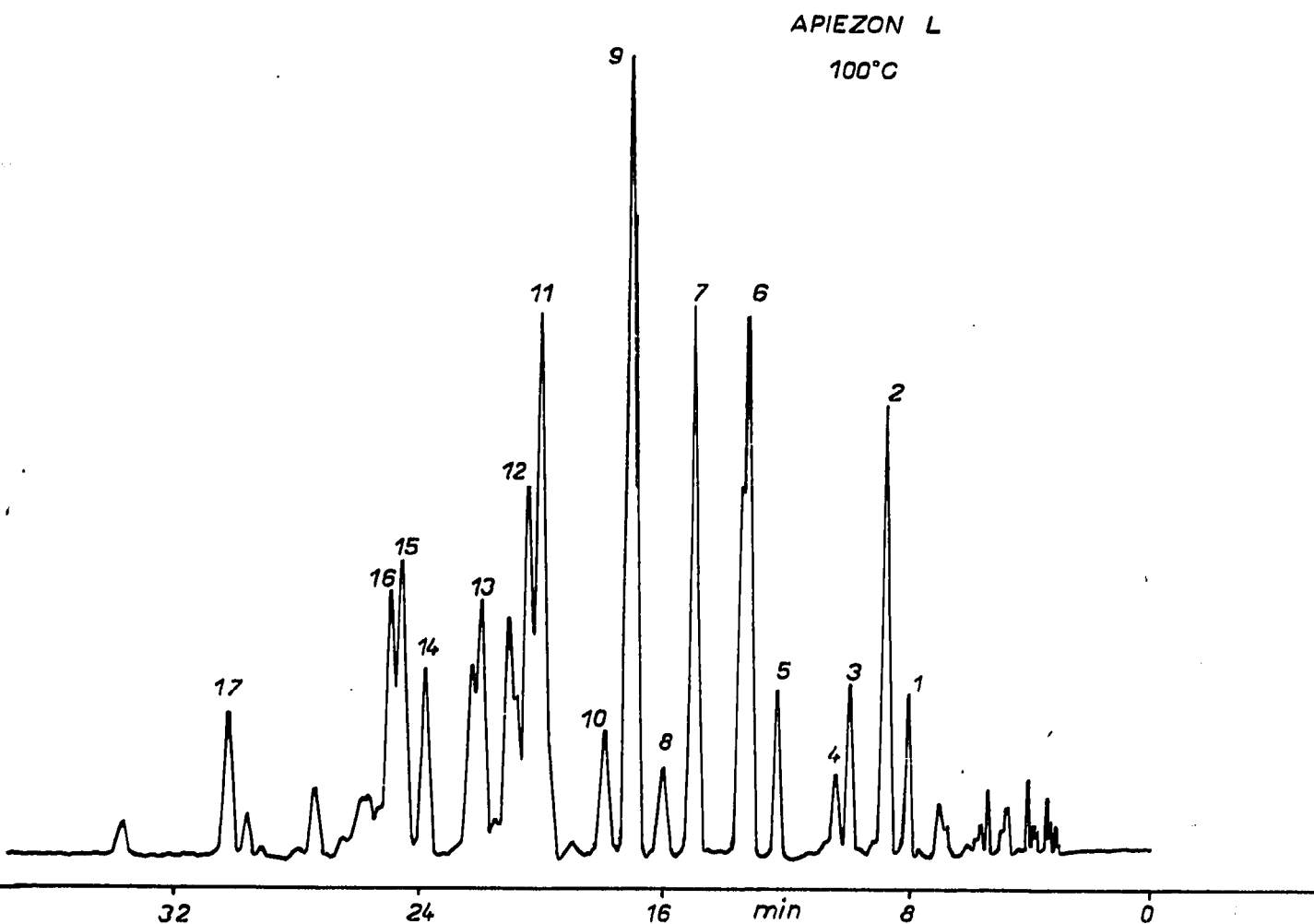


Fig. 3. Chromatogram of an aromatic concentrate (135–200°) isolated from the kerosene fraction of Romashkino petroleum.

200°, is shown in Fig. 3. The numbers 1–17 designate the main chromatographic peaks for which the mass spectra were measured in the same order as they left the chromatographic column. In this case, the identification was reduced to a comparison of seventeen mass spectra with the Spectrum Catalogue⁵. The results of the previous identification of the main components obtained by means of gas chromatography only are compared with those of their mass spectra provided by the LKB-9000 apparatus measurements, and are shown in Table VI. As may be seen, the basic structures of the components determined in accordance with the retention times and with the mass spectra, do agree in all cases. Mass spectrometry does not always differentiate exactly the isomers of aromatic hydrocarbons, for example xylenes, ethyltoluenes, trimethylbenzenes. On the other hand, it supplies more data about the higher boiling components when their identification by means of standards was not possible.

If several components elute in one chromatographic peak, the possibility of their identification by mass spectrometry is strictly limited. Peak 7, for example, apart from 1,3,5-trimethylbenzene contains about 20 % of *o*-ethyltoluene. This substance was incompletely identified by mass spectrometry as trimethylbenzene. In peak 9 three hydrocarbons (1,2,4-trimethylbenzene, isobutylbenzene and *sec.*-butylbenzene) were eluted simultaneously. In this case, where the components differ in molecular weight, it was possible by means of mass spectrometry to distinguish the presence of butylbenzene with a molecular weight of 134 apart from the trimethylbenzene.

TABLE VI

HYDROCARBONS DETERMINED IN AN AROMATIC CONCENTRATE (135–200°) FROM THE KEROSENE FRACTION OF ROMASHKINO PETROLEUM

Peak No.	Gas chromatograph internal standards CHROM I	Gas chromatograph-mass spectrometer LKB-9000
1	Ethylbenzene	Ethylbenzene
2	<i>p</i> -Xylene	Dimethylbenzene
	<i>m</i> -Xylene	
3	<i>o</i> -Xylene	Dimethylbenzene
4	Isopropylbenzene	Isopropylbenzene
5	<i>n</i> -Propylbenzene	<i>n</i> -Propylbenzene
6	<i>m</i> -Ethyltoluene	Methylethylbenzene
	<i>p</i> -Ethyltoluene	
7	1,3,5-Trimethylbenzene	Trimethylbenzene
	<i>o</i> -Ethyltoluene	
8	<i>tert.</i> -Butylbenzene	Butylbenzene
9	1,2,4-Trimethylbenzene	Trimethylbenzene
	Isobutylbenzene	Butylbenzene
	<i>sec.</i> -Butylbenzene	
10	<i>p</i> -Cymene	Methylisopropylbenzene
11	1,2,3-Trimethylbenzene	Trimethylbenzene
12		Methylpropylbenzene
13		Dimethylethylbenzene
14		Dimethylethylbenzene
15		Dimethylethylbenzene
16		Dimethylethylbenzene
17		Tetramethylbenzene

From the comparison of both methods, it follows that the main advantage of the analysis of unknown mixtures by combined gas chromatography and mass spectrometry consists in the rapidity of the identification of the components, and also in the far larger independence of the necessity of standard substances.

As a final illustration of applicability of the gas chromatograph-mass spectrometer LKB-9000 to the solution of problems concerning the composition of petroleum, we would like to mention the mass spectra measurements on hydrocarbons prepared in very low concentrations by the methylene insertion method.

The method of methylene insertion was reported by DVORETZKY, RICHARDSON AND DURRETT⁶ several years ago, and rapidly took its place in the field of gas chromatography where it is frequently used today. The method allows one to prepare a mixture of all methyl derivatives from any basic hydrocarbon, by the use of diazomethane.

Because of the necessity of working with a large surplus of the initial hydrocarbon, as compared with diazomethane, only about a 1% solution of methyl derivatives is produced, while the ratio of the isomers present agrees with that of the C-H bonds in methyl-, methylene-, and methine-groups of the initial hydrocarbon. The low concentrations of the methyl derivatives prepared in the way described, however, permit the measurement of their retention times by gas chromatography, but the concentrations are too low for it to be possible to isolate single reaction products or measure their other properties.

The gas chromatograph-mass spectrometer provided a new opportunity for the application of this reaction. The sensitivity of the mass spectrometer in the LKB-9000 apparatus is such that it will measure the mass spectrum of 1 γ of a substance. This is sufficient for measuring even the mass spectra of the low concentrations of methylene insertion reaction products, after separating the particular methyl derivatives on a preliminary chromatographic column.

We have used this procedure for measuring the mass spectra of methyl derivatives of diamantane. Diamantane⁷ is a crystalline pentacyclic naphthene with a high melting point, 237°, and with an empirical formula of C₁₄H₂₀, found in petroleum⁸ like adamantane from which it is structurally derived. We have needed the mass spectra of methyl-diamantanes for the identification of hydrocarbons which we have isolated from petroleum, together with the diamantane, since amongst them the presence of methyl-diamantanes may be expected.

We prepared the methylene insertion products from a cyclopentane solution of diamantane by the use of diazomethane⁹. As expected, in addition to the unreacted diamantane, three methyl-diamantanes in the ratio of 1:3:6 agreeing with that of different C-H bonds in diamantane, were found in the reaction product by gas chromatography.

The product of the methylene insertion was separated on a 50 m long squalane column in the LKB apparatus, and the mass spectra of diamantane and of all the three methyl-diamantanes were measured. In order to eliminate the distortion of the mass spectra caused by traces of the stationary phase volatilizing from the chromatographic column, in the case of all the measured spectra, the background of the instrument was deducted, *i.e.* the mass spectrum obtained when only the pure carrier gas was passing through the column. For checking purposes, the mass spectra of the methyl-diamantanes were even measured after their separation on a capillary column with a silicone coating. After the background was deducted (this was lower when the silicone column was used), spectra agreeing with those of the substances separated on a squalane column were obtained. Although the concentrations of the individual methyl-diamantanes leaving the capillary column are only about 10⁻⁸ g, the mass spectra obtained were quite clear and easily reproducible. The mass spectra of methyl-diamantanes are shown in Fig. 4. In these spectra the structure patterns of individual hydrocarbons (1-methyl-diamantane, 4-methyl-diamantane, 3-methyl-diamantane) are also designated.

The spectra also show the different kinds of fragmentation of the methyl-diamantanes. In derivatives having their methyl group bounded to the tertiary carbon of the diamantane skeleton (1-methyl-diamantane and 4-methyl-diamantane), the fragmented ion 187, corresponding to M minus CH₃, is dominant. On the other hand, in the spectra of 3-methyl-diamantane with the methyl group bonded to a

secondary carbon, the dominant peak is that of the molecular ion 202. Here the fragment ion corresponding to the elimination of the methyl group is only the second of the most obvious ions.

These mass spectra, even when not as good as those measured by the usual way, give a clear picture of differences in the course of fragmentation of the methyl-diamantanes, and are quite adequate for distinguishing individual isomers when identifying them in petroleum.

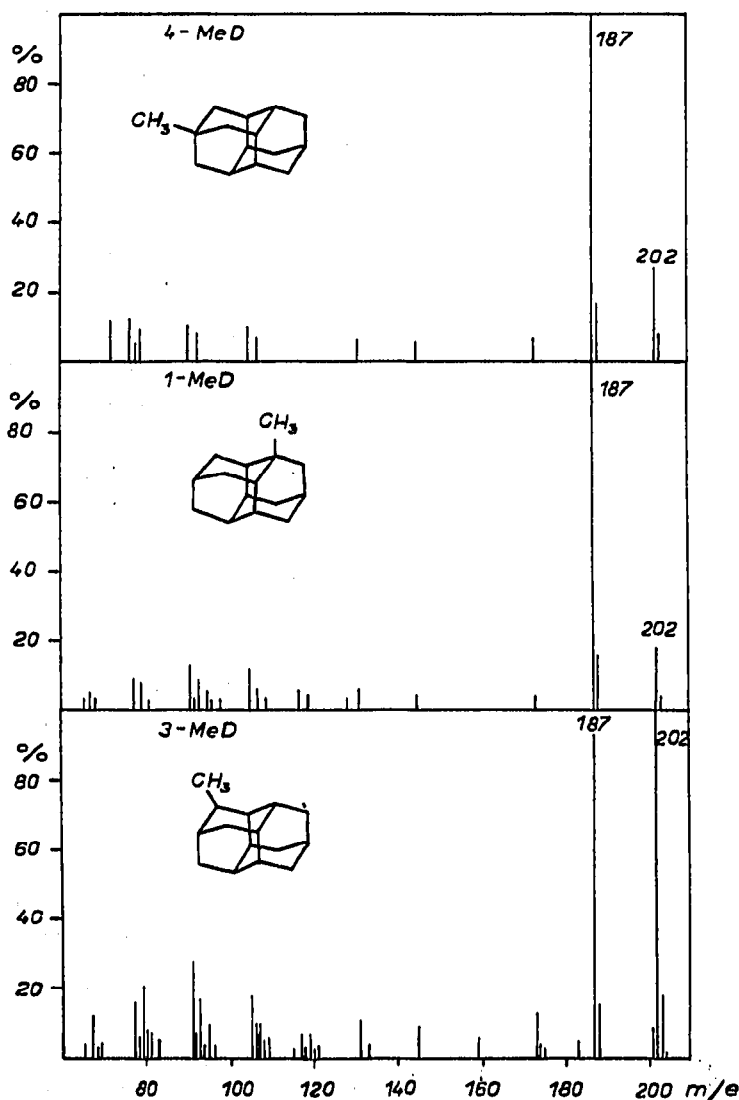


Fig. 4. Mass spectra of methyl-diamantanes. (70 eV.)

The exploitation of methylene insertion in combination with the gas chromatograph-mass spectrometer provides a simple and, above all, rapid means of obtaining the mass spectra of even such methyl derivatives of hydrocarbons whose complete syntheses are either very laborious, or have not yet been reported.

REFERENCES

- 1 R. L. SNYDER, H. E. HOWARD AND W. C. FERGUSON, *Anal. Chem.*, 35 (1963) 1676.
- 2 H. E. LUMPKIN AND T. ACZEL, *11th Annual Meeting of ASTM Committee E-14, San Francisco, 1963*.
- 3 J. MOSTECKÝ, M. POPL AND M. KURAŠ, *Erdöl Kohle*, 22 (1969) 388.
- 4 S. HÁLA, M. KURAŠ AND S. LANDA, *Scientific Papers of the Inst. Chem. Technology, Prague, Technol. Fuel*, D 9 (1966) 3.
- 5 A. CORNU AND R. MASSOT, *Compilation of Mass Spectral Data*, Heyden and Son Ltd., London, 1966.
- 6 I. DVORETZKY, D. B. RICHARDSON AND L. R. DURRETT, *Anal. Chem.*, 35 (1963) 545.
- 7 C. CUPAS, P. R. SCHLEYER AND D. J. TRECKER, *J. Am. Chem. Soc.*, 87 (1965) 917.
- 8 S. HÁLA, S. LANDA AND V. HANUŠ, *Angew. Chem.*, 78 (1966) 1060.
- 9 S. HÁLA, J. NOVÁK AND S. LANDA, *Scientific Papers of the Inst. Chem. Technology, Prague, Technol. Fuel*, D 19 (1969) 19.

J. Chromatog., 51 (1970) 45-57