CHROM. 14,948

GAS CHROMATOGRAPHIC–MASS SPECTROMETRIC INVESTIGATIONS OF HIGH-BOILING CRUDE OIL ALKANE FRACTIONS*

JANUSZ SZAFRANEK* and JÓZEF KUSMIERZ

Mass Spectrometry Laboratory, University of Gdańsk, ul. Sobieskiego 18, 80-952 Gdańsk (Poland)

and

WOJCIECH CZERWIEC

Technical College, Radom (Poland)

(First received October 23rd, 1981; revised manuscript received April 3rd, 1982)

SUMMARY

Capillary columns containing the thermostable stationary phases Dexsil 300, OV-1 and SE-30 were evaluated for the separation of high-boiling alkane mixtures. The best results were achieved with the Dexsil 300 column. A highly efficient ($N = 175 \cdot 10^3$ effective plates for tridecane with $k = 3.4$ and $TZ = 56$ for C_{12}/C_{13}) and thermostable (up to 370°C) glass capillary column was prepared and used for the separations of the alkane fraction of oil lubricants. The individual components of the fractions were identified by means of gas chromatography–mass spectrometry.

INTRODUCTION

We have attempted to separate high-boiling oil fractions in order to relate their properties to the chemical structures of the compounds present in the mixtures. The structural analysis of high-boiling (400°C) oil fractions is very difficult, owing to the presence of a large number of isomers with a wide molecular mass range. The most frequently used technique is the combination of a precise distillation with a chromatographic separation into fractions by elution with *n*-pentane and then mixtures of *n*-pentane with benzene[1]. The fractions are analysed by mass spectrometry with electron-impact (EI) ionization for group analysis. Owing to the nature of the electron ionization phenomenon, the mass spectra obtained in this way, in spite of the use of energy close to the ionization energy, constitute a very detailed record as a result of the presence of a molecular ion as well as of fragmentation ions.

Although the results for aromatic compounds obtained by EI mass spectrometry (MS) are satisfactory, one cannot apply this technique to saturated hydrocarbons[2,3]. Field ionization (FI) gives better results[4], and has proved useful both for aromatic compounds in the products of coal liquefaction[5] and for saturated hydro-

---

carbons[6]. However, analysis by MS results in the common detection of all isomers that have the same molecular weight.

Gas chromatography (GC) on packed and capillary columns has long been used for oil analysis. Stationary phases with high temperature limits allow one to analyse oil fractions with boiling temperatures up to $538°C$[1]. The efficiency of the packed column used, however, did not allow the identification of the components except for *n*-alkanes, whose peaks dominated in the background of the "hump".

The increasing risk of environmental pollution by oil and its products has led to the development of precise methods for the "fingerprinting" and identification of oil sources¯, and methods for identifying oil pollutants at trace concentrations have been devised. The main problem is the identification of oil pollutants in the presence of a background of hydrocarbons that exist naturally in the environment[8].

The use of capillary columns greatly increases analytical capabilities. Thus, GC–MS with a capillary column has become a routine technique in the oil-refining industry. The temperature limit however, is, $300°C$. It was our aim to increase this limit to $360–370°C$ with retention of the efficiency of the columns. In this paper we present the results of our experiments on the application of capillary columns containing Dexsil 300 as the stationary phase to the analysis of *n*- and isoalkane fractions of petroleum with the use of GC–MS.

EXPERIMENTAL

Gas chromatography

The separation of the mixtures examined and the capillary column tests were carried out with a Varian Aerograph Model 1400 gas chromatograph, which had been modified to accept a glass capillary column. An all-glass inlet system with splitting ratio of 1:20 was used. The glass injector was filled with a small amount of GC packing in order to break the aerosol formed during the injection, which helped to avoid the injection discrimination of high-boiling compounds. Helium was used as the carrier gas. The capillary column was joined to a flame-ionization detector through a make-up system with an additional gas flow of 25 cm^3/min. A Philips PM 8220 recorder was employed.

Column preparation

Soda-lime or borosilicate glass capillaries were drawn from 1.2-m tubes using Hewlett-Packard glass-drawing and coiling apparatus. The tubes to be drawn were prepared according to Novotný and Zlatkis[9] by successive rinsing with acetone, methylene chloride, 1% aqueous potassium hydroxide and methanol and drying under vacuum. Capillary columns of 100 m × 0.03 cm I.D. were drawn. Smooth or roughened inner wall capillaries were used for coating following the deactivation step. The inner walls were modified by leaching with 20% hydrochloric acid at $150°C$ for 12 h[10], deposition of Silanox 101 particles by a dynamic method[11] or during the drawing procedure[12] or by deposition of barium carbonate[13]. The glass capillaries were deactivated according to one of the following treatments: with trimethylchlorosilane at ambient temperature[14], with hexamethyldisilazane at $400°C$[15] or with Carbowax 20M at $300°C$[16].

The coating with stationary phases was carried out by a dynamic or static

method (vacuum employed at room temperature). The columns were tested before use for acid–base behaviour by means of the Grob test mixture[17].

Mass spectrometry

Direct MS analyses of alkane fractions were carried out with a Varian-MAT 711 double-focusing mass spectrometer. Electron-impact mass spectra of alkane mixtures were recorded at ionization voltage 10 V, acceleration voltage 8 kV, trap current 100 μA and ion source temperature 260°C. The samples were introduced into the ion source through a reference inlet system at 200°C. Field desorption (FD) fingerprinting was obtained with a combined FD–FI–EI source with an accelerating voltage of 8 kV and an additional potential of 3 kV. The emitter was a 10-μm tungsten wire activated in a Varian apparatus.

Gas chromatography–mass spectrometry

GC–MS analyses were performed using an LKB 2091 mass spectrometer coupled with a Pye 104 gas chromatograph through a two-stage jet separator. The capillary column was connected to the injection port with a splitting ratio of 1:10 and to a separator with an additional make-up flow of 20 cm^3/min. The mass spectrometer was operated at a source temperature of 270°C, molecular separator temperature 250°C, ionizing voltage 70 V, accelerating voltage 3.5 kV and trap current 50 μA. An MS–computer system provided cyclic scanning from m/e 10 to 680 in 2 sec. Gas chromatograms were obtained as the computer-reconstructed traces of ion currents. The decrease in capillary column efficiency in a GC–MS run did not exceed 15% of that in GC.

Alkane samples

The alkane fractions involved in these experiments were prepared from vacuum-distilled oil lubricant fractions of crude oil by successive steps of refining and deep deparaffination. Then the use of vacuum at successively lower pressures and higher temperatures provided distillates having boiling ranges of ca. 390–405, 405–420, etc., up to 550°C. The conditions of the distillation were such as to avoid any measurable sample decomposition.

The next step, liquid–solid chromatography on a column containing both silica gel and alumina, separated the fractions into subfractions. Elution with n-pentane provided n-, iso- and cycloalkane fractions, which were subjected to subsequent experiments.

RESULTS AND DISCUSSION

GC analyses of high-boiling crude oil alkane fractions require two main features of the columns employed, viz., high thermal stability and a high efficiency at elevated temperatures. The latter demand stems from the fact that these mixtures consist of a large number of n- and isoalkane isomers that usually elute in the same mass range. Thus in GC analysis they appear as unresolved humps characterizing crude oils. The procedure employed here for sample preparation enriched them in isoalkanes, which made their GC separation extremely difficult.

The thermostable liquid stationary phases SE-30, OV-1 and Dexsil 300 were

chosen for separation studies. Table I shows the methods of preparation of the columns. Soda-lime and borosilicate (Pyrex) glasses were used for drawing capillaries. The glass tubes were deactivated by treatment with trimethylchlorosilane (TMCS), Carbowax 20M or hexamethyldisilazane (HMDS) and dynamic or static methods of coating were employed (Table I).

TABLE I

CHARACTERISTICS OF THE COLUMNS

No.	Glass	Surface treatment	Deactivation	Stationary phase	Coating procedure	Length (m)	I.D. (mm)
1	Pyrex	Silanox 101*	TMCS	SE-30	DM, 2%**	30	0.3
2	Pyrex	20% HCl***, BaCO$_3$	Carbowax 20M	SE-30	SM, 0.2%$^\text{s}$	20	0.23
3	Soda-lime	Silanox 101	HMDS	SE-30	DM, 2%**	20	0.28
4	Soda-lime	20% HCl	HMDS	OV-1	SM, 0.2%$^\text{s}$	30	0.27
5	Soda-lime	20% HCl	HMDS	Dexsil 300	SM, 0.2%$^\text{s}$	30	0.25
6	Soda-lime	Silanox 101$^\text{ss}$	HMDS	Dexsil 300	SM, 0.2%$^\text{s}$	40	0.3
7	Soda-lime	Silanox 101$^\text{ss}$	HMDS	Dexsil 300	SM, 0.11%$^\text{s}$	35	0.23

* Dynamic method of Silanox deposition, 1.6% in carbon tetrachloride.
** Dynamic method, 2% in isooctane.
*** 20% hydrochloric acid leaching.
$^\text{s}$ Static method, 0.2% (or 0.11% as indicated) in n-pentane.
$^\text{ss}$ Torline and Schnautz method of Silanox deposition[12].

The performance of the columns (Table II) was described by the number of theoretical plates (n), the number of effective plates (N) and the separation number "Trennzahl", (TZ). The separation number was calculated using the retention times

TABLE II

COLUMN PERFORMANCE

Carrier gas: helium. t_R = retention time; t_R' = adjusted retention time = $t_R - t_M$; t_M = hold-up time; $w_{0.5}$ = peak width at half height.

No.	Stationary phase	Temperature (°C)	k for C$_{24}$	$n \cdot 10^3$*	n, m	$N \cdot 10^3$**	N/m	TZ*** (C_{23}/C_{24})	u (cm/sec)	Film thickness (μm)
1	SE-30	250	2	100	3.3	40	1.3	10	17	0.1
2	SE-30	250	2.6	64	3.2	25	1.25	7	13	
3	SE-30	250	2.5	39	1.95	14	0.7	6	12	
4	OV-1	240	2.7	66	2.2	26	0.9	8	17	0.13
5	Dexsil 300	250	1.7	115	3.8	46	1.53	10.4	16	0.12
6	Dexsil 300	250	1.8	77	1.9	32	0.8	9	17	0.15
7	Dexsil 300	230	2.66	140	4	51	1.43	12	16	0.11

$$* \; n = 5.54 \left(\frac{t_R}{w_{0.5}} \right)^2.$$

$$** \; N = 5.54 \left(\frac{t_R'}{w_{0.5}} \right)^2.$$

$$*** \; TZ = \frac{t_{R(B)} - t_{R(A)}}{w_{0.5(A)} + w_{0.5(B)}} - 1.$$

of two neighbouring n-alkane peaks in an isothermal run, and varied from 6 to 12 (Table II). This value and the theoretical plate number indicated a preference for SE-30 (Nos. 1 and 2), OV-1 (No. 4) or Dexsil 300 (HCl leach, No. 5, or Silanox, No. 7) capillary columns for the separation of alkanes.

Fig. 1 shows the separation between C_{23} and C_{24} of mixture 1 on 20-m SE-30, 30-m OV-1 and 30-m Dexsil 300 capillary columns. The separation on Dexsil 300 is much better than that on OV-1 or SE-30. For example, the separation of components D and E (Fig. 1) expressed as the ratio of the corrected retention times was found to be 1.0275, 1.0276 and 1.0376 for the SE-30, OV-1 and Dexsil 300 columns, respectively.
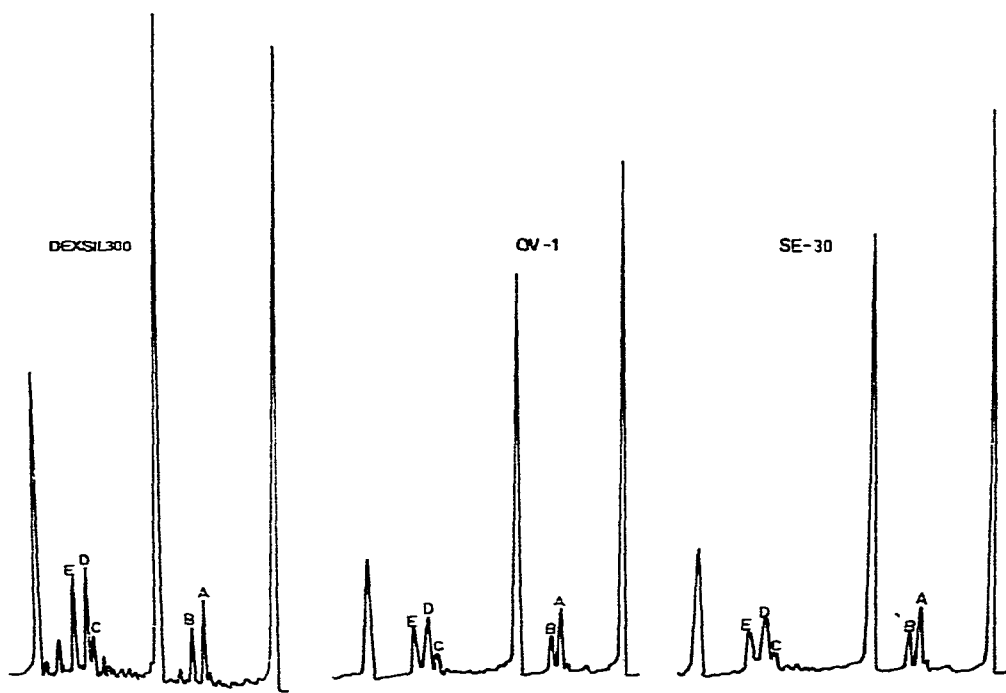

Fig. 1. Comparison of separation of hydrocarbons on Dexsil 300, OV-1 and SE-30 columns.

The usefulness of these stationary phases for alkane separations is even more pronounced if one compares the efficiencies required for baseline separation (resolution 1.5) of the critical peak pairs. The values of N_{req} obtained lie in the range 30,000–140,000 plates; however, those for SE-30 and OV-1 are roughly double those for Dexsil 300.

For the Dexsil 300 column, a thermalstability test was run[18], the column being heated between 300 and 410°C for 0.5 h at 10°C intervals and cooled to 240°C after each heating period for evaluation of the efficiency. No changes in the theoretical plate numbers were found, but small decreases in the capacity ratios (k values) were obtained (Fig. 2). However, deactivation disappeared entirely on exposure of the column to temperatures above 330°C. Nevertheless, the column was still of good quality and the GC peak profiles were unaffected.
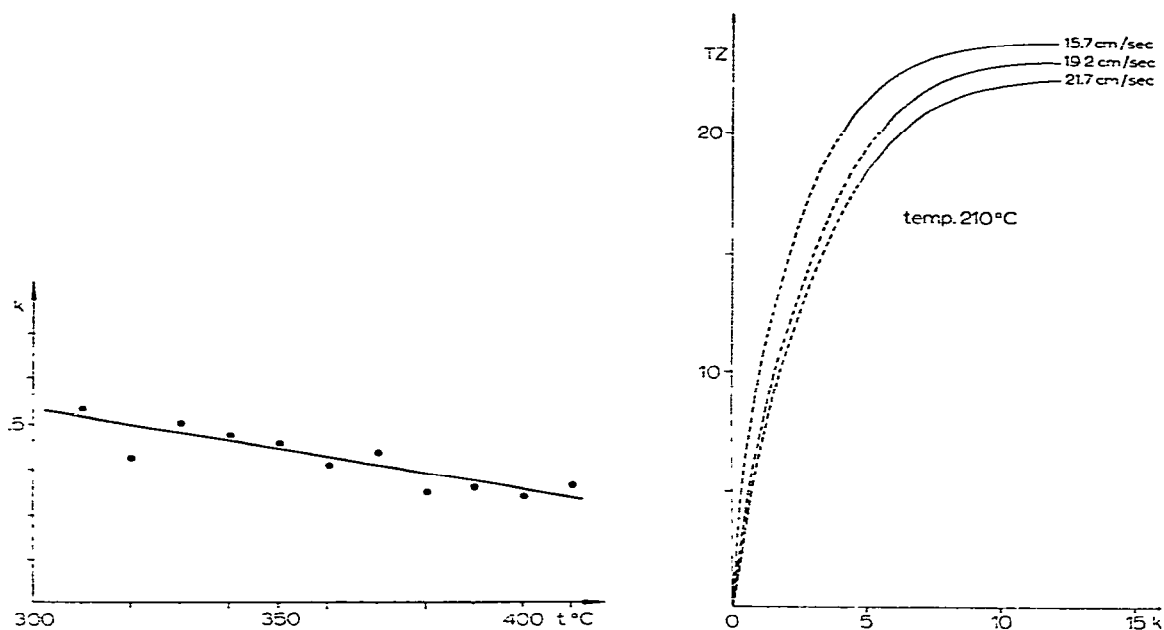
Fig. 2. Capacity ratio of C_{24} alkane standard at 240 C after successive heating between 300 and 400 C.

Fig. 3. Effect of linear velocity of carrier gas on separation number.

It was concluded that the Dexsil 300 column was the most suitable for the separation of high-boiling alkanes.

Fig. 3 shows the effect of the linear velocity of the carrier gas on the separation number for *n*-alkanes with a 50-m Dexsil 300 column. The range of the velocity modification was restricted to 24 cm/sec because the longer columns show a sharp decrease in efficiency above 30 cm/sec[19]. The maximum resolution curve for C_{21}/C_{22} to C_{24}/C_{25} alkane pairs was obtained for a linear velocity of 16 cm/sec. However, a velocity of 19 cm/sec, which results in the optimal efficiency and is the most practical gas velocity, was chosen for separation studies.

The gas chromatograms of alkane fractions are shown in Figs. 4 and 5 and the retention indices of the most abundant peaks are listed in Tables III and IV. The common feature of the chromatograms is a pattern of elution which consists of *n*-alkane and branched-chain and cyclic saturated hydrocarbons. This is a typical fingerprint of the samples and the retention indices can be used for structural elucidation.

The preliminary low-voltage and FD direct MS analysis of samples 1 and 2 (Figs. 6–8) provided an important initial indication of types of compound structures and molecular weight distributions. A comparison of the two ionization spectra of sample 1 indicates a preference for the FD rather than the EI technique because exclusively molecular ions and their isotopic species are present in the FD spectra.
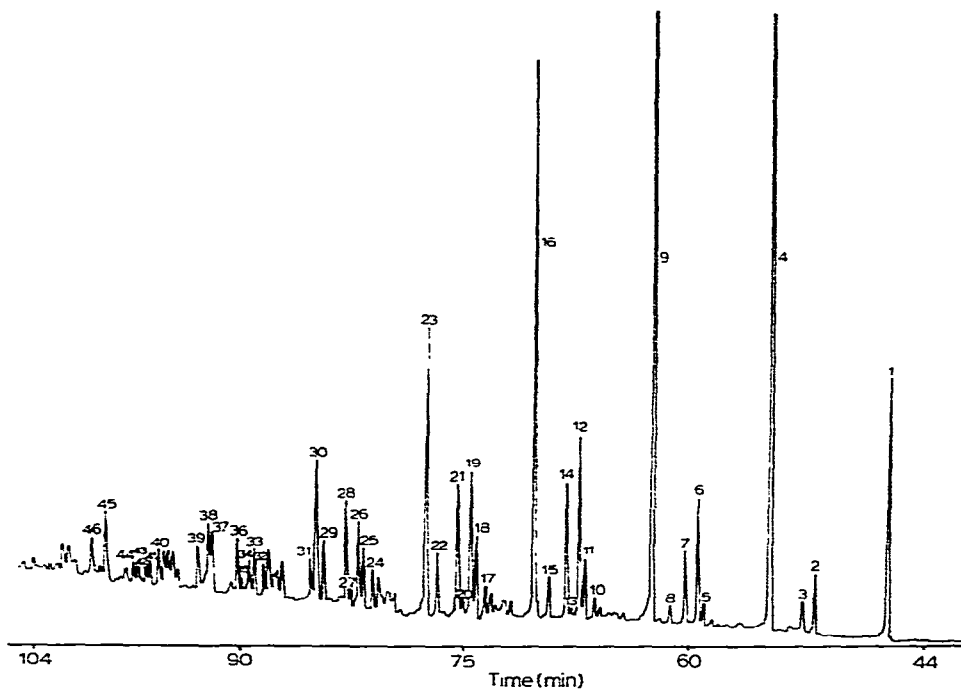
Fig. 4. Linear temperature-programmed separation of sample 1 on a 90-m Dexsil 300 column programmed from 170°C at 1°C/min. For peak identification see Table III.

Unfortunately, n- and isoalkanes are indistinguishable because of identical mass-to-charge ratios. The molecular weight distribution of sample 1 (Fig. 7) ranges from 296 a.m.u. (C_{21} alkane) to 380 a.m.u. (C_{27} alkane). In addition, some species with unsaturation sites are present in the sample. Those with one unsaturation site may represent cyclopentane and cyclohexane derivative homologous series. A progressive increase in the ratio of their ion currents to alkane currents with increase in molecular
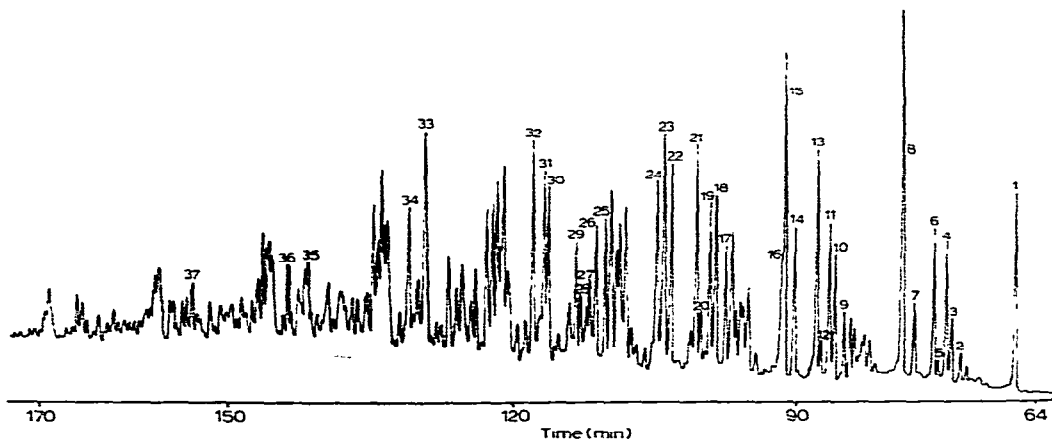

Fig. 5. Linear temperature-programmed separation of sample 2 on a 90-m Dexsil 300 column programmed for 185°C at 0.5°C/min. For peak identification see Table IV.

TABLE III

COMPOUNDS IDENTIFIED IN SAMPLE 1 AND THEIR KOVÁTS RETENTION INDICES (*I*) ON DEXSIL 300 AT 210°C

I could not be determined for compounds 24–46 at 210°C.

Peak No.	Compound	I	Peak No.	Compound
1	*n*-Heneicosane	2100	24	5-Methylpentacosane
2	2-Methylheneicosane	2160.3	25	4-Methylpentacosane
3	3-Methylheneicosane	2171.1	26	2-Methylpentacosane
4	*n*-Docosane	2200	27	3-Ethyltetracosane
5	4-Methyldocosane	2254.6	28	3-Methylpentacosane
6	2-Methyldocosane	2259.2	29	Eicosylcyclopentane
7	3-Methyldocosane	2269.3	30	*n*-Hexacosane
8	Heptadecylcyclopentane	2284.5	31	Nonadecylcyclohexane
9	*n*-Tricosane	2300	32	5-Methylhexacosane
10	5-Methyltricosane	2347.8	33	4-Methylhexacosane
11	4-Methyltricosane	2355.9	34	2-Methylhexacosane
12	2-Methyltricosane	2360.7	35	3-Ethylpentacosane
13	3-Ethyldocosane	2366.2	36	3-Methylhexacosane
14	3-Methyltricosane	2371.6	37	Heneicosylcyclopentane
15	Octadecylcyclopentane	2386.4	38	*n*-Heptacosane
16	*n*-Tetracosane	2400	39	Eicosylcyclohexane
17	5-Methyltetracosane	2447.1	40	5-Methylheptacosane
18	4-Methyltetracosane	2455.6	41	4-Methylheptacosane
19	2-Methyltetracosane	2460.5	42	2-Methylheptacosane
20	3-Ethyltricosane	2466.6	43	3-Ethylhexacosane
21	3-Methyltetracosane	2471.4	44	3-Methylheptacosane
22	Nonadecylcyclopentane	2486.1	45	*n*-Octacosane
23	*n*-Pentacosane	2500	46	Heneicosylcyclohexane

TABLE IV

COMPOUNDS IDENTIFIED IN SAMPLE 2 AND THEIR KOVÁTS RETENTION INDICES (*I*) ON DEXSIL 300 AT 220°C

I could not be determined for compounds 16 and 24–37 at 220°C.

| Peak No.	Compound	I	Peak No.	Compound	I
1	*n*-Tetracosane	2400	20	3-Ethylpentacosane	2666.7
2	5-Methyltetracosane	2448.4	21	3-Methylhexacosane	2670.8
3	4-Methyltetracosane	2455.7	22	Heneicosylcyclopentane	2690.6
4	2-Methyltetracosane	2462.2	23	*n*-Heptacosane	2700
5	3-Ethyltricosane	2467.8	24	Eicosylcyclohexane	
6	3-Methyltetracosane	2471.8	25	5-Methylheptacosane	
7	Nonadecycyclopentane	2488.9	26	4-Methylheptacosane	
8	*n*-Pentacosane	2500	27	2-Methylheptacosane	
9	5-Methylpentacosane	2539.9	28	3-Ethylhexacosane	
10	4-Methylpentacosane	2555.4	29	3-Methylheptacosane	
11	2-Methylpentacosane	2560.1	30	Docosylcyclopentane	
12	3-Ethyltetracosane	2567.3	31	*n*-Octacosane	
13	3-Methylpentacosane	2570.9	32	Heneicosylcyclohexane	
14	Eicosylcyclopentane	2590.2	33	*n*-Nonacosane	
15	*n*-Hexacosane	2600	34	Docosylcyclohexane	
16	Nonadecylcyclohexane		35	*n*-Triacontane	
17	5-Methylhexacosane	2647.6	36	Tricosylcyclohexane	
18	4-Methylhexacosane	2655.2	37	*n*-Hentriacontane	
19	2-Methylhexacosane	2659.5			
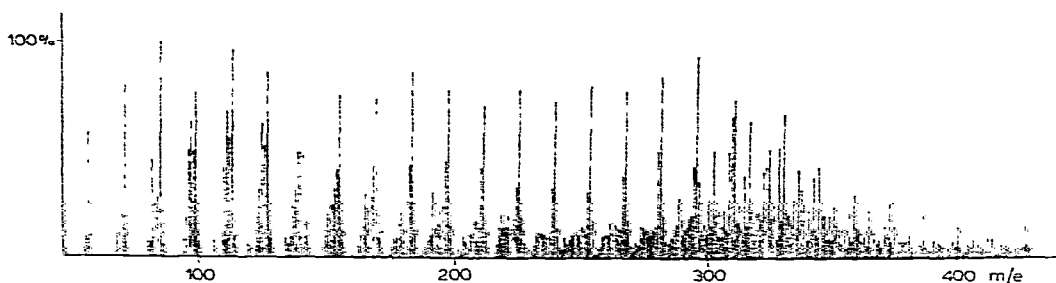
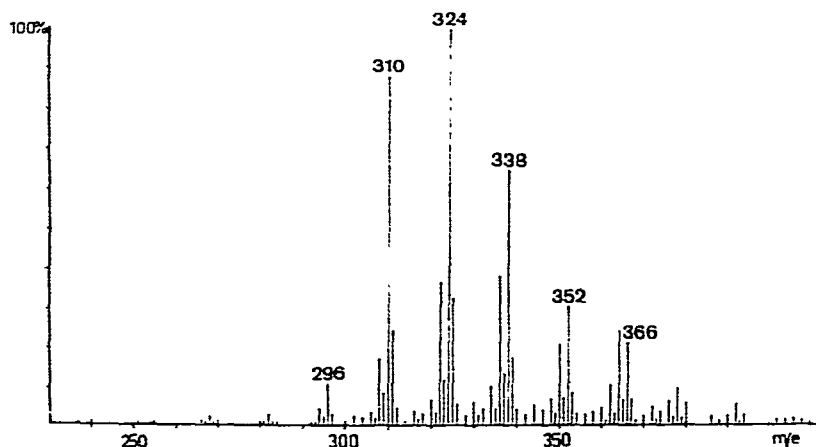Fig. 6. EI mass spectrum (10 eV) of sample 1.

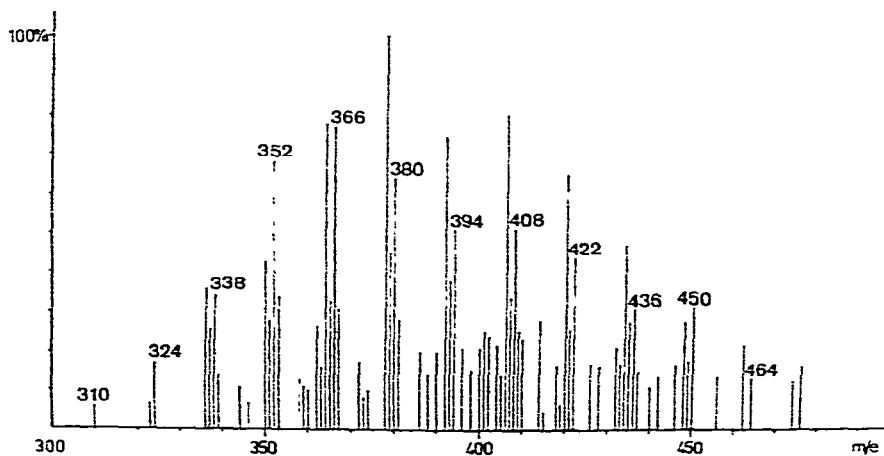Fig. 7. FD mass spectrum of sample 1.

Fig. 8. FD mass spectrum of sample 2.

weight is observed, and was found to be 20 % and 114 % for C_{22} and C_{26}, respectively.

The mass spectrum of sample 2 (Fig. 8) features cyclopentane and cyclohexane species ranging from m/e 336 (C_{24}) to m/e 462 (C_{33}) as the most abundant ions. Moreover, some ions with two unsaturation sites are also present and may correspond to cycloalkanes with two condensed rings.

The results of direct MS group analysis were found to correlate with those of GC–MS studies (Tables III and IV). The mass spectra of the compounds labelled in Figs. 4 and 5 were recorded by GC–MS. Co-injection of standards with samples 1 and 2 identified the n-alkane peaks, which were confirmed by mass spectrometry also. All n-alkane mass spectra showed a small but measurable molecular peak, the intensity of which varied from 1.6% for C_{22} to 0.5% for C_{29}. The other mass spectral features were typical of unbranched alkanes[20].

The mass spectra of some GC peaks appearing between n-alkane peaks (Figs. 4 and 5) revealed branched site features. These are seen to be described by the ions of M–X at higher mass ranges[20]. Thus prominent ions corresponding to $M - 43$ and $M - 15$ suggest a 2-methylalkane, but the $M - 29$, $M - 15$ and $M - 57$ ions indicate a 3-methyl isomer. In turn, 4- and 5-methyl isomers could be fairly easily characterized by $M - 43$ and $M - 57$ ions, respectively. The remaining branched isomer, which revealed $M - 29$ and $M - 71$ ions, might be a 3-ethyl isomer. Cyclopentane and cyclohexane homologous alkanes provided mass spectra with significant molecular ions. The saturated ring in a hydrocarbon mass spectrum is demonstrated by the most abundant ions at m/e 69 and m/e 83 for cyclopentyl and cyclohexyl structures, respectively (Tables III and IV). n-Alkanes, isoalkanes and cycloalkanes constitute the only or dominating components of the samples studied. Their elution sequence as groups or individual isomers seems to be structure-dependent. Branched-chain hydrocarbons elute before n-alkanes, but cycloalkanes elute after n-alkanes according to the differences in their boiling temperatures.

The relationship between the retention coefficients and the structures of the compounds studied will be the subject of a separate paper. We also plan to synthesize model compounds, which will be used for the verification of the proposed structures.

REFERENCES

1 H. J. Coleman, J. E. Dooley, D. E. Hirsch and C. J. Thompson, *Anal. Chem.*, 45 (1973) 1724.
2 W. A. Chupka and J. Berkowitz, *J. Chem. Phys.*, 47 (1967) 2921.
3 M. Vestal, in P. Ausloos (Editor), *Fundamental Processes in Radiation Chemistry*, Wiley-Interscience, New York, 1968, Ch. 2.
4 H. D. Beckey, *Principles of Field Ionization and Field Desorption Mass Spectrometry*, Pergamon Press, Oxford, New York, Toronto, Sydney, Paris, Frankfurt, 1977.
5 S. E. Scheppele, P. L. Grizzle, G. J. Greenwood, T. D. Marriott and N. B. Perreira, *Anal. Chem.*, 48 (1976) 2105.
6 S. E. Scheppele, C. S. Hsu, T. D. Marriott, P. A. Benson, K. N. Detwiler and N. B. Perreira, *Int. J. Mass Spectrom. Ion Phys.*, 28 (1978) 335.
7 J. G. Pym, J. E. Ray, G. W. Smith and E. V. Whitehead, *Anal. Chem.*, 47 (1975) 1617.
8 M. Dastillung and P. Albrecht, *Mar. Pollut. Bull.*, 7 (1976) 1617.
9 M. Novotný and A. Zlatkis, *Chromatogr. Rev.*, 14 (1971) 1.
10 K. Grob and G. Grob, *J. Chromatogr.*, 125 (1976) 471.
11 A. L. German and E. C. Horning, *J. Chromatogr. Sci.*, 11 (1973) 76.
12 P. Torline and N. Schnautz, *J. High Resolut. Chromatogr. Chromatogr. Commun.*, 1 (1978) 301.
13 K. Grob, Jr., G. Grob and K. Grob, *J. High Resolut. Chromatogr. Chromatogr. Commun.*, 1 (1978) 149.
14 M. Novotny and K. Tesarik, *Chromatographia*, 1 (1968) 332.
15 Th. Welsch, W. Engewald and Ch. Klaucke, *Chromatographia*, 10 (1977) 22.
16 D. A. Cronin, *J. Chromatogr.*, 97 (1974) 263.
17 K. Grob, Jr., G. Grob and K. Grob, *J. Chromatogr.*, 156 (1978) 1.
18 G. Schomburg, R. Dielmann, H. Borwitzky and H. Husmann, *J. Chromatogr.*, 167 (1978) 337.
19 K. Yabumoto and W. J. A. VandenHeuvel, *J. Chromatogr.*, 140 (1977) 197.
20 F. R. Heller and G. W. A. Milne, *EPA/NIH Mass Spectral Data Base*, U.S. Government Printing office Washington, DC, 1978.