Analysis of multicomponent mixtures by high-resolution capillary gas chromatography and combined gas chromatography–mass spectrometry

I. Aromatics in a hydrocarbon matrix

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ABSTRACT

   Achievements and problems of qualitative analysis of multicomponent mixtures are demonstrated on a complex hydrocarbon sample. Emphasis is given to the analysis of aromatics with the broader range of boiling points in a complex hydrocarbon matrix. In the petroleum fraction (150–350°C) used as the raw material for the analysis of *n*-alkanes by gas chromatography–mass spectrometry with electron-impact ionization using paraffins, olefins, naphthenes and aromatics (PONA) columns under optimized temperature-programmed conditions, it was found out that the sample consists of a multicomponent mixture of hydrocarbons belonging to various hydrocarbon groups at about the same concentration level: alkanes, naphtenes and aromatics. As the sample was very complex, the detailed analysis of aromatic hydrocarbons was performed in aromatic concentrate from liquid chromatography fraction. Identification was based on combination of isothermal retention data (on OV-101) and mass spectral data measured under temperature-programmed conditions using PONA columns. Higher-boiling-point aromatics were characterized using only mass spectral data. The 256 aromatics were characterized as to group (alkylbenzenes, indanes, tetralins, indenes, naphthalenes or acenaphthenes) and further with carbon atom number or the type of substituents. The precise structure with assignment of position of substituents was determined for 51 aromatics.

INTRODUCTION

   The definition and criteria of complex organic systems were given by Schomburg [1]. The first categories of these systems represent multicomponent samples and constituents with very similar physical and/or chemical properties (as optical

enantiomers and structural isomers). Natural and synthetic hydrocarbon samples are real multicomponent mixtures (the component number depending on group-type composition and on the range and distribution of boiling points of the components present in the mixture) with a large number of position isomers and enantiomers, numbers of which rapidly increase with increasing carbon atom number.

High-resolution capillary gas chromatography (HRCGC) is the most generally useful method for the analysis of complex hydrocarbon mixtures with the ultimate aim of complete component analysis, thus providing a true paraffins, olefins, naphthenes and aromatics (PONA) analysis. The disadvantage of this method is that every peak must be identified or at least classified according to the chemical group to which it belongs. Peak identification in a chromatogram is carried out on the basis of retention data and gas chromatography–mass spectrometry (GC–MS) [2,3]. MS has gained wide acceptance in petroleum chemistry as a means of providing structural data on the constituents of hydrocarbon mixtures. Its success is based on the principle that any given hydrocarbon type can be recognized by a set of specific spectral peaks [4–6].

Aromatics represent an important group of hydrocarbons in various petroleum products. Detailed information on their composition in feed materials, intermediates and commercial products is required for process development and quality control programs. The other important area of component identification is the environment used. Generally, aromatic hydrocarbons may be analysed directly in various hydrocarbon samples by HRCGC on a single column with non-polar, medium-polarity and polar stationary phases under isothermal and temperature-programmed GC conditions, using multidimensional GC (switching system with two or more columns) or in aromatic concentrates from liquid chromatography fractions using a column with various polarities of the stationary phase. Surveys of their application were published by Kumar *et al.* [7] and Matisová [8]. The individual aromatics were separated, identified and/or quantified, mostly with carbon atom numbers up to 10.

Single-column capillary GC [7,9,10] and multidimensional GC systems [11–16] (with packed and capillary columns) usually employ a very polar (*e.g.* Carbowax 1540, TCEP, SP-2340, OV-275) column to separate the aromatic from the saturated/olefinic hydrocarbons. However, in the case of very complex hydrocarbon mixtures with carbon atom numbers over 12 these systems fail to separate aromatics from compounds of other hydrocarbon groups. Therefore, for the analysis of higher-boiling-point fractions it is necessary to use off-line or on-line combination of liquid chromatography (LC) with capillary GC.

The aim of this paper was to show the possibilities of using single column capillary GC (with commercially available, chemically bonded, non-polar silicone capillary columns) for the detailed analysis of aromatic hydrocarbons in a petroleum fraction with boiling range 150–350°C, with the stress on identification of aromatics with boiling range 150–270°C in the concentrate from a liquid chromatography (LC) fraction using combined retention and mass spectral data. In this study the concentration of aromatics was approximately equal to the constituents of other hydrocarbon groups. The analysis of multicomponent mixture of trace aromatics in a hydrocarbon matrix will be the subject of Part II.

EXPERIMENTAL

GC measurements were performed on an HP Model 5890A gas chromatograph equipped with a split–splitless injection system, a flame ionization detection (FID) system and an HP Model 3396A integrator (Hewlett-Packard, Avondale, PA, U.S.A.). The analysis was carried out on a PONA fused-silica capillary column (Hewlett-Packard) which is a special-purpose cross-linked methyl silicone column with 0.5 μm film thickness for the separation of paraffins, olefins, napthenes and aromatics (50 m × 0.2 mm I.D.) and on glass capillary column (52 m × 0.25 mm I.D.) with statically coated OV-101 dimethylsilicone phase [17] having a film thickness of 0.38 μm. Hydrogen was used as a carrier gas at a linear velocity of 40 cm for the isothermal measurements (80–160°C) and TPG conditions adjusted to the initial temperature of the temperature programme (70 to 160°C at 1.5°C/min, then to 280°C at 15°C/min, and then held for 15 min). The other instrumental conditions were: injector temperatures, 250°C and 300°C, respectively; detector temperature, 300°C; split ratio, 1:70.

GC–MS measurements with electron-impact (EI) ionization (70 eV ionization energy) were performed on an HP Model 5890A gas chromatograph equipped with a split–splitless injection system and a Model 5970 mass-selective detector (Hewlett Packard) with the direct interface. All experimental work was done on a PONA column of the given temperature programmed conditions with helium as carrier gas at a linear gas velocity of 38 cm/s at the initial temperature of the programme run. The other instrumental conditions were: injector and detector temperatures, 300°C and 275°C respectively; split ratio, 1:70.

The raw material for analysis of n-alkanes (fraction of crude oil imported from the U.S.S.R. with boiling range 150–350°C) was the sample used for the analysis of aromatic hydrocarbons. From this multicomponent hydrocarbon mixture (0.6–0.7 ml) the aromatic fraction was isolated by column LC on silica gel (50 × 1.2 cm; particle size 70–100 μm) according to the modified [18] ASTM method D 2549-68 [19], with n-pentane (80 ml) for the elution of paraffinic and naphthenic fraction; the aromatic fraction was eluted with 80 ml of dichloromethane or methanol with a flow-rate of 1 ml/min. The aromatic fraction was evaporated using a Model RVO-64 rotary evaporator (Mikrotechna, Prague, Czechoslovakia) to a final volume of 0.5 ml.

The raw material sample (0.5 μl) was injected with a 1-μl Hamilton syringe; isolated aromatic fractions (1.5-2.0 μl) were injected with a 10-μl Hamilton syringe. For measurements of retention data n-alkanes were injected together with the isolated aromatic fraction. Methane was used for the determination of the gas hold-up time.

RESULTS

Analysis of multicomponent hydrocarbon mixture

In recent years n-alkanes have been extensively used in the manufacture of detergents, fatty acids, alcohols, petroproteins and various speciality chemicals. The technology of n-alkanes C_9–C_{22} is based on their selective adsorption on molecular sieves from the petroleum fraction (a multicomponent mixture of hydrocarbons consisting of n-alkanes, branched alkanes, napthenes and aromatics) and the following extraction. During the adsorption process of n-alkanes from the raw material small

amounts of aromatic hydrocarbons are also retained on molecular sieves. The presence of aromatics in the final product, the light fraction of *n*-alkanes C_9-C_{15}, was confirmed by UV spectrometry and their concentration was found to be in the range 10^2-10^3 ppm. As aromatics are potential carcinogens, it is very important to know their composition in *n*-alkanes. Therefore, it was necessary to perform qualitative analysis of aromatics in the raw material (petroleum fraction) and to determine their distribution in the technological process and mainly in the final product. The trace analysis of individual aromatics in an *n*-alkane matrix will be the subect of Part II.

Hewlett-Packard PONA fused-silica capillary columns, which are special-purpose cross-linked methyl silicone phase columns tailored for hydrocarbon (paraffins, olefins, napthenes and aromatics) analysis, were chosen for capillary GC and combined GC–MS analysis. Due to the large number of components present in the raw material and their broad range of boiling points (150–350°C) experimental conditions of capillary GC under temperature-programmed conditions with hydrogen as carrier gas were optimized in such a way that a considerably large number of peaks was resolved in a brief period of analysis. From capillary GC profiles it was evident that it would be problematic to perform qualitative analysis of aromatics using retention data measurements as a consequence of a very high probability of co-elution of components of the multicomponent hydrocarbon mixture. Much information on the composition of the raw material was received from the combined GC—MS technique with EI ionization under similar chromatographic conditions. By monitoring selective ions characteristic for certain hydrocarbon groups such as paraffins, napthenes and aromatics from the acquired mass spectra, mass chromatograms were obtained. From the results it was clear that the co-elution of many components of various hydrocarbons groups is taking place and in most cases GC–MS measurements produced complex mixed spectra which are fairly difficult to interpret. Therefore the qualitative analysis of aromatic hydrocarbons was performed in the aromatic fraction of the raw material.

Analysis of multicomponent mixture of aromatic hydrocarbons

Aromatic hydrocarbons were isolated by off-line adsorption column liquid chromatography on silica gel using a modification of the American Society for Testing and Materials (ASTM) method D2549-68 [19]. The reason for choosing this modified method[18] was its good reproducibility and the production of stock solution of aromatics suitable for repeat GC and GC–MS analyses.

For qualitative capillary GC analysis it is necessary to use a capillary column with the defined stationary phase which gives the opportunity of measurements of reliable retention data with good interlaboratory reproducibility and with good selectivity towards analysed compounds. There is little information available on standards for aromatic hydrocarbons (especially for carbon atom numbers over 9, where is the large number of possible isomers), so for identification purposes the only possibility is to use published retention data on non-polar silicone stationary phases. With regard to these requirements we first decided to use a PONA column with chemically bonded dimethyl silicone phase for its good temperature stability and other column qualities.

Due to the fact in the literature there are certain data on the dependence of retention characteristics on the cross-linking method and film thicknesss of bonded non-polar phase, and to the small number of published isothermal retention data for

aromatic hydrocarbons on PONA columns [20] and generally on bonded dimethylsil-icones, we have verified the agreement of retention indices of a sample of alkylben-zenes with known composition with those on OV-101 columns [21], as alkylbenzenes represent the major part of the monoaromatic fraction of natural and synthetic hy-drocarbon mixtures. The four PONA columns tested [22] showed reproducible chro-matographic properties, capacity ratios and high efficiencies. The standard deviation of the retention indices measured on a single column ($n = 4$) was 0.03 i.u., with confi-dence interval, $L_{1,2}(I) \pm 0.05$ i.u. ($\alpha = 0.05$), and the differences among the columns were found to be up to 0.3 i.u. Indices determined on conventionally coated di-methylsilicone columns are slightly but significantly lower, the difference being in most cases about 1 i.u. As most published retention indices of aromatics are on conventional non-polar silicone capillary columns [21–27], measurements were per-formed on an OV-101 glass capillary column. The chromatogram of aromatics isolat-ed from the raw material and n-alkanes C_7–C_{13} at 100°C is given in Fig. 1.

Isothermal measurements were also performed at temperatures in the range 80–160°C. In our laboratory we optimized experimental conditions (isothermal tem-perature in the range 80–130°C) for the analysis of multicomponent mixture of alkyl-benzenes on an OV-101 glass capillary column and the only optimum was found to be at 100°C [28]. Analysing aromatics of the raw material (the fraction with carbon atom numbers over 9 with boiling points in the range 150–350°C) at higher temperatures there was co-elution of many peaks. Peak numbering at various temperatures and the assignment of peak numbers both for isothermal GC and temperature programmed GC–MS for positive peak identification was difficult. Therefore, for the qualitative analysis of higher-boiling-point compounds the stress was on GC–MS measurements. The measured retention indices of aromatics at 100°C and their temperature coeffi-cients are given in Table I. Compound characterization was based on the comparison of the measured data with those in the literature [21,25,27].

Qualitative analysis by combination of GC–MS with EI ionization was the next step in the identification of aromatics in the aromatic fraction of the multicomponent hydrocarbon mixture studied. The total ion current (TIC) chromatogram is given in Fig. 2. Identification using the combined technique was based on information ob-tained from interpretation of the acquired mass spectra; mass chromatograms of selective ions of characteristic aromatics groups found in the mixture (alkylbenzenes, indanes/tetralins, indenes, naphtalenes and acenapthenes/biphenyls), examples for indanes/tetralins and napthalenes are given in Figs. 3 and 4 and mass chromatograms of molecular ions of alkylbenzenes, the most frequently occurring compounds in the aromatic fraction of the raw material (Fig. 5). The acquired mass spectra and mass chromatograms of molecular ions of some types of compounds made possible the determination of molecular weights and carbon atom numbers of the individual com-ponents and/or the type and number of substituents. In many cases mixed mass spectra were obtained and from mass chromatograms of selective ions it was possible to confirm the number or the type of compounds eluted in one peak.

More detailed structure with the assigned position of substituents was deter-mined using the combined retention and mass spectral data (Table I). It has to be pointed out that in the case of mixed spectra interpretation was not possible for a compound with low content. Further, the assignment of a corresponding peak num-ber under temperature-programmed GC–MS and isothermal GC conditions was not
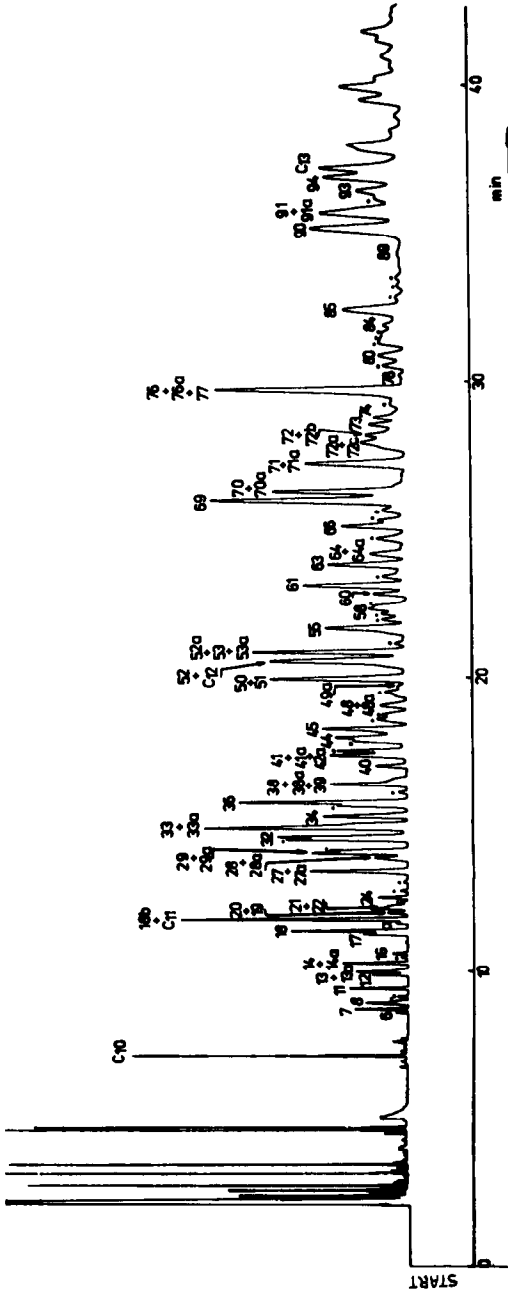
Fig. 1. Chromatogram of aromatics in aromatic fraction of the raw material isolated by LC on silica gel eluted between *n*-alkanes C_{10}—C_{13} at 100°C on OV-101 capillary column with as carrier gas hydrogen at a linear velocity of 40 cm/sec.
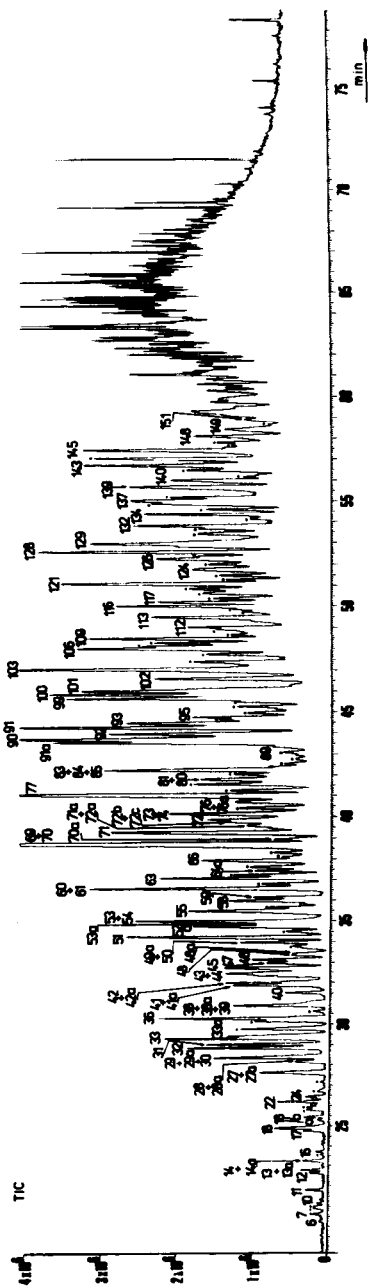
Fig. 2. Total ion current (TIC) chromatogram by GC–MS analysis of aromatic fraction of the raw material isolated by LC on silica gel; measurements were performed on a PONA column under the temperature-programmed conditions: $t_1 = 70°C$; $G_1 = 1.5°C/min$; $t_2 = 160°C$; $G_2 = 15°C/min$; $t_3 = 280°C$; 15 min isothermal; carrier gas, helium at 38 cm/s.
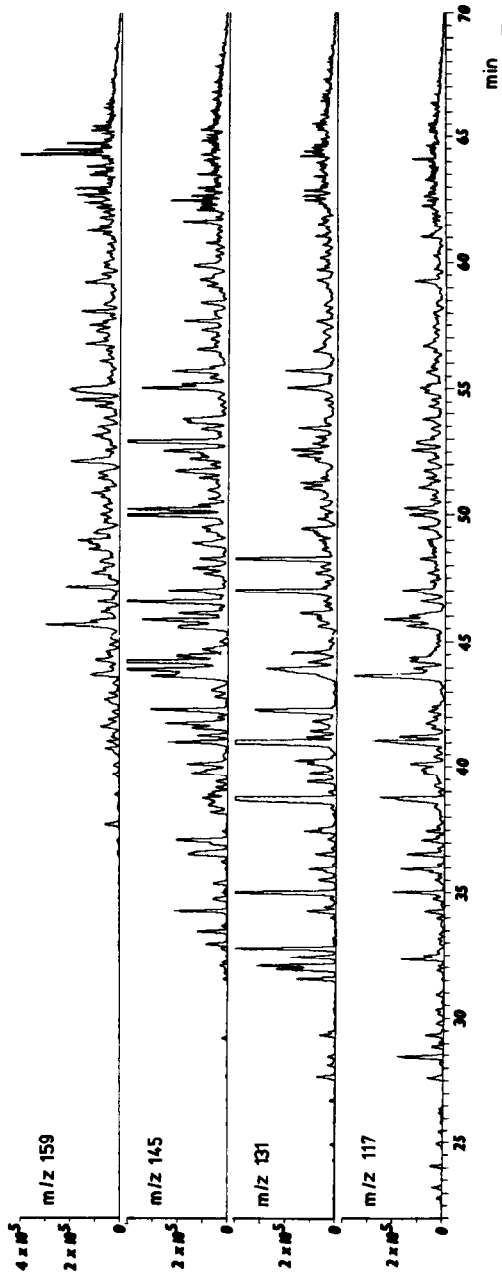
Fig. 3. Mass chromatogram of selective ions of indanes/tetralins in aromatic fraction of the raw material; experimental conditions as in Fig. 2.
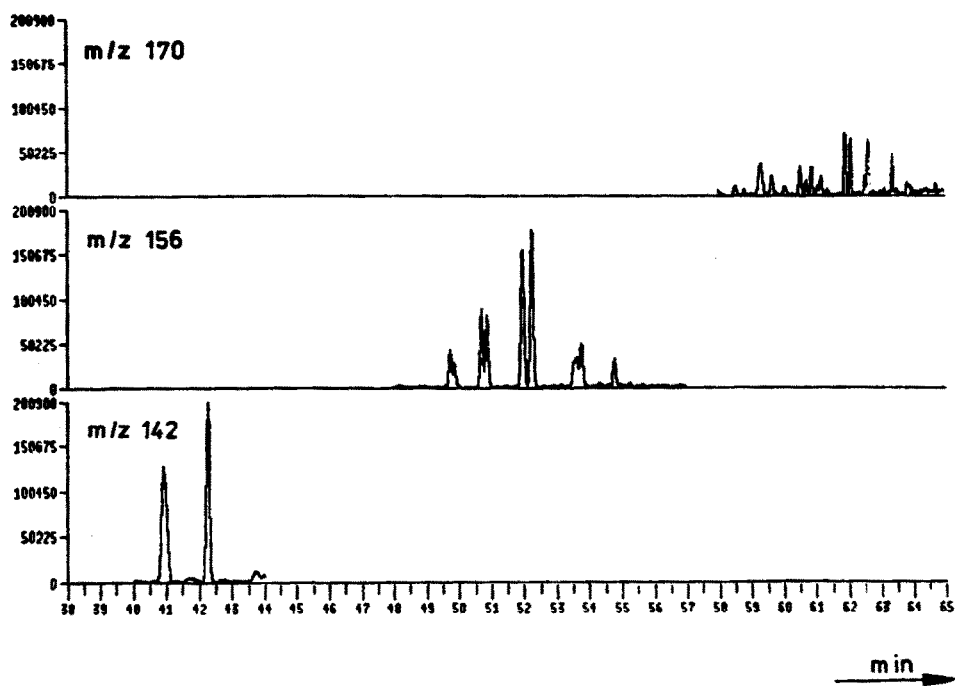
Fig. 4. Mass chromatogram of selective ions of napthalenes in aromatic fraction of the raw material; experimental conditions as in Fig. 2.

TABLE I

RETENTION INDICES (I) OF AROMATIC HYDROCARBONS DETERMINED IN AROMATIC FRACTION OF THE RAW MATERIAL OF THE TECHNOLOGY OF n-ALKANES ON OV-101 STATIONARY PHASE AT 100°C AND THEIR TEMPERATURE COEFFICIENTS ($\mathrm{d}I/\mathrm{d}T$)

Peak No.	Compound[a]	I	$\mathrm{d}I/\mathrm{d}T$	Peak No.	Compound[a]	I	$\mathrm{d}I/\mathrm{d}T$
6	1,3-DiEtB	1039.2	0.265	15	Unidentified	1078.2	0.270
7	1-Me-3-nPrB	1041.8	0.265	16	1,3-DiMe-2-EtB	1080.4	0.365
8	1,4-DiEtB + 1-Me-4-nPrB	1046.6	0.295	17	Me-iBuB or 2-Ph-3-MeButane	1091.9	0.290
9	nBuB	1048.0	0.225	18	1-Me-3-sBuB + 1,2-DiMe-3-EtB	1093.7	0.315
10	1,2-DiEtB	1051.3	0.325	18a	1-Et-2-iPrB + Me-iBuB		
11	1-Me-2-nPrB	1057.2	0.335		or 2-MePhButane	1098.0	0.305
12	1,4-DiMe-2-EtB	1066.7	0.290	18b	1-Me-4-sBuB	1100.0	0.305
13	1,3-DiMe-4-EtB	1068.6	0.310	19	1-Et-4-iPrB	1103.4	0.285
13a	Indane C_{10}	1069.7	0.445	20	Indane C_{10}	1103.4	—
14	1,2-DiMe-4-EtB	1074.4	0.300	21	2-Me-2-PhButane	1105.6	0.380
14a	Indane C_{10}	1074.4	0.460	22	1,2,4,5-TetraMeB + AB C_{11}	1106.4	0.380

TABLE I (*continued*)

Peak No.	Compound[a]	I	dI/dT	Peak No.	Compound[a]	I	dI/dT
23	1,2,3,5-TetraMeB	1108.7	0.440	57	Indane C_{11}	1212.4	0.450
24	iPeB	1111.1	0.320	58	Indane C_{11} + AB C_{12}	1213.4	0.385
25	Indane C_{11}	1114.4	0.440	59	1,2,4-TriMe-3-EtB	1214.5	0.475
26	1,4-DiMe-2-iPrB	1118.7	0.225	60	Indane C_{12}	1217.7	0.665
27	1-Et-3-nPrB	1124.4	0.265	61	1,4-Di-nPrB	1220.0	0.320
27a	5-MeIndane	1124.4	0.455	62	AB C_{12}	1222.2	0.325
28	1,2-DiMe-4-iPrB	1130.3	0.315	63	AB C_{12} + Indane C_{12}	1225.2	0.375
28a	1,3-DiEt-5-MeB	1130.3	–	64	AB C_{12}	1227.7	0.325
29	1,3-DiMe-5-nPrB	1132.4	0.345	64a	Indane C_{12}	1227.7	0.630
29a	AB C_{11}	1132.4	0.210	65	AB C_{12}	1231.7	0.360
30	Indane C_{10}	1133.5	0.560	66	1-Me-3-nPeB	1234.1	0.310
31	1-Me-3-nBuB	1139.4	0.265	67	AB C_{12}	1235.3	0.355
32	1,2,3,4-TetraMeB	1138.3	0.440	68	AB C_{12}	1237.7	0.340
33	Tetralin C_{10} + 1,4-DiEt-2-MeB (traces)	1143.2	0.550	69	Indane C_{11} + AB C_{12}	1240.2	0.585
33a	nPeB	1143.2	0.335	70	HeB (branched)	1242.0	0.335
34	1,4-DiMe-2-nPrB	1147.7	0.325	70a	Indane C_{12} + Indene C_{11} + AB C_{12}	1242.0	0.660
35	1,3-DiMe-4-nPrB	1152.0	0.330	71	1-Me-2-nPeB	1247.8	0.370
36	1-Me-2-nBuB	1153.0	0.335	71a	Indane-unidentified	1247.8	0.555
37	1,3-DiEt-2-MeB	1156.8	0.390	72a	AB C_{12} + AB C_{13}	1251.9	0.350
38	1,3-DiMe-2-nPrB	1160.1	0.330	72b	AB C_{12} + AB C_{13}	1253.4	0.275
38a	AB C_{11}	1160.1	0.330	72c	Indane C_{12}	1251.9	0.630
39	Indene-unidentified + Naph(traces)	1161.7	0.550	72	AB C_{12}	1253.4	0.440
40	MeIndane C_{11}	1666.6	0.465	73	Indane C_{12}	1255.5	0.325
41	Indane C_{11}	1170.4	0.465	74	AB C_{12}	1257.0	0.375
41a	1,2-DiEt-3-MeB + Indane C_{11} + 1-Et-3-sBuB	1170.4	0.275	75	AB C_{13} + Indane C_{12} (traces)	1259.7	0.315
42	Indane C_{11} + AB C_{12} (traces)	1171.9	0.480	76	AB C_{12}	1262.7	0.350
42a	AB C_{11}	1170.4	0.365	76a	AB C_{12}	1262.7	0.410
43	1-iPr-3-nPrB + Indane C_{11}	1175.3	0.545	77	Indane C_{11} + 2-MeNaph	1262.7	0.660
44	1,2-DiMe-3-nPrB	1176.3	0.505	78	AB C_{13} + Indane C_{12}	1265.1	0.625
45	MeIndane C_{11} + AB C_{12}	1179.3	0.510	79	Indane C_{12} + AB C_{12}	1267.0	0.670
46	1,3,5-TriMe-2-EtB + AB C_{12}	1182.3	0.355	80	Indane C_{12}	1268.9	0.710
47	1,2,5-TriMe-3-EtB + AB C_{12}	1183.5	0.295	81	AB C_{12} + AB C_{13}	1271.2	0.595
48	1-Et-4-sBuB	1186.4	0.310	82	AB C_{12} + Indane C_{12} (traces)	1272.0	0.655
48a	Indane C_{12} + AB C_{12}	1186.4	0.560	83	1-MeNaph	1273.0	0.825
49	1,4-DiMe-2-sBuB	1190.6	0.265	84	AB C_{12}	1274.3	0.710
49a	AB C_{12}	1191.7	0.210	85	Indane C12	1277.1	0.545
50	1,2,3-TriMe-5-EtB	1194.7	0.265	86	AB C_{13}	1279.0	–
51	MeTetralin + AB C_{12}	1194.7	0.570	87	AB C_{13} + Indane C_{12}	1281.0	–
52	1,3-DiMe-4-sBuB + AB C_{12}	1198.1	0.305	88	Indane C_{12} + AB C_{13}	1282.3	–
52a	AB C_{11} + Indane C_{12} (traces)	1202.2	0.335	89	AB C_{13}	1286.3	–
53	Indane C_{11}	1202.2	0.590	90	AB C_{13} + Indane C_{12}	1290.7	0.650
53a	MePeB	1202.2	0.277	91	Indane C_{12} + AB C_{13}	1293.1	0.810
54	AB-unidentified	1204.4	0.225	91a	MeHeB + Indane C_{12}	1293.1	0.345
55	1,3-Di-nPrB	1208.7	0.355	92	Indane C_{12}	1295.5	0.540
56	nPrMeEtB	1210.9	0.245	93	Indane C_{12} + AB C_{13}	1296.5	0.560
				94	AB C_{12} + Indane C_{12}	1298.5	0.735

[a] Abbreviations: Me = methyl; Et = ethyl; Pr = propyl; Bu = butyl; Pe = pentyl; He = hexyl; B = benzene; AB = alkylbenzene; Ph = phenyl; Naph = naphthalene.
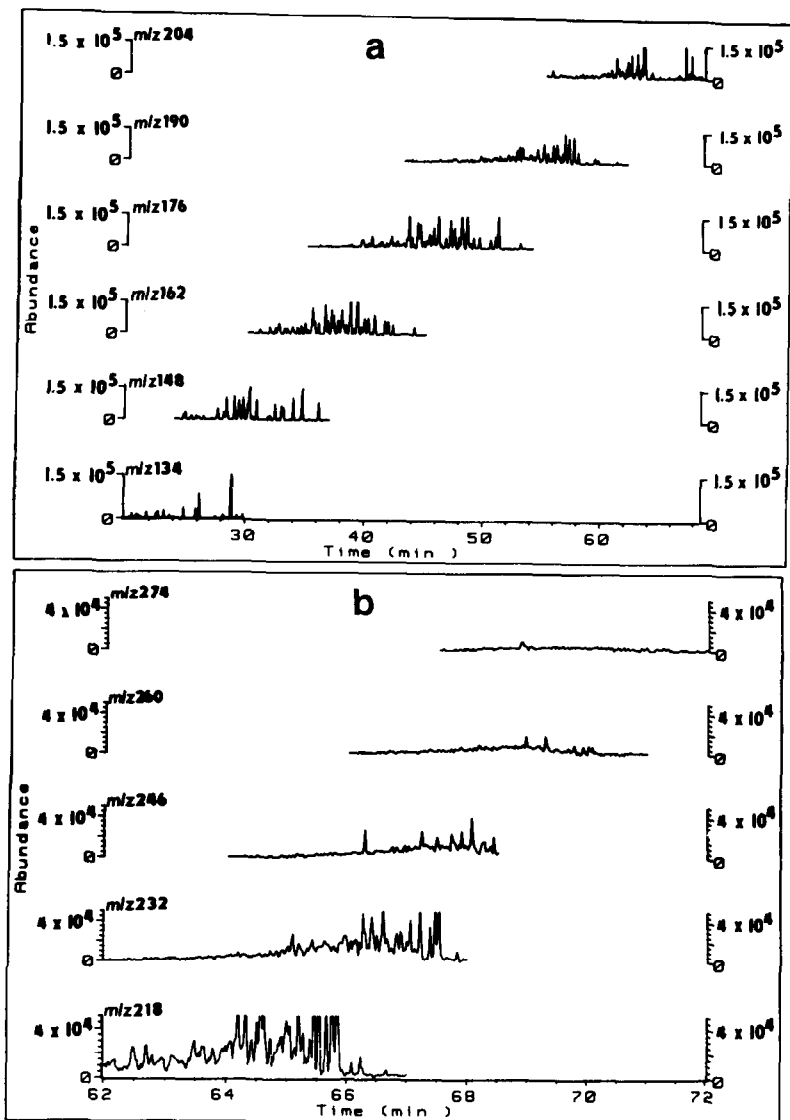
Fig. 5 (a) Alkylbenzene map C_nH_{2n-6}, where $n = 10–14$, of the aromatic fraction of the raw material; experimental conditions as in Fig. 2 (b). Alkylbenzene map C_nH_{2n-6}, where $n = 15–20$, of the aromatic fraction of the raw material; experimental conditions as in Fig. 2.

always possible. In these cases, using mass spectra and mass chromatograms, only the type of compound was determined. This comprises mainly the aromatics eluting in the upper part of the fraction with boiling points up to 270°C. In this region there is also a lack of published retention data (Table II).

As in the light fraction of the *n*-alkanes $C_9–C_{15}$ (boiling points range 151–270°C) higher-boiling-point aromatics of the petroleum fraction do not occur, de-

TABLE II

CHARACTERIZATION OF AROMATIC HYDROCARBONS BY GC–MS

Peak No.	Compound[a]	Peak No.	Compound[a]
95	Indene C_{12} + AB C_{13}	124	Indane C_{13} + AB C_{14}
96	AB C_{13} + Indane C_{13}	125	Naph C_{12} + Indane C_{13}
97	AB C_{13} + Indene C_{13} (traces)	126	Naph C_{12} + Indane C_{14}
98	AB C_{13} + Indane C_{12}	127	Indane C_{14} + Indene C_{13} + AB C_{14}
99	AB C_{13} + Indane C_{13}	128	Indane C_{13} + AB C_{14} + Acen C_{14}
100	Indane C_{13}	129	Indane C_{14} + AB C_{14}
101	AB C_{13}	130	Indane C_{13}
102	Indane C_{13} + AB C_{13}	131	Indane C_{14} + AB C_{14} + Naph C_{12}
103	Indane $C_{12,13}$ + AB C_{13}	132	Indane C_{13} + AB C_{14} + Naph C_{12}
104	AB C_{13}	133	Indane C_{14} + AB C_{14}
105	AB C_{13} + Indane C_{13}	134	AB C_{14} + Indane C_{13} + Indene C_{13}
106	AB C_{13}	135	Indane C_{13} + Naph C_{12}
107	Biphenyl + AB C_{13}	136	AB C_{14} + Indane C_{13}
108	Indane C_{12}	137	Indane C_{13}
109	AB C_{13}	138	Indane C_{13} + AB C_{14}
110	Indane C_{13} + AB C_{14}	139	Indane C_{13}
111	Indane C_{13} + AB C_{13}	140	Long chain AB C_{14}
112	Indane C_{13} + AB C_{13}	141	Long chain AB C_{14}
113	Indane C_{13} + AB C_{13}	142	AB C_{14} + Indane C_{13} (traces)
114	Indene C_{13} + Naph C_{12}	143	AB C_{14}
115	Naph C_{12} + Indane C_{13} + AB C_{14}	144	Long chain AB C_{14}
116	Indane C_{12} + Acen C_{13}	145	Acen C_{13} + AB C_{14}
117	Indane C_{12}	146	Indane C_{13}
118	AB C_{13} + Indane C_{14}	147	AB C_{14}
119	Indane C_{13} + AB C_{14} + Naph C_{12}	148	Indane C_{14} + Acen C_{13} (traces)
120	AB C_{13} + Naph C_{12}	149	Indane C_{14} + AB C_{15} (traces)
121	AB C_{13} + Indane C_{13} (traces)	150	AB C_{15} + Indene C_{14} + Indane C_{14-} +
122	Indane C_{14} + AB C_{14} + Indene C_{13}		Acen C_{14} + Naph C_{13}
123	Indane C_{13}		

[a] Abbreviations: AB = alkylbenzene; Naph = naphthalene; Acen = acenapthene.

tailed analysis of compounds eluted at the rapidly increasing portion of the temperature program (15°C/min) was not performed.

CONCLUSIONS

In the analysis of multicomponent samples the choice of separating system is very important, mainly in the case of single-column analysis. Though PONA columns are specially tailored for hydrocarbon analysis and offer high quality with respect to efficiency and thermal stability, they are insufficient to resolve complex hydrocarbon mixtures with a broader range of boiling points under optimized experimental conditions. The combination of GC–MS with EI ionization (mass fragmentography, selected-ion monitoring) is of great help in distinghuising various groups of compounds eluting in one peak (as alkanes, napthenes or aromatics). For the detailed identification of aromatic hydrocarbons it is necessary to separate different groups of com-

pounds to collect retention and mass spectral data which can be easily and unambiguously interpreted. In the petroleum fraction studied aromatic hydrocarbons were analysed in concentrate from the LC fraction. From measured isothermal retention data $(I, dI/dT)$ and mass spectral data (mass spectra, mass chromatograms) the following compounds of several aromatics groups were identified: 51 alkylbenzenes with carbon atom number C_9–C_{12}, one indane, three napthalenes and one biphenyl with the assignment of exact structure. The other components were characterized by carbon atom number and/or type of substituents but without assignment of final structures: 93 C_{11}–C_{15} alkylbenzenes, 82 C_{10}–C_{14} indanes/tetralins, nine C_{10}–C_{13} indenes, ten C_{11}–C_{13} napthalenes and six C_{12}–C_{14} acenapthenes/biphenyls.

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REFERENCES

1 G. Schomburg, *LC · GC*, 5 (1987) 304.
2 I. M. Whittemore, in K. H. Altgelt and T. H. Gouw (Editors), *Chromatography in Petroleum Analysis*, Marcel Dekker, New York, 1979, pp. 50–70.
3 E. M. Steward and E. W. Pitzer, *J. Chromatogr. Sci.*, 26 (1988) 218.
4 M. E. Fitzgerald, V. A. Cirillo and F. J. Galbraith, *Anal. Chem.*, 34 (1962) 1276.
5 E. J. Gallegos, J. W. Green, L. P. Lindeman, R. L. Le Turneau and R. M. Teeter, *Anal. Chem.*, 39 (1967) 1833.
6 S. Zadro, J. K. Haken and W. V. Pinczewski, *J. Chromatogr.*, 323 (1985) 305.
7 B. Kumar, R. K. Kuchhal, P. Kumar and P. L. Gupta, *J. Chromatogr. Sci.*, 24 (1986) 99.
8 E. Matisová, *J. Chromatogr.*, 438 (1988) 131.
9 C. L. Stuckey, *J. Chromatogr. Sci.*, 7 (1969) 177.
10 E. Matisová, J. Krupčík, P. Čellár and A. Kočan, *J. Chromatogr.*, 346 (1985) 17.
11 M. G. Block, R. B. Callen and J. H. Stockinger, *J. Chromatogr. Sci.*, 15 (1977) 504.
12 P. van Arkel, J. Beens, H. Spaans, D. Grutterink and R. Verbeek, *J. Chromatogr. Sci.*, 26 (1987) 141.
13 F. P. Di Sanzo, J. L. Lane and R. E. Yoder, *J. Chromatogr. Sci.*, 26 (1988) 206.
14 F. P. Di Sanzo and V. J. Giarrocco, *J. Chromatogr. Sci.*, 26 (1988) 258.
15 J. Curvers and P. van der Sluys, *J. Chromatogr. Sci.*, 26 (1988) 267.
16 J. Curvers and P. van der Engel, *J. Chromatogr. Sci.*, 26 (1988) 271.
17 E. Matisová, M. Rukgrílová, J. Krupčík, E. Kovačicová and Š. Holotík, *J. Chromatogr.*, 455 (1988) 301.
18 P. Kuráň, *Thesis*, Faculty of Chemical Technology, Slovak Technical University, Bratislava, 1989.
19 *Annual Book of ASTM Standards*, Part 24, American Society for Testing and Material, Philadelphia, PA, 1975, method D2549-68.
20 J. A. Lubeck and D. L. Sutton, *J. High Resolut. Chromatogr. Chromatogr. Commun.*, 6 (1983) 328.
21 E. Matisová, E. Kovačicová, P. T. Ha, E. Kolek and W. Engewald, *J. Chromatogr.*, 475 (1989) 113.
22 E. Matisová and P. Kuráň, *Chromatographia*, 30 (1990) 328.
23 A. F. Sljachov, B. I. Anvaer, O. V. Zolotareva, N. N. Romina, N. N. Novikova and R. I. Koreskova, *Zh. Anal. Chim.*, 30 (1975) 788.
24 W. Engewald, L. Wennrich and E. Ritter, *J. Chromatogr.* 174 (1979) 315.
25 V. A. Gerasimenko, A. V. Kirilenko and V. M. Nabivach, *J. Chromatogr.*, 208 (1981) 9.
26 V. A. Gerasimenko and V. M. Nabivach, *Zh. Anal. Khim.*, 37 (1982) 110.
27 T. Tóth, *J. Chromatogr.*, 279 (1983) 157.
28 E. Matisová, E. Kovačicová, J. Garaj and G. Kraus, *Chromatographia*, 27 (1989) 494.