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

II. Trace aromatics in an *n*-alkane matrix

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ABSTRACT

The achievement of and problems with the trace analysis of multi-component mixtures are demonstrated on a complex organic mixture containing trace amounts of numerous aromatic substances in an *n*-alkane matrix with a boiling range of 151–270°C. Qualitative analysis of trace aromatics was performed, after a preseparation step, on a preconcentrated LC fraction by high-resolution capillary GC–MS with electron impact ionization from mass spectra, mass chromatograms using a single-column separation system (HP-PONA column) and splitless injection. With direct injection of the sample and selected-ion monitoring of aromatics there were problems with interferences from ions of the matrix. 185 aromatic compounds belonging to various aromatic groups (mainly alkylbenzenes, indanes, tetralins, naphthalenes and acenaphthenes) were identified at concentrations of individual aromatics in the range 10^{-3}–10^{-6}%.

INTRODUCTION

In a previous paper [1] we demonstrated the achievement of and problems with the qualitative analysis of multi-component mixtures for a complex hydrocarbon sample. We have shown the possibilities of using single-column capillary GC (with a commercially available, chemically bonded, non-polar silicone capillary column) for the detailed analysis of aromatic hydrocarbons in a petroleum fraction with a boiling range of 150–350°C, which is the raw material for the production of *n*-alkanes. The emphasis was placed on identification of aro-

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matics with a boiling range of 150–270°C. The concentration of the aromatics was approximately equal to that of the constituents of other hydrocarbon groups (alkanes, naphthenes). Single-column high-resolution capillary GC [2–4] and multi-dimensional GC systems fail in the separation aromatics from compounds of other hydrocarbon groups in complex mixtures with broad ranges of boiling points [5]. For highly complex samples, aromatics were analysed in the concentrate from a liquid chromatographic fraction. Capillary columns with non-polar silicone stationary phase were chosen for their good selectivity towards alkylbenzenes and good inter-laboratory reproducibility [6,7].

For better selectivity of non-polar silicones (compared with squalane), donor–acceptor interactions of the free electron pairs of oxygen and π-electrons of the aromatic ring [8] should be responsible. With squalane there are only dispersion forces. The characterization of individual aromatics (256) was based on a combination of isothermal retention data (on OV-101) and mass spectral data measured under optimized temperature-programmed (TPG) conditions using PONA fused-silica capillary columns, which are special-purpose cross-linked methylsilicone phase columns tailored for hydrocarbon analysis (alkanes, alkenes, naphthenes, aromatics). Mass spectral data for aromatic compounds can be unambiguously interpreted [9–11]. It was shown that a combination of GC–MS with electron impact (EI) ionization (mass chromatography, mass fragmentography) is a great help in distinguishing various groups of compounds eluting in one peak [1,12].

This part of the work was intended to show the possibilities and difficulties of the analysis of aromatics in multi-component mixtures at trace concentrations. During the preparation of *n*-alkanes from the raw material [1], small amounts of aromatics pass into the final product. As aromatics are potential carcinogens, the quality of *n*-alkanes, utilized as the raw materials in various other technologies, depends also on the composition and content of aromatics.

For trace analysis it was necessary to take into consideration the nature and concentration of the compounds being analysed and the nature of the sample matrix in deciding whether a preseparation and/or preconcentration step was needed and in choosing the correct system for sample introduction, separation and detection [13–17]. In this paper stress is laid on qualitative analysis. With respect to the appropriate sample amounts for GC (for identification purposes), coupling with mass spectrometry (GC–MS) is the best choice of coupled techniques.

EXPERIMENTAL

Gas chromatography was performed with a Model 5890A Series II gas chromatograph equipped with split–splitless injection, flame ionization detection (FID), a Model 3396A integrator and Vectra Model ES/12 personal computer (Hewlett-Packard, Avondale, PA, USA). The analysis was carried out on a PONA fused-silica capillary column (Hewlett-Packard) with 0.5-μm film thickness (50 m × 0.2 mm I.D.). Hydrogen was used as carrier gas at a linear velocity of 40 cm/s for TPG conditions adjusted to the initial temperature of the temperature programme. In the split injection mode (1:70) the TPG conditions were from 70 to 160°C at 1.5°C/min, then to 220°C at 15°C/min and held for 15 min. With splitless injection the septum purge flow-rate was 2 ml/min and a flow of 49 ml/min passed the split outlet; the split valve was closed for 1.0 min during injection. Splitless injections (liner, 7.8 cm × 2 mm I.D.) were performed with the column at 35°C; this temperature was held for 1 min, then increased at 10°C/min to 70°C, at 1.5°C/min to 160°C and finally at 15°C/min to 220°C, which was held for 15 min. The injector and detector temperatures were 270 and 300°C, respectively.

GC–MS measurements with 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 5970B mass-selective detector (MSD) (Hewlett-Packard) with a direct interface. All experimental work was done on a PONA column under the given TPG conditions with helium as the carrier gas at a linear velocity of 38 cm/s at the initial temperature of the temperature programme. The other instrumental conditions were as follows: in the total ion current (TIC) and SIM modes, detector temperature 275°C, electron multiplier voltage 2200 V and treshold 1000; in the TIC mode, scan speed 1.4 scans/s; in the SIM mode, scan speed 2.8 scans/s and dwell time 100 ms.

Trace aromatics were analysed in a C_9–C_{14} *n*-

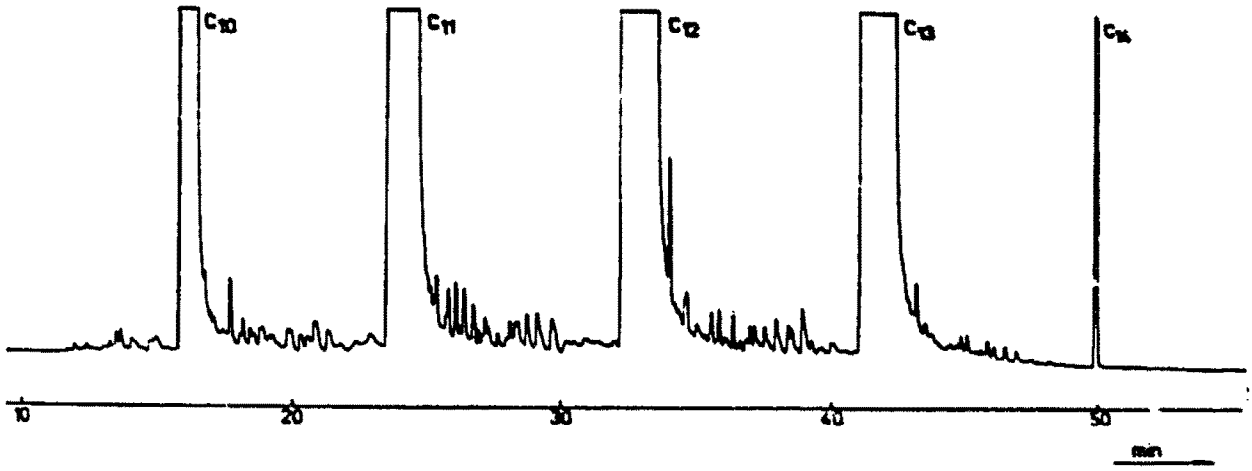

Fig. 1. Gas chromatogram of the light fraction of *n*-alkanes on an HP PONA column with temperature programming from 70°C at 1.5°C min to 160°C; carrier gas, hydrogen at 40 cm/s; split injection (1:70); volume injected, 0.15 μl; detection FID.

alkane matrix with the following composition: C_9, 0.004%; C_{10}, 15.541%; C_{11}, 32.720%; C_{12}, 30.195%; C_{13}, 21.314%; and C_{14}, 0.031% (boiling range 151–270°C). Aromatics were isolated by column liquid chromatography on silica gel and preconcentrated in dichloromethane [18]. Isolated aromatic fractions in dichloromethane were injected (1 μl) with a 10-μl Hamilton syringe with a 0.8-μl plug of solvent using the hot needle injection technique. In direct injection of the final product of *n*-alkanes, 0.15–0.2 μl was injected with a 1-μl Hamilton syringe; the analytical column was connected with a retention gap (2 m × 0.53 mm I.D. fused-silica uncoated tubing) using a press-fit connector.

RESULTS

The study of the composition of trace aromatics in a complex *n*-alkane matrix by direct measurement of GC retention data is impossible. As an il-

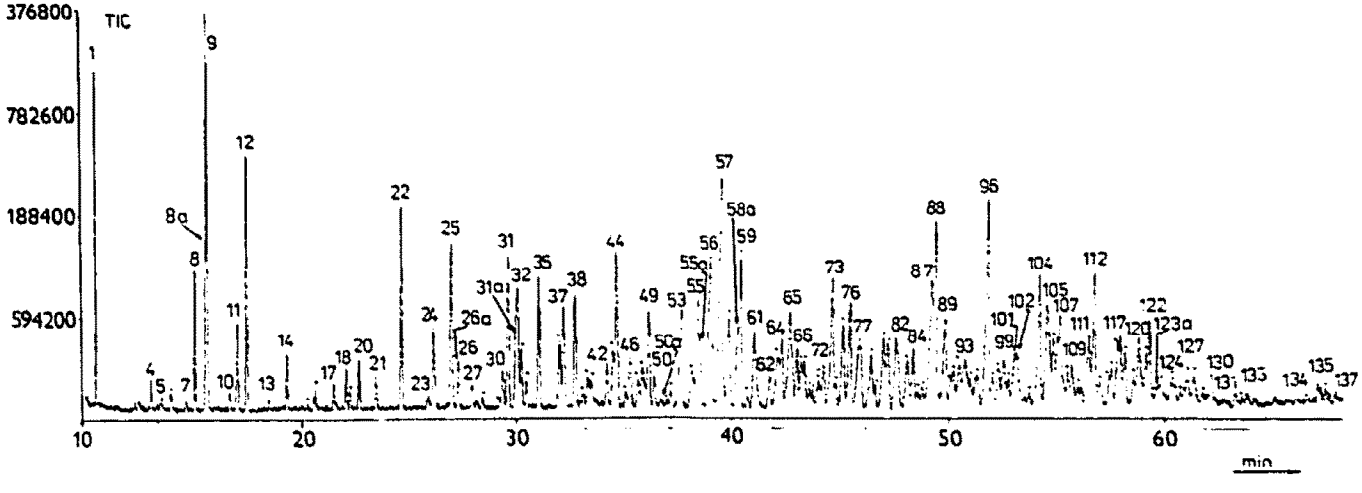

Fig. 2. TIC chromatogram of isolated trace aromatics in dichloromethane on an HP PONA fused-silica capillary column; carrier gas, helium at 38 cm/s; splitless injection; temperature programme, 35°C, held for 1 min, then increased at 10°C min to 70°C, at 1.5°C min to 160°C and at 15°C min to 220°C, held for 15 min. Peak designation is given in Table I; peaks that are not included there come from the blind experiment on the isolation procedure [17].

lustration, the gas chromatogram of the light fraction of *n*-alkanes on a PONA column under TPG conditions with split injection is shown in Fig. 1.

To follow the qualitative distribution of aromatics from the raw material (a petroleum fraction) to the final product of *n*-alkanes, GC–EI-MS as a fundamental method was utilized. Qualitative analysis of trace aromatics was performed in two ways: after preseparation in the LC fraction, by GC–MS collecting mass spectra and mass chromatograms, and by the direct injection of the sample (without preseparation) by selected-ion monitoring (SIM). A single high-resolution column with immobilized polydimethylsilicone was used. The experimental conditions (splitless injection, TPG conditions) were optimized using FID.

Analysis of trace aromatics after preseparation from the matrix

For the detailed analysis of individual aromatics, it was necessary to collect mass spectra. From Fig. 1 it follows that owing to the overwhelming concentration of *n*-alkanes (a matrix consisting of 99.81% C_9–C_{14} *n*-alkanes plus a small amount of isoalkanes) there is co-elution with several aromatics, and with the use of splitless injection the co-elution

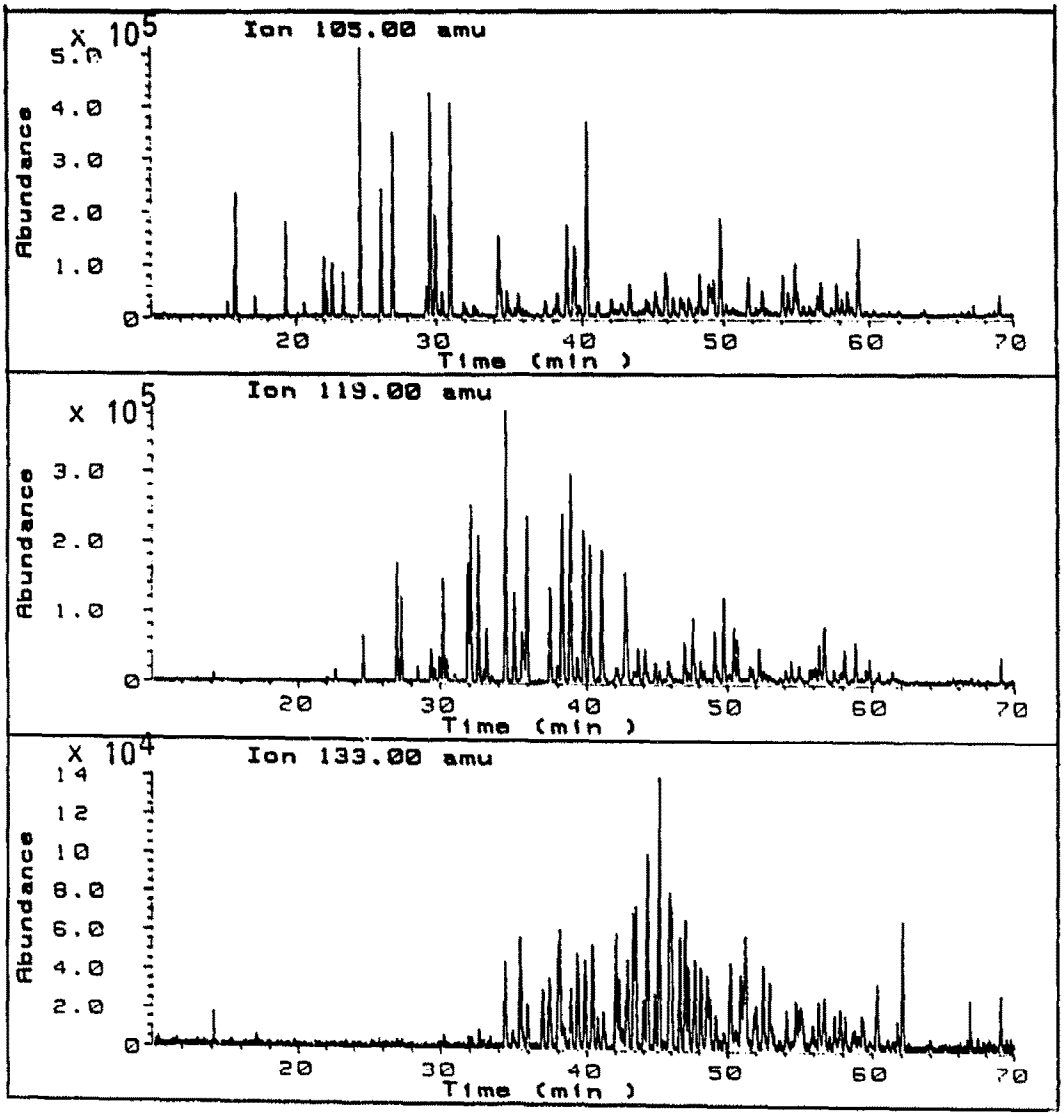

Fig. 3. Mass chromatograms of selected ions of alkylbenzenes of isolated trace aromatics. Experimental conditions as in Fig. 2.

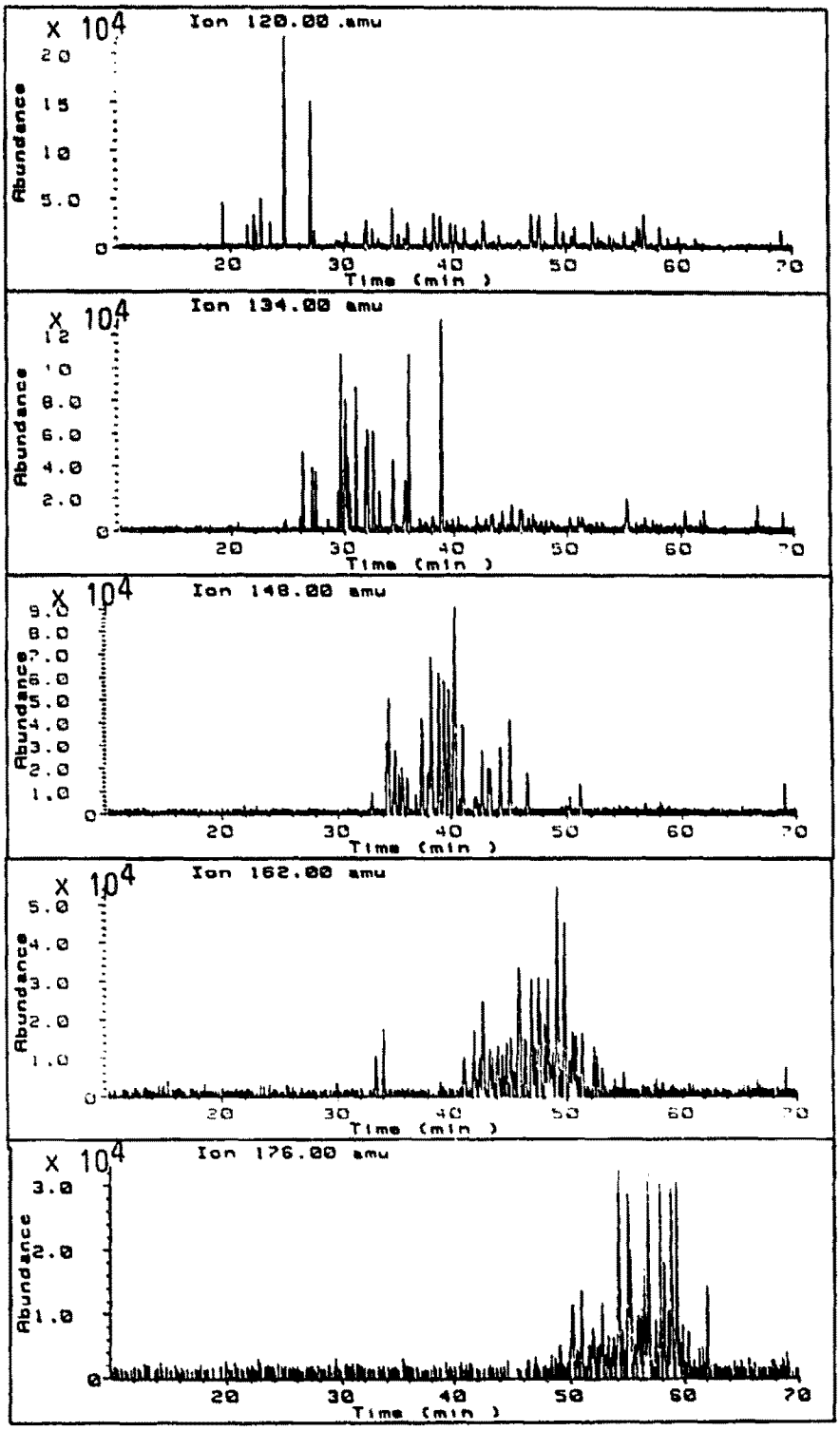

Fig. 4. Mass chromatograms of molecular ions of alkylbenzenes of isolated trace aromatics. Experimental conditions as in Fig. 2.

TABLE I

RESULTS OF ANALYSIS OF TRACE AROMATICS IN *n*-ALKANE MATRIX

Peak No.	Compound[a]	$\bar{X}$ (10^{-4}%)[b]	R.S.D. (%)
1	MeB	10.48	4.3
8	EtB	6.01	4.8
8a	1,3-DiMeB	5.34	5.1
9	1,4-DiMeB	16.61	4.8
10	C_8H_8 (styrene)	0.71	5.3
11	1,2-DiMeB	3.77	6.0
14	iPrB	4.28	6.7
17	nPrB	1.87	4.1
18	1-Et-3-MeB	3.29	4.9
19	1-Et-4-MeB	1.53	6.2
20	1,3,5-TriMeB	3.17	9.2
21	1-Et-2-MeB	1.82	5.7
22	1,2,4-TriMeB	17.00	10.0
23	tBuB	1.44	31.0[c]
24	sBuB	6.74	2.1
25	1,2,3-TriMeB + 1-Me-3-iPrB	15.04	5.5
26	1-Me-4-iPrB	3.50	4.9
27	Indane C_9	1.89	6.5
28	1-Me-2-iPrB	8.19	6.8
29	1-Me-3-nPrB	0.49	26.3[d]
30	1,3-DiEtB	2.89	6.4
31	1-Me-4-nPrB	11.11	5.4
31a	1,4-DiEtB	5.00	5.2
32	nBuB	10.02	6.6
33	1,3-DiMe-5-EtB	4.43	6.5
34	1,2-DiEtB	2.42	7.1
35	1-Me-2-nPrB	9.92	5.3
36	1,4-DiMe-2-EtB	4.91	5.4
37	1,3-DiMe-4-EtB	8.48	5.1
38	1,2-DiMe-4-EtB + indane C_{10}	9.47	7.4
39	1-Et-PrB	1.29	12.1[c]
40	1,3-DiMe-2-EtB	2.35	7.0
43	1-Et-3-iPrB	4.78	3.5
44	1-Me-3-sBuB + 1,2-DiMe-3-EtB	14.52	4.9
45	1-Et-2-iPrB	1.25	4.1
46	1-Me-4-sBuB	3.82	4.7
47	1,3-DiMe-5-iPrB	2.27	4.7
48	1,2,4,5-TetraMeB + AB C_{11}	3.92	5.4
49	1,2,3,5-TetraMeB	8.21	4.7
50	iPeB	2.79	4.5
52	1,4-DiMe-2-iPrB	1.21	6.1
53	1-Et-3-nPrB	9.91	5.8
54	1,2-DiMe-4-iPrB	2.56	7.5
55	1,3-DiMe-5-nPrB	16.77	5.2
55a	Me-indane		
56	1,2,3,4-TetraMeB + AB C_{11}	11.02	5.5
57	1,4-DiEt-2-MeB + tetralin C_{10}	16.98	5.1
58	1,4-DiMe-2-nPrB	10.06	10.9
59	1-Me-2-nBuB	13.65	4.4
60	1,3-DiEt-2-MeB	0.81	11.2[c]
61	DiMe-nPrB + Naph + AB C_{12}	8.06	4.3
62	DiMe-indane C_{11} + AB C_{12}	2.96	3.6

TABLE I (continued)

Peak No.	Compound[a]	$\bar{X}$ (10^{-4}%)[b]	R.S.D. (%)
63	DiMe-indane C_{11}	7.14	3.3
64	DiMe-indane C_{11}	7.06	3.0
65	1,2-DiMe-3-nPrB + DiMe-indane C_{11}	11.75	4.8
66	DiMe-indane C_{11}	9.13	4.6[d]
67	1,2,5-TriMe-3-EtB + indane C_{12}	9.63	18.8[d]
68	1,3,5-TriMe-2-EtB + AB C_{12}		
69	1-Et-4-sBuB	2.51	31.7[d]
70	Indane C_{12}		
71	DiMe-sBuB	3.26	6.3
72	1,2,3-TriMe-5-EtB	3.88	5.3
73	Me-tetralin C_{11}	12.13	5.0
74	1,3-DiMe-4-sBuB	4.49	10.4
75	1,2,4-TriMe-3-EtB	5.81	5.2
76	Indane C_{11}	10.79	4.9
77	1,3-Di-nPrB	9.14	6.4
78	AB C_{12} + indane C_{11}	4.77	6.4
79	1,2,3-TriMe-4-EtB	1.79	7.0
80	1,2,4-TriEtB	11.88	4.5
81	1-Me-3-nPeB + indane C_{11}		
82	1-Et-4-nBuB + indane C_{12}	6.97	4.5
83	1,2,3-TriEtB + indane C_{12}	2.48	4.9
84	1-Me-2-nPeB	4.84	5.0
85	AB C_{12}	1.53	5.1
86	AB C_{12} + AB C_{13}	1.95	3.8
87	AB C_{12}	27.83	5.6
88	Indane C_{11}		
89	AB C_{12}	9.57	5.5
90	AB C_{13} + indane C_{12}	1.36	9.9
91	AB C_{12} + AB C_{13}	3.64	8.2
92	AB C_{12} + indane C_{12}	4.93	7.0
93	AB C_{12} + indane C_{12}	5.73	6.0
94	AB C_{13}	3.53	9.4
95	AB C_{12}	3.61	7.6
96	Indane C_{11} + MeNaph	22.10	5.4
97	AB C_{13} + indane C_{12}	3.29	7.4
98	AB C_{12} + AB C_{13} + indane C_{12}	4.81	6.0
99	AB C_{13} + AB C_{12} + indane C_{12}	3.55	31.5[c]
100	AB C_{13} + indane C_{12}	2.72	8.0
101	AB C_{13} + indane C_{12}	9.01	5.6
102	Indane C_{12} + MeNaph		
103	AB C_{13} + indane C_{13}	0.83	9.4[c]
104	AB C_{13}	15.76	3.9
105	Indane C_{12}	9.81	6.6
106	Indane C_{12}	7.29	7.6
107	AB C_{13} + indane C_{12}	3.99	10.3
108	Indane C_{12}	1.22	15.0[d]
109	Indene C_{12}	2.03	9.6
110	AB C_{13}	1.23	13.4[c]
111	AB C_{13} + indane C_{12} + indane C_{11}	6.80	5.6
112	AB C_{13} + indane C_{12}	7.40	5.6[d]
113	Indane C_{12} + indane C_{13}	7.52	17.0[c]
114	AB C_{13} + indane C_{12} + indane C_{13}	4.10	11.4[c]
115	Indane C_{12}		

(Continued on p. 316)

TABLE I *(continued)*

Peak No.	Compound[a]	$\bar{X}$ (10^{-4}%)[b]	R.S.D. (%)
116	AB C_{13}	9.74	7.0
117	Indane C_{12}		
118	AB C_{13}	3.35	11.8[d]
119	AB C_{13} + indane C_{13}	3.11	15.4[d]
120	AB C_{13}	5.72	7.6
121	AB C_{14} + biphenyl	2.92	10.6[d]
122	AB C_{13} + indane C_{12}	4.80	10.1
123	AB C_{14} + indane C_{13}	0.99	17.9[d]
124	Indane C_{13} + AB C_{13} + AB C_{14}	1.42	20.6[c,d]
125	AB C_{13} + AB C_{14} + indane C_{13}	3.49	20.7[d]
126	AB C_{14} + indane C_{13}	1.00	23.8[d]
127	Indane C_{12} + Naph C_{12} + MeAcen	2.66	11.7[e]
128	Indane C_{12} + indane C_{13}	1.93	15.7[e]
129	AB C_{13} + AB C_{14}	0.69	30.0[d]
130	AB C_{13} + DiMeNaph	1.64	16.1[e]
131	Naph C_{12}	1.01	10.3[e]
132	AB C_{14} + Naph C_{12}	0.60	11.5[e]
133	Indane C_{12} + indane C_{13} + MeAcen	0.38	11.8[e]
134	AB C_{14} + indane C_{13}	0.23	12.6[e]
135	AB C_{14}	1.22	10.4[e]
136	AB C_{14}	0.32	11.8[e]
137	AB C_{15} + indane C_{13} + MeAcen	0.43	12.9[e]

[a] Abbreviations: Me = methyl; Et = ethyl; Pr = propyl; Bu = butyl; Pe = pentyl; B = benzene; AB = alkylbenzene; Naph = naphthalene; Acen = acenaphthene; n = normal; i = iso-; s = sec.-; t = *tert.*-.

[b] $\bar{X}$ (%) = mean value of aromatics content from four GC determinations (n = 4) in mass%.

[c] Small peaks.

[d] Poorly resolved peaks.

[e] Pair of compounds which in some analyses were integrated as individual peaks and in other analyses were integrated as one peak.

is much more apparent. Therefore, a preseparation step was used [18]. Aromatics were isolated from the matrix by column LC on silica gel. The recovery of components across the complete boiling point range was greater if preconcentration of the dichloromethane fraction was performed by distillation rather than vacuum evaporation. Recoveries for the whole procedure were thoroughly studied using a model mixture and were found to be 80.67% within the confidence interval $L_{1,2}$ (R) ± 8.26% at a significance level of 95% (α = 0.05).

The TIC chromatogram of aromatics in concentrated form (LC fraction) is given in Fig. 2. Identification using the combined technique was based on information obtained from interpretation of the acquired mass spectra and mass chromatograms of selected ions of characteristic aromatic groups found in the mixture (alkylbenzenes, indanes/tetralins, indenes, naphthalenes and acenaphthenes/biphenyls); examples for alkylbenzenes, the most frequently occurring compounds in the multi-component mixture studied, are given in Figs. 3 and 4.

The acquired mass spectra and mass chromatograms of the molecular ions of trace aromatics made possible the determination of the molecular mass and carbon numbers of the individual components and/or the type and number of substituents. In many instances mixed mass spectra were obtained and from the mass chromatograms of selected ions it was possible to confirm the number or the type of compounds eluted in one peak. The data obtained for trace aromatics in the *n*-alkane matrix (Table I) were compared with those published in Part I (aromatics in a petroleum fraction at percentage concentrations) [1]. The concentration of individual aromatics in the light fraction of *n*-alkanes is included in Table I and was found to be in the range 10^{-3}–10^{-6}%, which corresponds to 10–10^{-2} ppm.

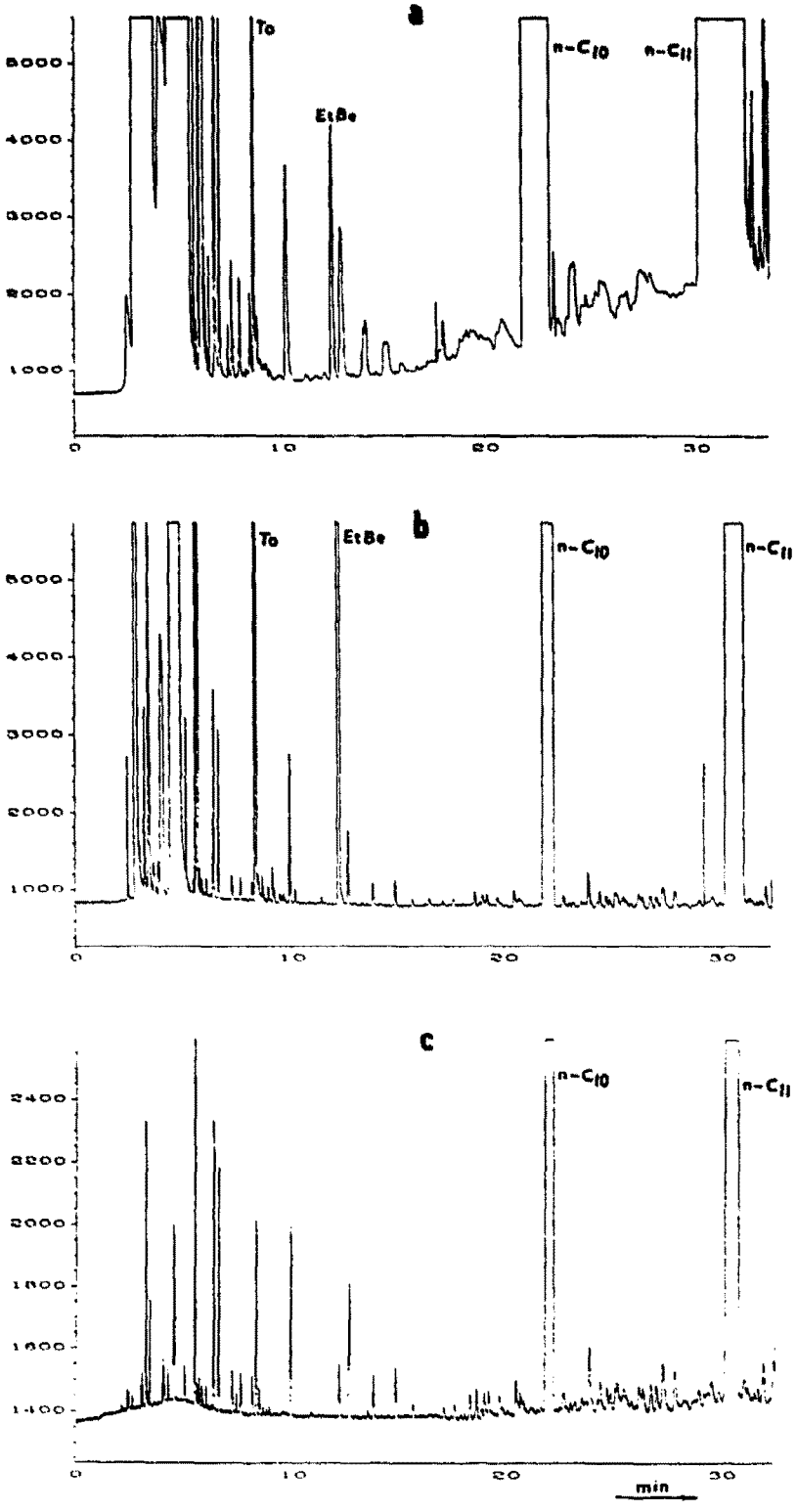

Fig. 5. Part of the chromatogram of the light fraction of *n*-alkanes on an HP PONA column under TGP conditions (as in Fig. 2) with hydrogen as carrier gas, splitless injection and FID. (a) Volume of sample injected 0.2 μl [with 10 ppm standard addition of toluene (To) and ethylbenzene (EtBe)] and $CHCl_3$ 0.8 μl; (b) same conditions as in (a) with a precolumn (2 m × 0.53 mm I.D. uncoated fused-silica tubing); and (c) same conditions as in (b) without standard additions in the sample and without any solvent.

We have discussed the reproducibility of the GC determination of individual trace aromatics and the overall aromatic content (including the isolation procedure) in a recent paper [18]. It can be concluded that most aromatics (within the given boiling point range) passed from the raw material into the *n*-alkane final product in about the same mutual relative abundance.

Direct analysis of trace aromatics in an n-alkane matrix by SIM

To establish the distribution of aromatics from the raw material to the final product of *n*-alkanes, we tried to apply SIM for two reasons: aromatics in the raw material were known [1] and to overcome the tedious preseparation step. The aim of SIM is not to obtain detailed data on the individual aromatics, but rather group-type information, carbon number. After the direct injection of the sample with splitless injection we encountered chromatographic problems (peak broadening; peak splitting) and problems with interferences from ions from the matrix.

The first question to be solved was peak broadening and peak splitting after direct sample injection. To improve the peak shape by utilizing the solvent effect we injected the sample (with standard addition of toluene and ethylbenzene to follow the effect) with a solvent. By trial and error we tested several solvents (dichloromethane, pentane, hexane, chloroform, benzene), various solvent combinations and optimized parameters of splitless injection [19], but without succes. On analysing aromatics in dichloromethane after the preseparation step there were no problems with peak shape when using splitless injection (Figs. 2–4). With direct injection the matrix of the sample (*n*-alkanes) gave problems in achieving good solvent effect for aromatic compounds. The best results were obtained with chloroform; a gas chromatogram obtained with FID is shown in Fig. 5a, although also in this instance the results were not sufficient for further GC–MS measurements. From the results obtained it can be concluded that it was difficult to find a solvent that fulfils the demands concerning its boiling point and

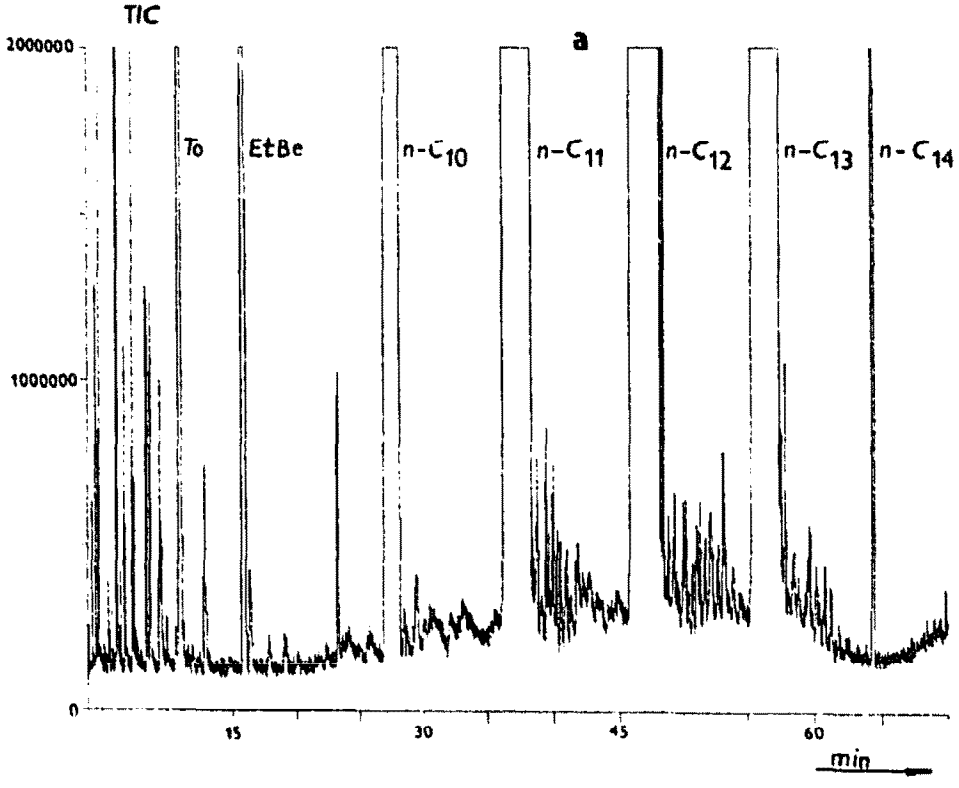

Fig. 6.

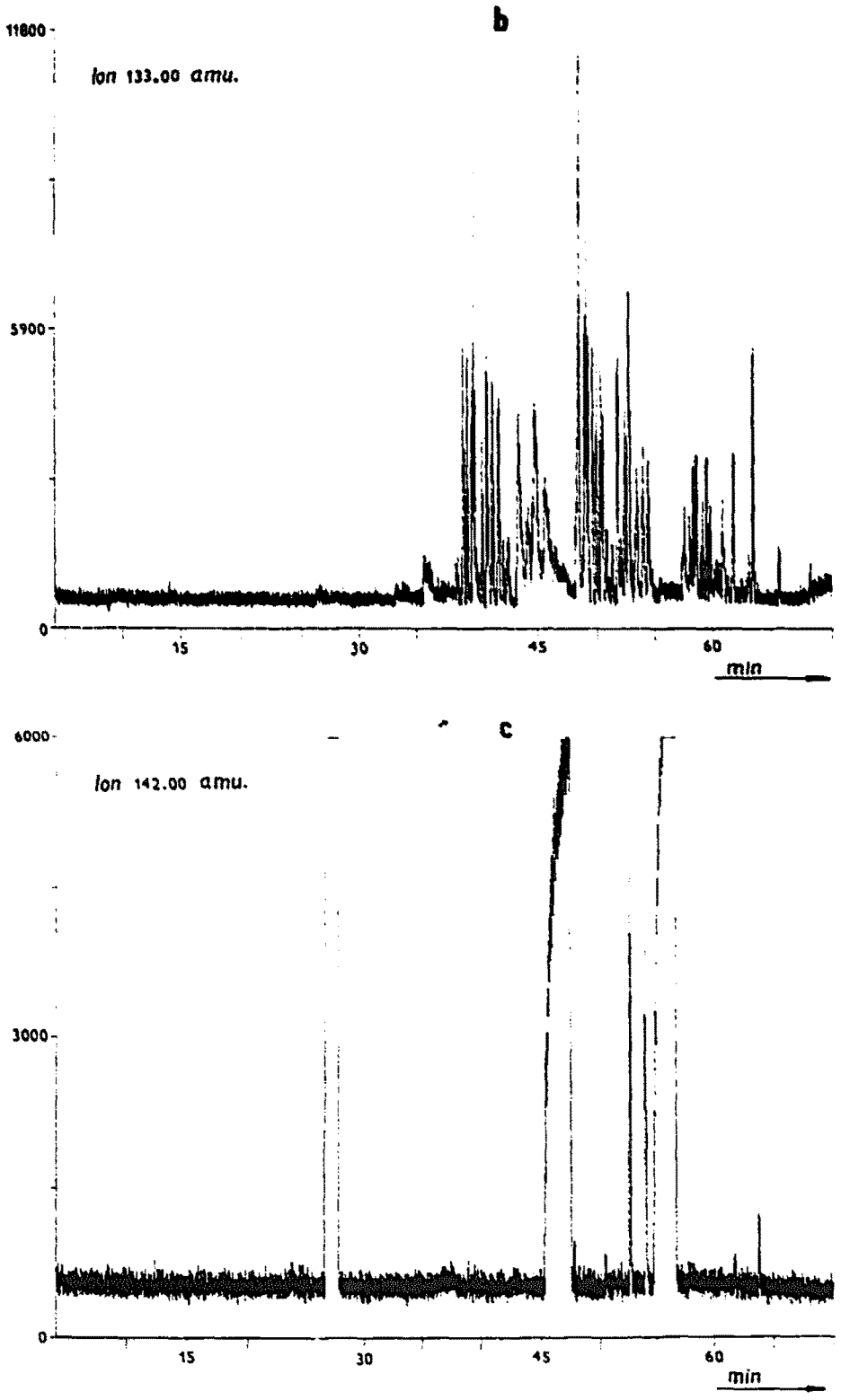

Fig. 6. GC–MS of the light fraction of *n*-alkanes by direct injection of the sample with the retention gap. Other experimental conditions as in Fig. 2. (a) TIC chromatogram with standard addition of toluene (To) and ethylbenzene (EtBe); (b) SIM of alkylbenzenes (ion of *m/z* 133); (c) SIM of naphthalenes (ion of *m/z* 142).

its polarity towards the analyte compounds, stationary phase and sample matrix. Band broadening in space can be suppressed by stationary phase focusing via a retention gap [20,21]. All the solutes that are spread over the flooded zone are carried on to the stationary phase where they are retained. In our case, after connection of the analytical column (using a press-fit connector) with a precolumn, all the problems were solved; good peaks shape were obtained with co-injection of the sample with any solvent (Fig. 5b) or without a solvent (Fig. 5c).

The second problem we encountered with SIM was interferences from ions from the matrix. Although *n*-alkanes show completely different characteristic ions to aromatics, a thorough study of the mass spectra of compounds of the matrix showed that there are small ions which at very high concentrations of matrix compounds are monitored in addition to specific ions of aromatic compounds at trace concentrations (*e.g.*, naphthalenes, indenes). Another problem was disturbances to the monitoring trace ions of aromatics during the elution of matrix compounds (alkylbenzenes, indanes/tetralins, acenaphthenes/biphenyls). Examples are given in Fig. 6.

CONCLUSIONS

In the analysis of multi-component organic mixtures with components present in trace concentrations in a complex sample matrix, the application of a single-column separation system with splitless injection of trace components by capillary GC and GC–EI-MS was useful. A preseparation step was found to be necessary.

For trace aromatics (in the range 10^{-3}–10^{-6}% by mass) in an *n*-alkane matrix (99.81% C_9–C_{14}) plus a small amount of isoalkanes, it was shown that the identification of individual aromatics is necessary after a preseparation step [18] for several reasons. Several aromatics are co-eluted with *n*-alkanes. Although we used a very efficient system (PONA columns under optimized conditions), it was insufficient to resolve complex mixtures. Group-type characterization according to classes of aromatic compounds (alkylbenzenes, indanes/tetralins, indenes, naphthalenes and acenaphthenes/biphenyls) by direct injection of the sample and SIM was not possible, although chromatographic problems (peak splitting, peak broadening) were solved, as there were serious problems with interferences from ions from the matrix. 185 individual C_7–C_{15} aromatics were characterized (from mass spectra and mass chromatogram) in the concentrate from the LC fraction.

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