Identification of C_2–C_4 alkylated benzenes in flash pyrolysates of kerogens, coals and asphaltenes*

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ABSTRACT

Pseudo-Kováts indices were determined for all positional isomers of C_2–C_4 alkylated benzenes using a non-polar capillary column (CP Sil-5). These indices were applied in combination with mass spectral data to identify these compounds in complex mixtures of a relatively non-polar nature generated upon flash pyrolysis of macromolecular sedimentary organic matter (kerogens, asphaltenes and coals). Alkylbenzene distribution patterns were constructed by integration of appropriate mass chromatograms. Generally, toluene is the major pyrolysis product. Other specific alkylated benzenes (*e.g.* 1,2,3,4-tetramethylbenzene and 1-methyl-4-isopropylbenzene) were found to be enhanced in flash pyrolysates of different samples. Flash pyrolysates of asphaltene and kerogen fractions isolated from the same oil shale exhibit similar alkylbenzene distributions.

INTRODUCTION

Complex mixtures of relatively non-polar organic compounds are commonly encountered in the analysis of the composition of soils, sediments and fossil fuels. High-resolution gas chromatography (GC) is nowadays commonly used to separate such complex mixtures, to enable the identification of the individual compounds present with mass spectrometry (MS). Similar complex mixtures are obtained by analytical pyrolysis (controlled thermal dissociation in an inert atmosphere) of high-molecular-weight, relatively non-polar material. Flash pyrolysis (Py) coupled on-line with GC–MS is frequently applied to characterize natural, high-molecular-weight substances present in kerogens and coals, and to screen polluted soil and sediment samples for anthropogenic substances [1,2].

Owing to the complexity of the mixtures [generally mixtures of *n*-alkenes, *n*-alkanes, saturated and aromatic (poly)cyclic hydrocarbons as well as heteroatom-containing compounds], it is often not possible to identify all compounds present using only mass spectral data. For example, isomeric alkylbenzenes have similar mass spectra and require additional retention time data for unequivocal identification.

The GC retention behaviour of aromatic hydrocarbons, including alkylbenzenes, has been the subject of many studies [3–7]. Many relatively polar stationary phases (Carbowax 20M; UCON-LB 550X; Tris-cyanoethoxypropane) and various temperature programmes have been used to achieve optimal GC separation and to determine accurate, reproducible retention indices [8]. However, to separate complex mixtures in extracts of soils, sediments and fossil fuels as well as pyrolysates of kerogens and coals, non-polar stationary phases (*e.g.* CP Sil-5; Squalane; DB-5; OV-101) are preferred. It is, therefore, apparent that retention indices for alkylbenzenes on non-polar stationary phases are essential for the reliable identification of these com-

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pounds in complex mixtures such as those obtained from pyrolysis of natural materials.

In this paper we report the relative retention indices of C_2–C_4 alkylated benzenes determined with a capillary column coated with CP Sil-5. These data enabled the full identification of these compounds in pyrolysates of kerogens, coals and asphaltenes. The samples described in this paper are representative examples of different types of organic matter ranging from aliphatic-rich substances to those mainly composed of condensed polyaromatic material (kerogen types I, II and III) [9]. The geochemical applications of this work will be discussed elsewhere [10].

EXPERIMENTAL

Origin and preparation of kerogen samples

The Mulhouse kerogen was isolated from a marl layer (No. 6) from the Mi_1-bed of the Salt IV unit from the Lower Oligocene Mulhouse Potash Basin (Alsace, France). The sample was selected from a suite of rock layers sampled in the Amélie Concession, Gallery 830 [11]. The Jurf ed Darawish Oil Shale (Jordan) is a Cretaceous deposit of immature bituminous calcareous marl stones [12]. The sample investigated is a composite sample from 156–157 m taken from a core. The organic matter present in this sample has a high sulphur content [13] and is marine-derived. The Estonian kerogen is from an Ordovician deposit [14], mainly comprising fossil remains of the extinct alga *Gloeocapsomorpha prisca*. The Beulah Zap coal is selected from the Argonne Premium coal set [15]. This coal sample was taken from the upper Palaeocene Sentinel Butte Formation (North Dakota, USA) [16].

The Mulhouse and Jurf ed Darawish kerogen samples were grounded in a rotary disc mill and extracted for 24 h in a soxhlet apparatus with methanol–toluene (3:1, v/v). The powdered Estonian kerogen was extracted for 12 h at room temperature by chloroform–methanol (2:1, v/v). The carbonate minerals present in the Mulhouse residue after extraction were removed by treatment with 6 M hydrochloric acid at room temperature. The neutralized and dried residue was re-extracted ultrasonically with methanol and dichloromethane to yield the concentrated Mulhouse kerogen fraction. All kerogen samples were dried in a vacuum stove at 40°C

overnight. The asphaltene fraction of the Jurf ed Darawish sample was isolated from the corresponding bitumen by precipitation with *n*-heptane [17]. The coal sample was powdered and used without further treatment for pyrolysis.

Authentic standards

Twenty-four alkylbenzene standards were commercially available from Aldrich. Ten C_4 alkylated benzenes were obtained from the collection of standards of the Organic Chemistry Division of Delft University (Delft, Netherlands).

The ethyldimethyl-substituted C_4 alkylated benzenes were kindly provided by Dr. T. Tóth (University of Budapest, Budapest, Hungary) and Dr. J. P. E. M. Rijks (Technical University Eindhoven, Eindhoven, Netherlands). The standards provided by Dr. Tóth were synthesized via a Friedel Crafts ethylation of the appropriate dimethylbenzene [18]. Fractional distillation of mixtures of alkylbenzenes was performed by Rijks [19] to obtain the pure isomers. Structural assignments were made by chromatographic and spectroscopic studies.

The synthesis of 1-methyl-3-propylbenzene and 1-methyl-4-propylbenzene was performed via a Grignard reaction. Two equivalents of ethylbromide were converted to the corresponding alkylmagnesiumhalide and subsequently coupled to 3-methylbenzaldehyde and 4-methylbenzaldehyde, respectively, in diethyl ether under reflux. The resulting secondary alcohol function was removed by ionic hydrogenolysis with triethylsilane in trifluoracetic acid [20,21]. The products were obtained in 80% overall yield.

Gas chromatography

GC was performed with a Hewlett-Packard 5890 Series II instrument, using an on-column injector. Detection was accomplished using a flame ionization detector. Helium was used as the carrier gas. Separation was achieved using a fused-silica capillary column (25 m × 0.32 mm I.D.) coated with CP Sil-5 (film thickness 0.45 μm). The alkylbenzene standards were injected at 0°C in hexane (*ca.* 0.05 μl/ml), except for benzene, which was injected in *n*-pentane. The gas chromatograph, equipped with a cryogenic unit, was held at its initial temperature of 0°C for 5 min and then programmed at a rate of 3°C/min to 320°C, at which temperature it was held for 10 min.

Gas chromatography–mass spectrometry

GC–MS was carried out using a Hewlett-Packard 5890 Series II gas chromatograph connected to a VG-70S mass spectrometer by direct insertion of the capillary column into the ion source. Electron-impact spectra were obtained at 70 eV using the following conditions: cycle time 1.8 s; resolution 1000; mass range m/z 50–900. Separation was achieved using the same capillary column and temperature programme as described for GC analyses.

Curie point pyrolysis–gas chromatography

Flash pyrolysis experiments were performed using a FOM-3LX Curie point pyrolysis unit [22] directly connected to the injector of a Hewlett-Packard 5890 Series II gas chromatograph. Samples were pressed on flattened ferromagnetic wires (iron–nickel alloy; Curie temperature 610°C) as described by Venema and Veurink [23]. The on-line flash pyrolysis was performed by inductive heating of the wire in 0.15 s to its final temperature using a high-frequency generator (Fischer, Model 9425).

Separation of the pyrolysis products was achieved using a fused-silica column (25 m × 0.32 mm I.D.) coated with CP Sil-5 (film thickness 0.45 μm). Helium was used as the carrier gas. The oven was programmed from 0°C (5 min) to 320°C (10 min) at a rate of 3°C/min.

Curie point pyrolysis–gas chromatography–mass spectrometry

Curie point Py–GC–MS analysis was performed using the same conditions as described for Py–GC, using a similar Curie point device and gas chromatograph connected to a magnetic sector mass spectrometer (VG-70S) as described above. Alkylbenzenes present in the kerogen pyrolysates were analysed by constructing accurate mass chromatograms using m/z values of 78, 92, 106, 120 and 134 (window 0.03).

Retention index measurements

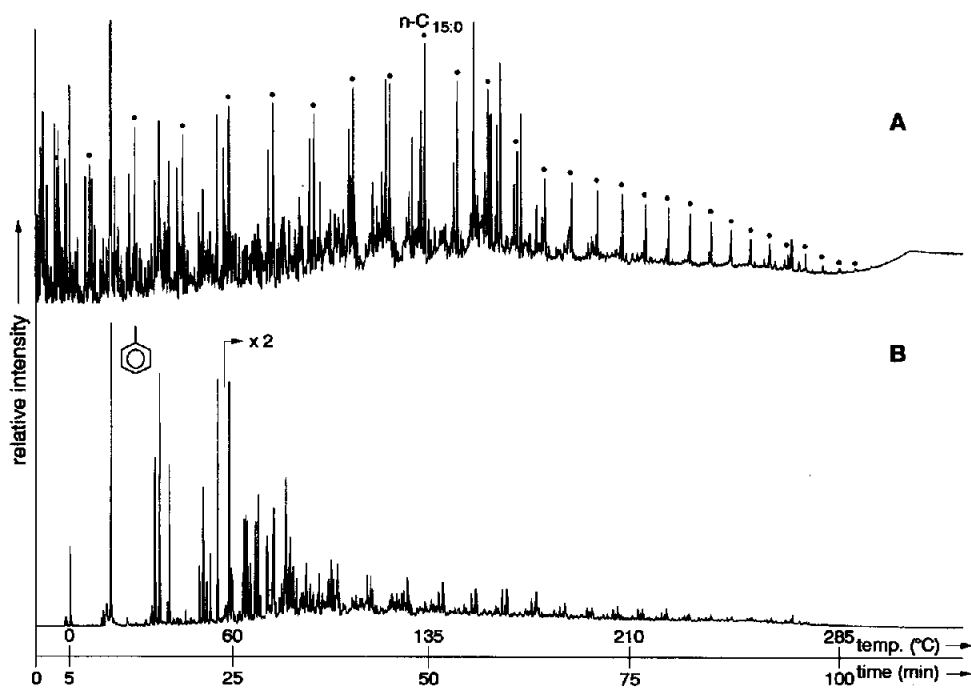The retention indices of all alkylbenzene standards were determined by co-injection of each indi-

Fig. 1. (A) Total ion current of the flash pyrolysate (Curie temperature 610°C) of the Mulhouse kerogen and (B) summed accurate mass chromatogram (m/z 78.12 + 91.13 + 92.14 + 105.16 + 106.17 + 119.18 + 120.19 + 133.21 + 134.22 + 147.23 + 148.24) showing the distribution of akylbenzenes. Dots indicate *n*-alkanes.

vidual standard with a mixture of n-alkanes (C_6–C_{15}) using a non-isothermal temperature programme of the GC oven from 0°C (5 min) to 320°C at a rate of 3°C/min. A function was obtained by fitting a third-order polynomial equation to the data points (retention times) of the homologous series of n-alkanes. Subsequently, the pseudo-Kováts indices of the alkylbenzene standards were calculated using this regression function. The measurements were performed four times to determine the standard deviation.

Calculation of the retention indices of alkylbenzenes present in flash pyrolysates was performed using the scan number of peaks in the reconstructed total ion current or mass chromatogram corresponding to these alkylbenzenes and the regression function generated using the homologous series of n-alkanes present in the pyrolysates.

RESULTS AND DISCUSSION

Fig. 1A shows the total ion current (TIC) trace of the flash pyrolysate of the Mulhouse kerogen. Accurate mass chromatograms of relevant m/z values show that the complex mixture of compounds generated is dominated by n-alkenes, n-alkanes and alkylbenzenes. Branched alkanes are also present in relatively high abundance. Alkylcyclohexanes, alkylnaphthalenes, alkylthiophenes and alkylbenzo[b]thiophenes are minor constituents of the pyrolysate.

Fig. 1B shows an accurate, summed mass chromatogram (m/z 78 + 91 + 92 + 105 + 106 + 119 + 120 + 133 + 134) to illustrate the complex distribution of the alkylbenzenes. The ions used to generate this mass chromatogram are the most abundant ions in the mass spectra of the alkylbenzenes. Therefore, this summed mass chromatogram provides a quantitatively representative picture of the alkylbenzene distribution present in the flash pyrolysate of the Mulhouse kerogen. An accurate mass chromatogram was constructed because a mass chromatogram using nominal m/z values also contains contributions from alkylated benzothiophenes. Although toluene is the single most abundant pyrolysis product, alkylbenzenes of higher molecular weight are also abundant. Mass chromatography using m/z values of the molecular ions is a useful tool to analyse individual clusters of alkyl-

benzenes with the same molecular weight in the pyrolysate of the Mulhouse kerogen. Fig. 2 has been constructed on this basis and shows the accurate mass chromatograms of m/z values 78, 92, 106, 120 and 134. Each individual cluster of alkylbenzenes with the same molecular weight has been normalized to the most abundant isomer present. This approach provides insight into the internal distribution of isomeric alkylbenzenes present in the pyrolysate.

Mass spectra of low-molecular-weight alkylbenzenes have been reported [24,25]. The base peak for most alkylated alkylbenzenes results from cleavage of the benzylic bond and loss of the largest alkyl substituent. Exceptions to this general rule are tri- and tetramethylated alkylbenzenes (e.g. Fig. 3F), which show base peaks at $M^+ - 15$. A rearrangement involving neighbouring methyl groups which leads to the stabilized tropylium ion explains this fragmentation behaviour [26]. Mass spectra of positional isomers are often very similar (e.g. compare Fig. 3D and E). As a result, it is possible to discriminate only isomers with different alkyl substituent(s) (Fig. 3). Complementary relative retention time data, therefore, are required to identify all positional isomers.

Determination of the retention indices of the C_0–C_4 alkylated benzenes was performed by co-injection of each individual alkylbenzene standard with a mixture of n-alkanes on a CP Sil-5 capillary column using a non-isothermal temperature programme of the GC oven (see Experimental section). It was decided to study the distribution of alkylated members only upon to C_4 because of the large number of isomers involved above C_4. For example, it is possible to have 51 isomers for C_5 alkylated benzene. Table I shows a list of the measured pseudo-Kováts indices of all isomers of the C_0–C_4 alkylated benzenes. The maximum standard deviation (calculated from four measurements) is 0.4 index units. The pseudo-Kováts indices of alkylbenzenes were in good agreement with those obtained from the pyrolysate, which were calculated using the scan numbers in the mass chromatograms of these compounds and the regression function generated using the scan numbers of the homologous series of C_6–C_{12} n-alkanes present in the pyrolysate.

The complete qualitative identification enabled a detailed quantitative investigation of the distribu-

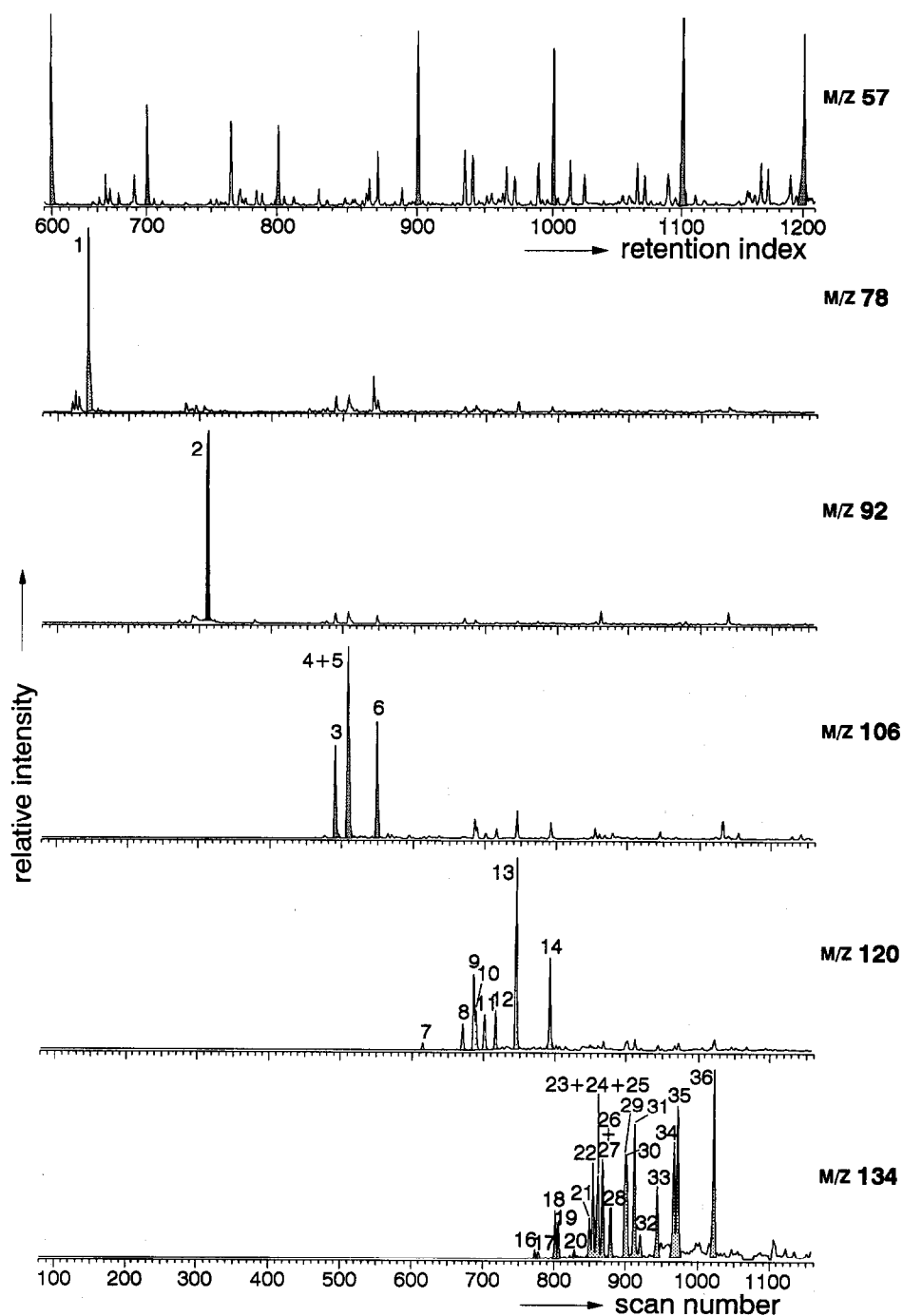Fig. 2. Partial accurate mass chromatograms of the flash pyrolysate (Curie temperature 610°C) of the Mulhouse kerogen showing the distribution of C_6–C_{12} n-alkanes (m/z 57) and the C_0–C_4 alkylated benzenes (m/z 78.12, 92.14, 106.17, 120.19 and 134.22). Peak numbers refer to compounds listed in Table I.
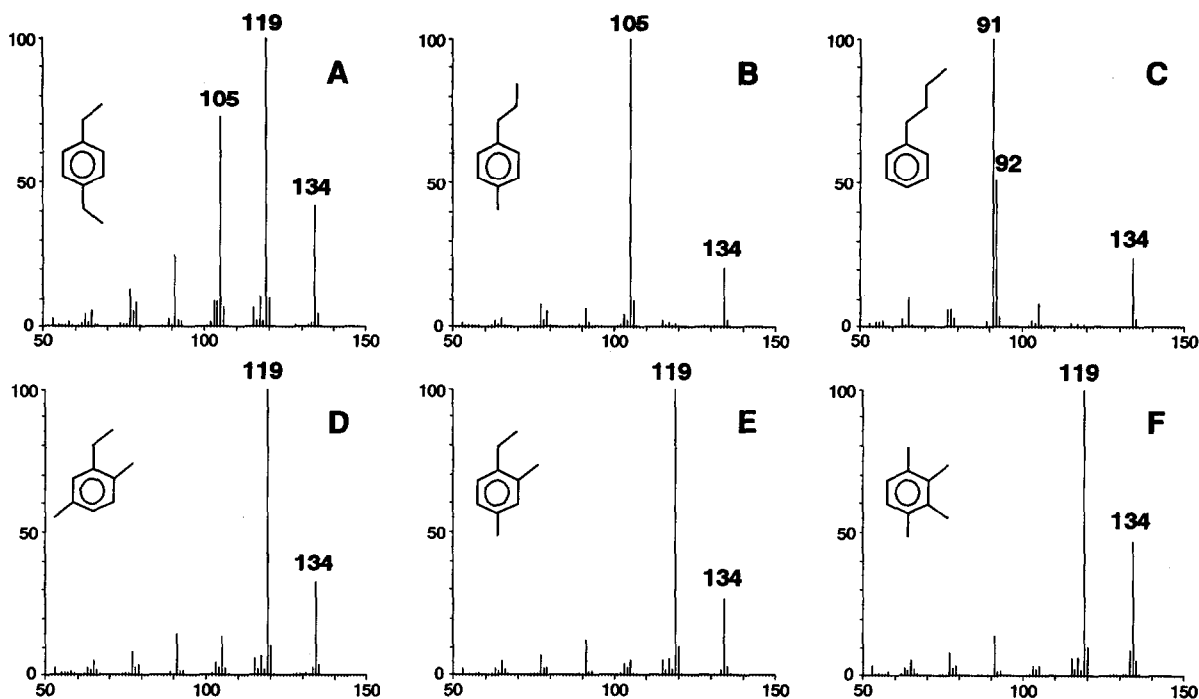
Fig. 3. Mass spectra of authentic C_4 alkylated benzenes: (A) 1,4-diethylbenzene, (B) 1-methyl-4-propylbenzene, (C) n-butylbenzene, (D) 1,4-dimethyl-2-ethylbenzene, (E) 1,3-dimethyl-4-ethylbenzene, (F) 1,2,3,4-tetramethylbenzene.

tion patterns of these compounds in flash pyrolysates by integration of peak areas from partial mass chromatograms (Fig. 2), taking into account different abundances of molecular ion peaks in the mass spectra of different alkylbenzenes (Fig. 3). These differences were taken into account by multiplying the obtained peak areas by a correction factor, calculated from the mass spectra of the authentic standards by taking the inverse of the percentages of the total ion current (Table I) of the relevant m/z value and multiplying it by 100. This approach was successfully applied for non-coeluting compounds.

To calculate peak areas of coeluting compounds, differences in their mass spectra were used. 1,4-Diethylbenzene, 1-methyl-4-propylbenzene and n-butylbenzene exhibit similar retention behaviour (see Table I).

Relative concentration of 1-methyl-4-propylbenzene and 1,4-diethylbenzene were calculated by integration of the peak areas in the partial mass chromatograms of m/z 105 and 119 separately. Mass fragment m/z 119 is almost absent in the mass spectrum of 1-methyl-4-propylbenzene (Fig. 3B). As a

result, the corresponding peak area in the partial mass chromatogram of m/z 119 is derived almost exclusively from 1,4-diethylbenzene. The peak area of 1-methyl-4-propylbenzene was calculated by correcting the peak area obtained from the partial mass chromatogram m/z 105 for the contribution of 1,4-diethylbenzene.

The relative concentration of n-butylbenzene was determined by integrating the peak area in the partial mass chromatogram of m/z 92. This characteristic mass fragment, resulting from a McLafferty rearrangement, can be attributed almost entirely to n-butylbenzene (Fig. 3C). Afterwards, the results of the calculation method used were checked. Calculated peak areas of 1,4-diethylbenzene, 1-methyl-4-propylbenzene and n-butylbenzene were converted to their corresponding peak areas of m/z 134 using their mass spectral data and subsequently summed. Comparison of this summed area with the peak area obtained by integration of the appropriate peak in the partial mass chromatogram m/z 134 showed a good match (error within 1%). In a similar manner the peak areas of 1,3-dimethyl-5-ethyl-

TABLE I

RETENTION INDICES OF LOW-MOLECULAR-WEIGHT ALKYLBENZENES IDENTIFIED IN KEROGEN PYROLY-SATES

No.[a]	Compound	Mol.wt.	I[b]	S.D. (n = 4)	Characteristic ions[c]
1	Benzene	78	640.0	0.0	77(7), 78(38)
2	Toluene	92	746.4	0.0	91(40), 92(29)
3	Ethylbenzene	106	841.8	0.1	91(44), 105(3), 106(14)
4	1,3-Dimethylbenzene	106	851.1	0.2	91(32), 105(9), 106(21)
5	1,4-Dimethylbenzene	106	851.3	0.1	91(33), 105(10), 106(21)
6	1,2-Dimethylbenzene	106	871.6	0.1	91(35), 105(6), 106(14)
7	Isopropylbenzene	120	906.2	0.2	91(3), 105(49), 120(13)
8	n-Propylbenzene	120	936.0	0.3	91(65), 105(2), 120(13)
9	1-Methyl-3-ethylbenzene	120	944.0	0.3	91(5), 105(43), 120(14)
10	1-Methyl-4-ethylbenzene	120	945.9	0.2	91(5), 105(46), 120(13)
11	1,3,5-Trimethylbenzene	120	951.8	0.3	105(35), 119(5), 120(21)
12	1-Methyl-2-ethylbenzene	120	960.2	0.1	91(5), 105(46), 120(14)
13	1,2,4-Trimethylbenzene	120	975.5	0.4	105(38), 119(5), 120(19)
14	1,2,3-Trimethylbenzene	120	1000[d]	–	105(40), 119(5), 120(19)
15	tert.-Butylbenzene	134	975.4	0.4	91(21), 119(37), 134(8)
16	Isobutylbenzene	134	991.5	0.4	91(44), 92(23), 134(11)
17	sec.-Butylbenzene	134	994.0	0.3	91(7), 105(51), 134(9)
18	1-Methyl-3-isopropylbenzene	134	1005.6	0.3	91(8), 119(45), 134(12)
19	1-Methyl-4-isopropylbenzene	134	1008.4	0.3	91(8), 119(46), 134(11)
20	1-Methyl-2-isopropylbenzene	134	1020.7	0.3	91(9), 119(44), 134(11)
21	1,3-Diethylbenzene	134	1032.1	0.3	105(24), 119(26), 134(12)
22	1-Methyl-3-propylbenzene	134	1034.5	0.3	105(51), 134(12)
23	1,4-Diethylbenzene	134	1038.0	0.3	105(20), 119(28), 134(12)
24	1-Methyl-4-propylbenzene	134	1038.1	0.4	105(58), 134(12)
25	n-Butylbenzene	134	1038.9	0.1	91(43), 92(22), 134(10)
26	1,3-Dimethyl-5-ethylbenzene	134	1041.6	0.2	119(40), 134(15)
27	1,2-Diethylbenzene	134	1042.5	0.3	105(23), 119(23), 134(11)
28	1-Methyl-2-propylbenzene	134	1048.6	0.3	105(55), 134(12)
29	1,4-Dimethyl-2-ethylbenzene	134	1059.5	0.3	119(43), 134(14)
30	1,3-Dimethyl-4-ethylbenzene	134	1060.7	0.3	119(49), 134(13)
31	1,2-Dimethyl-4-ethylbenzene	134	1066.7	0.3	119(43), 134(13)
32	1,3-Dimethyl-2-ethylbenzene	134	1071.7	0.3	119(44), 134(12)
33	1,2-Dimethyl-3-ethylbenzene	134	1085.2	0.3	119(42), 134(13)
34	1,2,4,5-Tetramethylbenzene	134	1097.8	0.3	119(39), 134(20)
35	1,2,3,5-Tetramethylbenzene	134	1100[d]	–	119(40), 134(20)
36	1,2,3,4-Tetramethylbenzene	134	1130.4	0.4	119(40), 134(19)

[a] Numbers refer to Figs. 3, 4, 5 and 6.
[b] Pseudo-Kováts index.
[c] Percentages of the total ion current are given in parentheses.
[d] Coelution with n-alkane.

benzene and 1,2-diethylbenzene were calculated.

It was not possible to determine mathematically the relative concentrations of 1,3-dimethylbenzene and 1,4-dimethylbenzene because of almost identi-cal retention behaviour and mass spectral data of these compounds.

This mathematical procedure enables the full identification of all C_0–C_4 alkylated benzene iso-
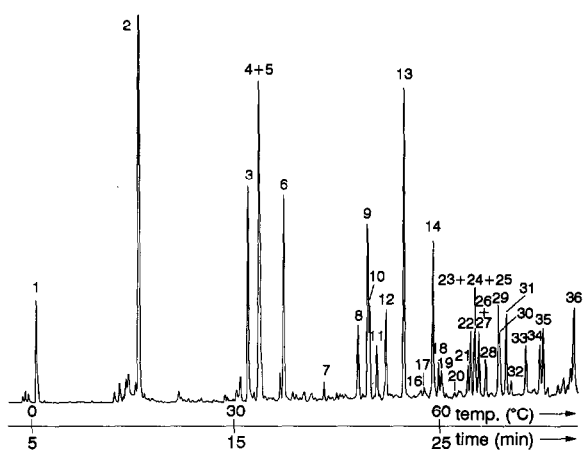
Fig. 4. Partial summed accurate mass chromatogram (m/z 78.12 + 91.13 + 92.14 + 105.16 + 106.17 + 119.18 + 120.19 + 133.21 + 134.22) of the flash pyrolysate (Curie temperature 610°C) of the Mulhouse kerogen illustrating the distribution of benzene, toluene and the C_2–C_4 alkylated benzenes. Peak numbers refer to the compounds listed in Table I.

mers present in complex mixtures of hydrocarbons. Fig. 4 shows a partial accurate mass chromatogram illustrating the distribution of the C_0–C_4 alkylated benzenes in the pyrolysate of the Mulhouse kerogen. Peak numbers refer to Table I. All alkylbenzene isomers were found to be present, except tert.-butylbenzene (compounds 15), the concentration of which is below the detection level of the method used.

In the way described above, distribution patterns of C_0–C_4 alkylated benzenes of kerogen, asphaltenes and coal pyrolysates can be obtained. Significant differences in distribution patterns were observed. For example, the alkylbenzene distribution of the pyrolysate of the Mulhouse kerogen (Fig. 5A) compared with the Estonian kerogen (Fig. 5B) shows considerable differences. The pyrolysate of the Estonian kerogen is dominated by a relatively higher abundance of homologous series of monosubstituted and ortho-disubstituted n-alkylbenzenes (compounds 6, 8, 12, 25 and 28). Also the relative abundance of C_4 alkylated benzenes in the pyrolysate is lower than that in the Mulhouse pyrolysate. The C_4 alkylated benzene distribution present in the pyrolysate of the Beulah Zap coal (Fig. 5C) is dominated by 1-methyl-4-isopropylbenzene and 1,2,3,4-tetramethylbenzene (compounds 19 and 36). Also noteworthy is the higher abundance of ben-
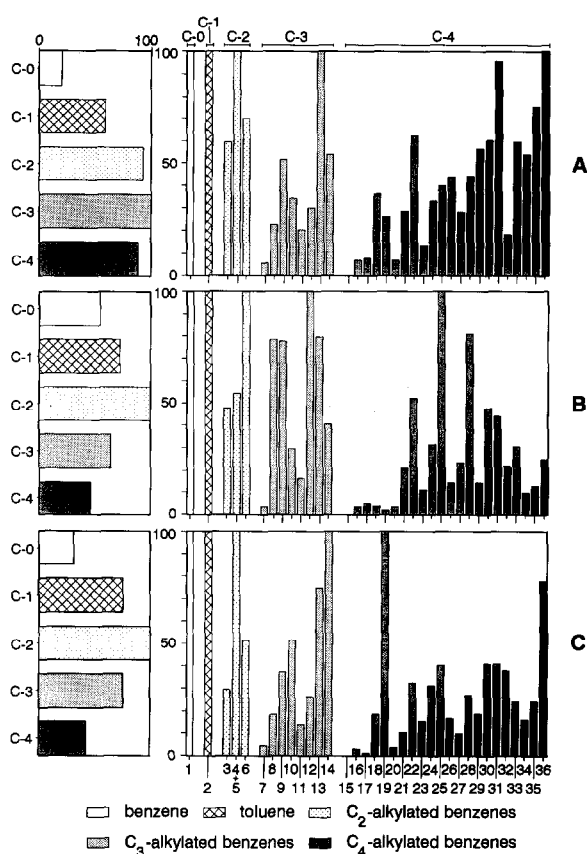

Fig. 5. Bar plots showing the carbon number distributions of benzene, toluene and the C_2–C_4 alkylated benzenes (left bar graphs) and the distribution of isomers (right bar graphs) generated upon flash pyrolysis (Curie temperature 610°C) of the Mulhouse kerogen (A), Estonian kerogen (B) and Beulah Zap coal (C). The distributions of the alkylated benzenes were normalized to the most abundant component. Numbers refer to compounds listed in Table I.

zene and toluene relative to C_2–C_4 alkylated benzenes in the pyrolysate of Estonian Kukersite compared with that of Mulhouse kerogen and Beulah Zap coal.

Fig. 6 shows the distributions of alkylbenzenes generated by flash pyrolysis of the asphaltene and the extracted kerogen fractions of the Jurf ed Darawish Oil Shale. The similarity of the alkylbenzene distributions is striking, although an enhanced relative abundance of the C_3 and C_4 alkylated benzenes in the pyrolysate of the asphaltene is observed. The observed similarity supports the idea that asphaltenes are structurally related to kerogen [27–30]. It
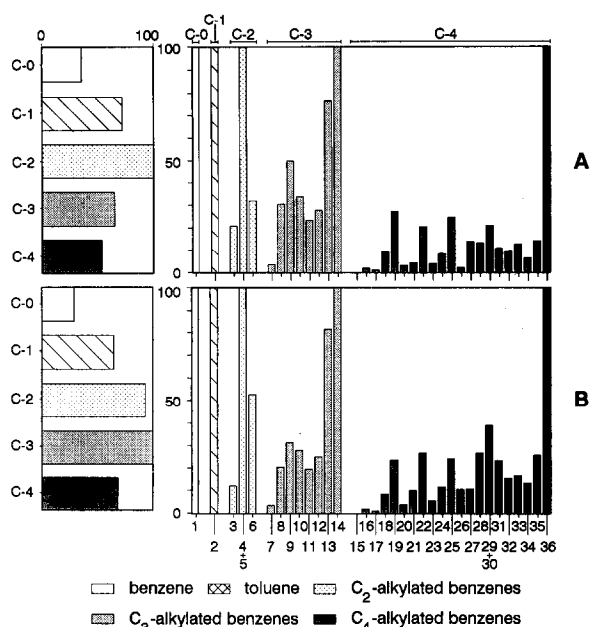
Fig. 6. Bar plots showing the carbon number distribution of benzene, toluene and the C_2-C_4 alkylated benzenes (left bar graphs) and the distribution of isomers (right bar graphs) generated upon flash pyrolysis (Curie temperature 610°C) of the asphaltenes (A) and kerogen (B) of the oil shale of Jurf ed Darawish. The internal distributions of the alkylated benzenes were normalized to the most abundant component. Numbers refer to compounds listed in Table I.

appears, therefore, that analysis of alkylbenzene distributions in pyrolysates of asphaltenes may be a useful tool for oil–source rock correlations. The full identification of alkylbenzenes in flash pyrolysates enables a comparative study of alkylbenzene distributions in order to give more information about the presence and origin of their natural precursors.

CONCLUSIONS

Pseudo-Kováts indices have been determined for all isomers of C_2-C_4 alkylated benzenes using a non-polar capillary column coated with CP Sil-5. In combination with mass spectral data, the identification of these compounds in flash pyrolysates of kerogens, coals and asphaltenes was achieved. To investigate in more detail the variations in the internal distributions of alkylbenzenes present in these flash pyrolysates, appropriate mass chromatograms were integrated and corrected for different MS re-

sponses. Benzene and toluene are generally the most abundant products. Significant differences were observed owing to the relatively high abundances of specific alkylbenzenes (e.g. 1,2,3,4-tetramethylbenzene and 1-methyl-4-isopropylbenzene). A higher abundance of "linear" alkylbenzenes was found in the pyrolysate of Estonian Kukersite. The alkylbenzene distributions present in flash pyrolysates of the asphaltene and kerogen fractions of the Jurf ed Darawish oil shale are very similar, confirming their structural relationship.

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