OCCURRENCE AND DISTRIBUTION OF METHYLNAPHTHALENES AND METHYPHENANTHRENES IN CRUDE OILS FROM EGYPT

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ABSTRACT

The distribution patterns of methylhomologs of naphthalene and phenanthrene in two Egyptian crude oil samples from Alamein and Badran oilfields have been examined by capillary column gas chromatography (GC) and combined gas chromatography-mass spectrometry (GC/MS). The total aromatic distributions are very similar for both oils and contained significant proportions of polycondensed aromatic hydrocarbons. The distribution was dominated by methylnaphthalenes and dimethylnaphthalenes followed in the order of decreasing relative abundance by trimethylnaphthalenes, dimethylphenanthrenes, methylphenanthrenes, ethylnaphthalenes and phenanthrene. The predominance of 1-methylphenanthrene and pimanthrene indicates preferential preservation in these samples of materials derived from conifers. Maturity parameters based on methylnaphthalene and methylphenanthrene isomers were almost identical. The values of the Methylphenanthrene Index (MPI 1) were in the range 0.87-0.89 corresponding to a calculated vitrinite reflectance (R_c) of 0.92-0.93% and are typical of organic matter derived from mixed Type II/III kerogens with a preponderant terrestrial components.

Key Words

aromatic hydrocarbons, crude oils, gas chromatography, methylnaphthalenes, methylphenanthrenes, thermal maturity, origin

INTRODUCTION

Aromatic hydrocarbons are common constituents of geological sources such as petroleum, coal, soils, and oilshales. Like many fossil organic molecules, aromatic hydrocarbons are believed to be derived from transformations of nonaromatic biological precursors, either through microbial processes in the initial stages of diagenesis, or during subsequent burial in which such precursors experience the effects of temperature, pressure and catalytic action of the mineral matrix [1-3].

The occurrence of alkyl aromatic compounds in sedimentary organic matter is of continuing interest to geochemists, since variations in the relative abundance of methyl aromatic series have been used solve oil-to-source rock correlations and to obtain information about the thermal maturity of sedimentary rocks, coal and crude oils. Radke *et al* [3-5] and Radke and Welte [6] reported that the relative distribution of monomethylphenanthrene (MP), dimethylphenanthrene (DMP) and methyldibenzothiophene (MDBT) isomers could be correlated with vitrinite reflectance data. Alexander *et al* [6-9] showed that the relative distribution of dimethylnaphthalene (DMN), trimethylnaphthalene (TMN) and alkylbiphenyl isomers in rock extracts are correlated with increasing depth and could be related to some extent to other parameters such as sterane ratios. Garrigues *et al* [10-12] also observed changes in the distributions of phenanthrene, anthracene, chrysene and pyrene derivatives in crude oils and rock extracts.

Recently [13] a preliminary organic geochemical study on crude oil samples from Alamein and Badran oilfields from Egypt were performed. These oils are thought to be derived from terrigenous source material and are classified as "paraffinic" oil. In the present paper, I have extended the previous work to a detailed examination of alkylnaphthalenes and alkylphenanthrenes in the same oils. A comparison of the relative abundances of these compounds in the two oils is also presented.

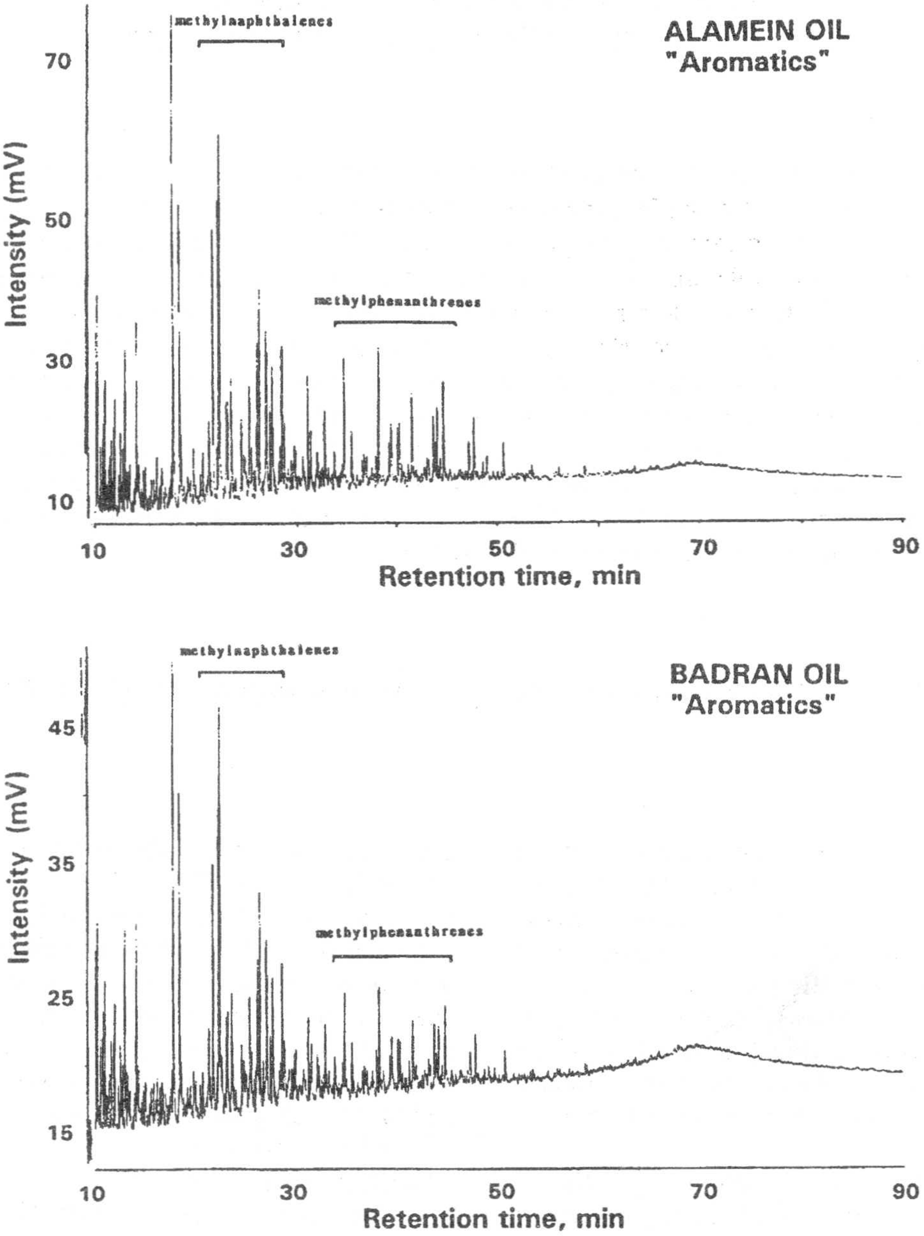

Figure 1. Capillary column gas chromatograms of the C_{11+}-aromatic hydrocarbon fractions of crude oils from Alamein and Badran oilfields.

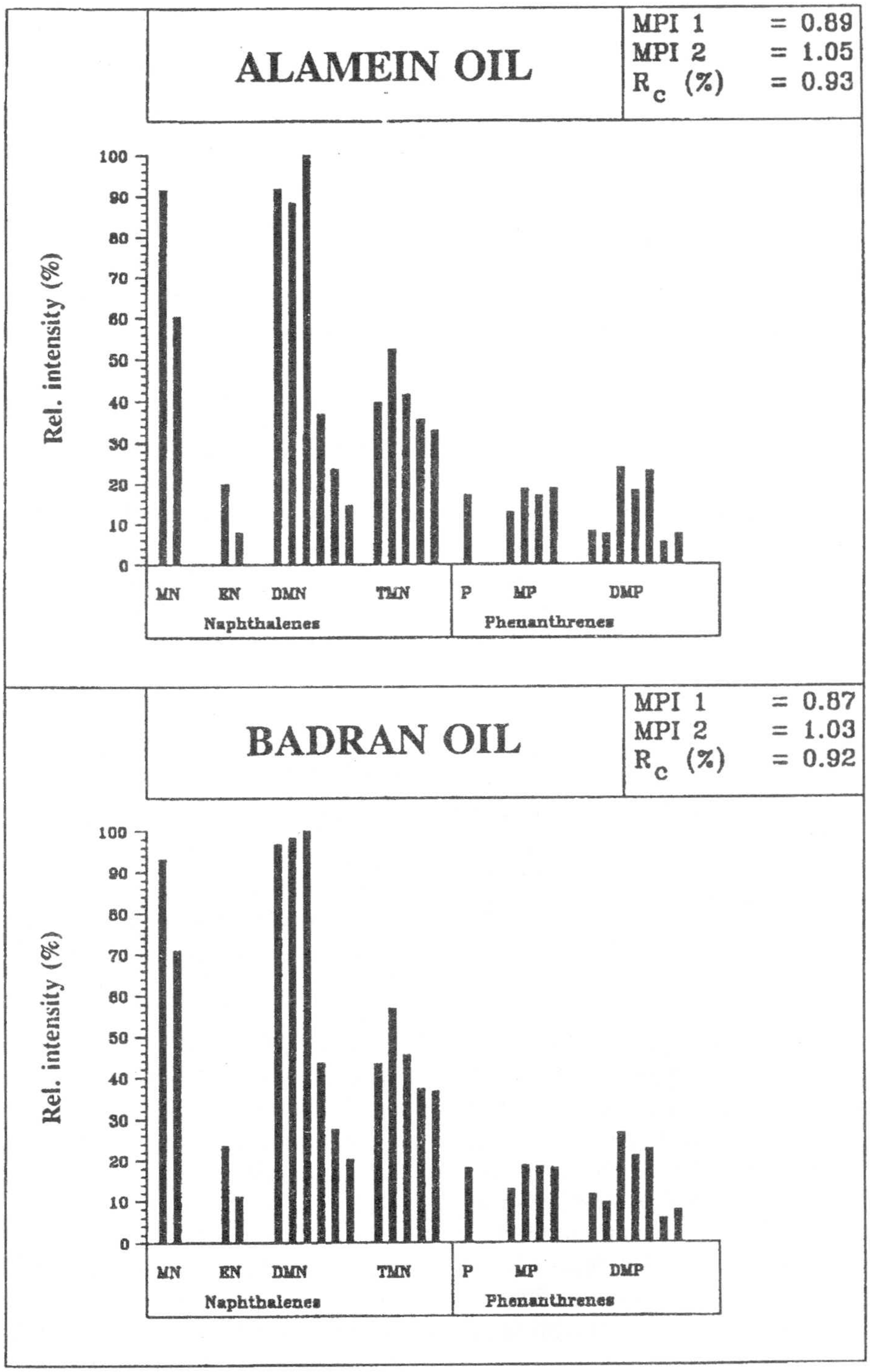

Figure 2. Standard bar diagram showing the distribution of selected methylnaphthalene, phenanthrene and their alkyl homologues in Alamein and Badran oils. Relative concentrations obtained from the gas chromatograms, presented in Figures 3 and 4, by integration of the respective peaks which were normalized to the most intense peak.

Table 1. Bulk Crude oil composition.

Crude oil	Location	Reservoir ages	API Graviy (60°)	Wt.% Sulfur	Gross Composition		%sat.	%Aro	%NSO	%Sat./Aro.
					$\% < C_{15}$	$\% > C_{15}$				
Alamein	Western Desert	Certaceous	32.9	1.35	30.4	69.6	68.0	26.5	5.5	2.6
Badran	Gulf of suze	Cretaceous	26.4	2.27	27.3	72.7	62.2	28.3	9.5	2.2

EXPERIMENTAL

Alamein crude oil sample is reservoired in Cenomanian sands at a depth 2580-2590 m in the western desert of Egypt, while the Badran sample is reservoired at a depth 3200-3400 m in the Cretaceous Nubian sands in the gulf of Suez. Bulk chemical properties of the oils are listed elsewhere. [13]

Procedure

The crude oil samples were separated by medium pressure liquid chromatography (MPLC) into C_{15+}-saturated and C_{11+}-aromatic hydrocarbon fractions and N,S,O-heterocomponents according to an established procedure.[14] Aromatic fractions were further analyzed by capillary gas chromatography (GC) and combined gas chromatography mass spectrometry (GC/MS).

Instrumental Methods

High resolution gas chromatographic analysis was performed on a Carlo Erba 6180 gas chromatograph equipped with an on-column injector, a flame ionization detector and a fused silica capillary column (25 m x 0.32 mm, film thickness = 0.25 μm) coated with polymethyl(95%)phenyl(5%)siloxane (CP-Sil 8). The temperature was programmed from 60 to 80°C at 30°C/min and from 80 to 300°C at 3°C/min with an initial hold time of 1 min and a final time of 20 min. GC data was stored and processed by a multichrom on-line data system (VG Instruments).

GC/MS analysis was carried out on a Carlo Erba Fractovap 4160 gas chromatograph coupled to a VG 7070E mass spectrometer operating at 70 eV. Samples were injected onto a fused silica capillary column (50 m x 0.32 mm, d*f* = 0.4 μm) coated with CP-Sil-5. Helium was the carrier gas and the temperature was programmed from 110 to 320°C at 3°C/min with an initial time of 2 min and a final hold time of 20 min. The magnetic field of the mass spectrometer was scanned over a mass range of m/z 900-45 at a rate of 2.5 s/scan. Data were acquired stored and processed using a Kratos DS 90 data system.

Identifications of individual polycyclic aromatic hydrocarbons were based on comparison of their GC retention or mass spectral data with literature values. [3,4,6,12,15-17].

RESULTS AND DISCUSSION

Quantitative results from MPLC analyses of the two oil samples are listed in Table (1). Both samples differ slightly in the yield of saturated and aromatic hydrocarbons and of N,S,O-compounds. The ratio of saturated/aromatic hydrocarbons is greater in the Alamein sample as is the concentration ratio of higher $(>C_{20})$ to the low molecular weight *n*-alkanes $(<C_{20})$ [13].

High-resolution GC of the total aromatic fractions from the both crude oils are shown in Figure (1). The appearances of the FID chromatograms for the most part were very similar, being dominated by the fairly typical mixtures of substituted naphthalenes and phenanthrenes. These polycondensed aromatic hydrocarbons were mainly represented by pseudohomologous series of mono-, di-, and tri-methylnaphthalenes and of phenanthrene, mono-, and dimethylphenanthrenes. Histograms showing the relative distribution of selected methylnaphthalene, phenanthrene and their alkyl homologs in both oil samples are presented in Figure (2). As shown in the latter Figure, the molecular distribution of C_{11+}-aromatic hydrocarbons in Alamein oil (western desert) in many respect was similar to that of Badran oil from the gulf of Suez. Specifically, the concentration ratio of phenanthrene and methylphenanthrenes over mono-, di- and trimethylnaphthalenes is the same in both oils (Figure 2).

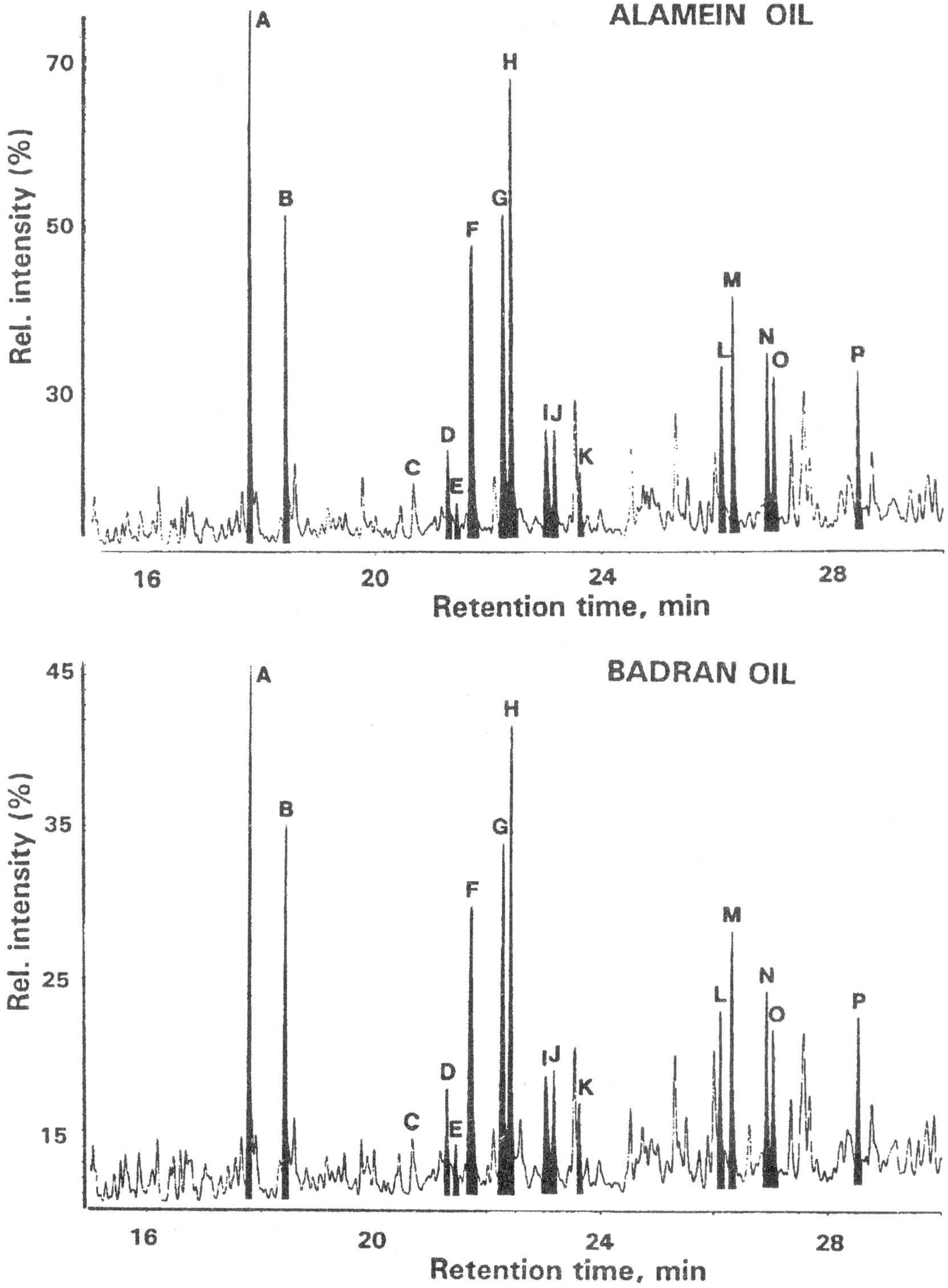

Figure 3. Partial capillary column gas chromatography of aromatic hydrocarbons showing the distribution and retention of methylnaphthalenes in Alamein and Badran oils. Peak assignements and relative abundances are given in Table 2 and Figure 2, respectively.

Table 2. Bicyclic aromatics identified in the crude oil samples (Figure 2)

Peak	Compound	Relative abundance (%)	
		Alamein	Badran
A	2-Methylnaphthalene	91.4	93.0
B	1-Methylnaphthalene	60.2	70.9
C	Biphenyl	13.9	12.1
D	2-Ethylnaphthalene	20.0	23.5
E	1-Ethylnaphthalene	7.8	11.2
F	2,6-2,7-Dimethylnaphthalene	91.9	96.8
G	1,3-/1,7-Dimethylnaphthalene	88.4	98.4
H	1,6-Dimethylnaphthalene	100.0	100.0
I	2,3-/1,4-Dimethylnaphthalene	37.0	43.5
J	1,5-Dimethylnaphthalene	23.6	27.5
K	1,2-Dimethylnaphthalene	14.7	20.2
L	1,3,7-Trimethylnaphthalene	39.7	43.3
M	1,3,6-Trimethylnaphthalene	52.5	56.9
N	1,3,5-/1,4,6 Trimethylnaphthalene	41.7	45.5
O	2,3,6-Trimethylnaphthalene	35.7	37.3
P	1,2,5-Trimethylnaphthalene	32.9	36.7

Alkylnaphthalene distributions

Alkylnaphthalenes were assigned by mass fragmentography of the molecular ions (*m/z* 143, 156, 170) and by comparison of retention times with those of authentic isomers [6,16,17]. Partial extended gas chromatograms of the aromatic fractions of Alamein and Badran crude oils are shown in Figure (3). Labeled peaks in the latter Figure are identified in Table 2. Because co-elution of the 2,6-, 2,7-DMN, 1,3-, 2,7-DMN and 1,4-, 2,3-DMN isomer pairs occurred, individual abundance of each isomer could not be given in Figure (2).

A high relative abundance of 1,6-dimethylnaphthalene (compound H, Figure (3)) was characteristic of aromatics in both oil samples. On the average, relative abundance of individual naphthalenes were not significantly different in both samples. On the other hand , the predominance of 2-methylnaphthalene (compound B) over 1-methylnaphthalene (compound A) was more pronounced for Alamein oil, as was the predominance of 1,6-DMN over the other DMN isomers. DMN and TMN concentrations were elevated for both, Alamein and Badran oils, that cannot be related to any specific biological source material.

It is apparent from these results that the β MN and β EN isomers are present in both samples at greater concentrations than are the α isomers. Further, one observes that the $\alpha\beta$ and $\beta\beta$ DMN isomers (1,3-, 1,6-, 1,7-, and 2,6-, 2,7-, DMN) are present at greater concentrations than the $\alpha\alpha$ isomers (1,4-DMN, 1,5-DMN). The major TMN isomer in both samples is 1,3,6-TMN ($\alpha\beta\beta$).

Alkylphenanthrene distributions

Identification of phenanthrene, methylphenanthrene and dimethyphenanthrene isomers was based on comparison of relative GC retention times with those reported in previous studies [3,12,16,17]. Partial capillary gas chromatograms showing the relative retention of the various methylphenanthrene isomers in Alamein and Badran crude oil samples are given in Figure (4).

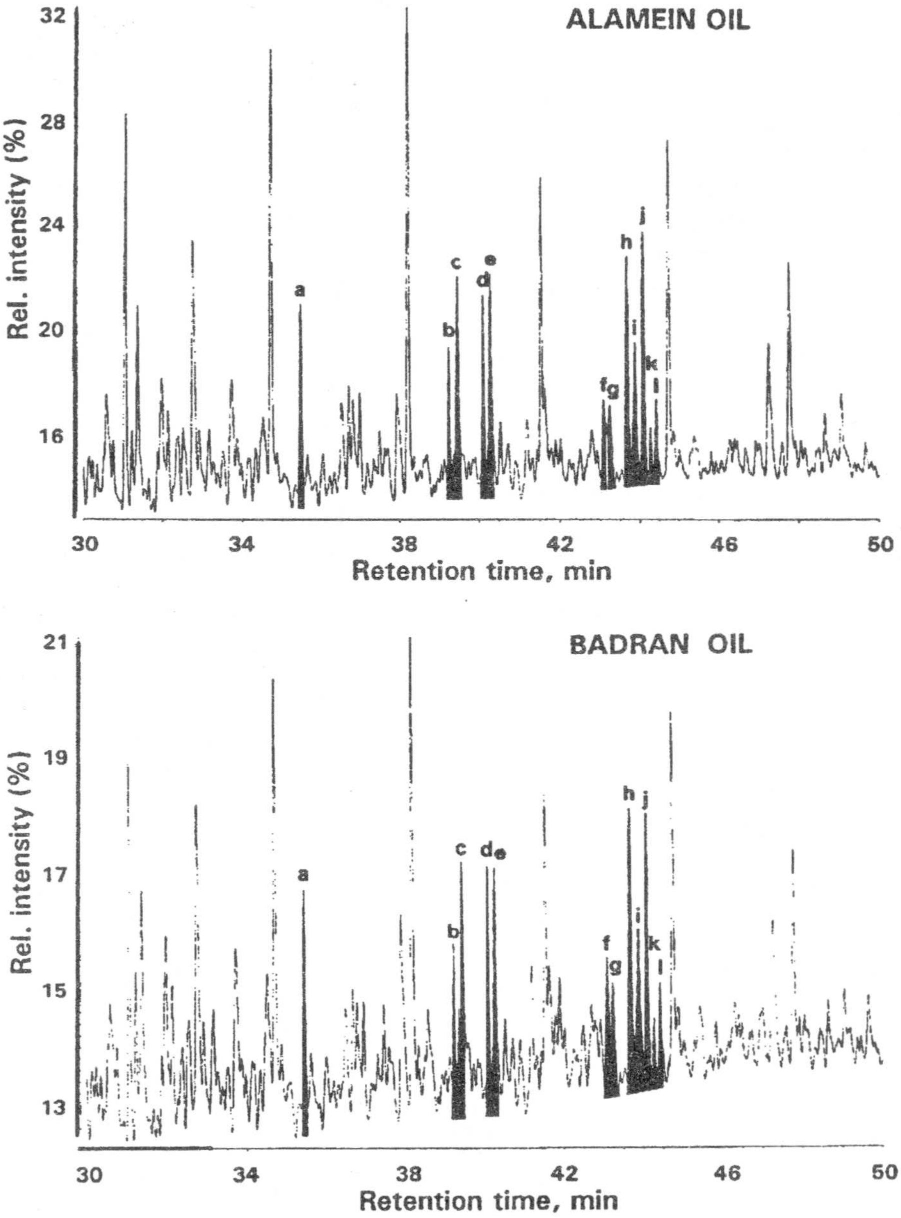

Figure 4. Partial capillary column gas chromatography of aromatic hydrocarbons showing the distributions and retentions of methylphenanthrenes in Alamein and Badran oils. Peak assignments and relative abundances are given in Table 3 and Figure 2, respectively.

Table 3. Tricyclic aromatics identified in the crude oil samples (Figure 2)

Peak	Compound	Relative abundance (%)	
		Alamein	Badran
a	Phenanthrene	71.3	17.9
b	3-Methylphenanthrene	12.9	12.9
c	2-Methylphenanthrene	18.7	18.5
d	9-Methylphenanthrene	17.1	18.0
e	1-Methylphenanthrene	18.9	11.6
f	2,6-/3,5-Dimethylphenanthrene	8.3	9.5
g	2,7-Dimethylphenanthrene	7.6	26.6
h	1,3-/2,10-/3,10-/3,9 Dimethyphenanthrene	23.9	21.0
i	1,6-Dimethyphenanthrene	18.3	22.7
j	1,7-Dimethylphenanthrene	23.1	5.9
k	2,3-Dimethylphenanthrene	5.6	7.7
l	2,3-Dimethylphenanthrene 1,9-Dimethylphenanthrene	7.5	

Table 4. Maturity indicators based on ratios of bicyclic and tricyclic aromatics.

Index name	Definition	Substitution pattern	Reference
Alkylnaphthalene ratios			
Methylnaphthalene ratio (MNR)	$\frac{[2\text{-MN}]}{[1\text{-MN}]}$	$\frac{\beta}{\alpha}$	3
Ethylnaphthalene ratio (ENR)	$\frac{[2\text{-EN}]}{[1\text{-EN}]}$	$\frac{\beta}{\alpha}$	3
Dimethylnaphthalene ratio (DNR)	$\frac{[2,6\text{-DMN}] + 2,7\text{-DMN}}{[1,5\text{-DMN}]}$	$\frac{\beta\beta + \beta\beta}{\alpha\alpha}$	3
Trimethylnaphthalene ratio (TNR)	$\frac{2,3,6\text{-TMN}}{[1,4,6\text{-TMN}] + [1,3,5\text{-TMN}]}$	$\frac{\beta\beta\beta}{\alpha\alpha\beta + \alpha\beta\alpha}$	8
Alkylphenanthrene ratios			
Methylphenanthrene ratio (MPR)	$\frac{[2\text{-MP}]}{[1\text{-MP}]}$	$\frac{\beta}{\alpha}$	4
Methylphenanthrene ratio* (MPR*)	$\frac{[2\text{-MP}]}{[9\text{-MP}]}$	$\frac{\beta}{\alpha}$	22
Methylphenanthrene Index 1 (MPI 1)	$\frac{1.5([2\text{-MP}] + [3\text{-MP}]}{[P] + [1\text{-MP}] + [9\text{-MP}]}$	$\frac{\beta + \beta}{\alpha + \alpha}$	4
Methylphenanthrene Index 2 (MPI 2)	$\frac{3[2\text{-MP}]}{[P] + [1\text{-MP}] + [9\text{-MP}]}$	$\frac{\beta}{\alpha + \alpha + \alpha}$	4
Calculated vitrinite reflectance (%)	$R_c = 0.60$ MPI 1 + 0.40		5

*Abbreviation used only in this work

The distribution patterns of phenanthrene and its alkyl homologs is fairly similar in both oil samples (see Figure 4). The predominance of 1-methylphenanthrene (compound e, Figure 4) over the other methylphenanthrenes in Alamein oil indicates enhanced contributions of abietic acid-type precursors to the formation of this isomer [18]. Another imprint of coniferous resins source material on the alkylphenanthrene distribution, i.e. the predominance of pimanthrene (1,7-DMP, compound j) over the other dimethyl phenanthrenes in the aromatic fraction of Alamein oil. As pointed out by several authors [18,19], abietic and/or pimaric acids, which are known resin constituents of many higher plants, are the most likely biogenic precursors of pimanthrene in sediments and oils. The predominance of 1-methylphenanthrene and 1,7-dimethylphenanthrene is less pronounced in Badran oil but is still perceivable, indicating preferential preservation in this sample of material derived from conifers. These results are in agreement with the proposed depositional model [13] assuming a higher plant source materials for both oils.

Maturity parameters

From previous publications on the MP and DMP isomer distributions [3,4] or the MN, EN, DMN and TMN isomer distributions [6-8], it follows that the α-substituted isomers are present in lower amounts than the β-substituted ones in mature geological samples. Indeed, the natural thermal maturation favors the most thermodynamically stable β-substituted compounds [4,8,20] Based on these observations , several indices has been proposed as described in detail in Table (4).

Methylnaphthalene indices

Changes observed in the relative abundances of methylnaphthalenes, dimethylnaphthalenes and trimethylnaphthalenes have been used to obtain information about thermal maturity of crude oils and sediments. Radke et al [3] reported that changes in the abundance of the isomer ratios MN, EN and DMN correlated with increase in coal rank. This can be explained in terms of the thermodynamically favorable methyl shift from the α- to the β-position of naphthalene. A corresponding rearrangement of 1,5-DMN, which is an isomer of the α,α-type, to yield α,β- and β,β-type isomers, would explain the increase of dimethylnaphthalene ratio (DNR) with increase of thermal maturity. Based on similar thermodynamic considerations, Alexander *et al* [8] showed that the TNR parameter was also a sensitive indicator of thermal maturity of sediments and petroleum.

The values of the methylnaphthalene indices are given for the Alamein and Badran oil samples in Table (5). It could be observed that the values of all methylnaphthalene indices were always slightly higher in Alamein than in Badran oil, indicating higher relative abundance of the thermodynamically more stable β-, $\beta\beta$- and $\beta\beta\beta$-type isomers in the former oil. This might suggest a slightly higher level of thermal maturity for Alamein oil.

Phenanthrene indices

Several ratios based on the phenanthrene distribution have been proposed as indicators of thermal maturity. The most frequently used indices appear in Table 4. Steroids and terpenoids have been proposed as biological precursors for the phenanthrenes found in fossil material. Partial de-alkylation of these molecules gives rise only to 1- and 2-methylphenanthrene [21]. The presence of 3- and 9-MP in sediment extracts and crude oils has been ascribed to methylation of phenanthrene and rearrangement of mono-MP. [3,4]. Radke *et al* [3-5] observed an increase in relative amounts of 2- and 3-methylphenanthrene compared to 1- and 9-MP with increasing depth. This can be explained in terms of a methyl shift from α- to β-position on the phenanthrene nucleus resulting in reduction of the steric strain which is lower in the β-type isomers (2-MP, 3-MP) than in the α-type isomers (1-MP, 4-MP, 9-MP).

The values of the phenanthrene indices are given for Alamein and the Badran samples in Table 5. MPI 1 (see abbreviations in Table 4) are in the range 0.87-0.89, whereas MPI 2 exhibits values in the range 1.03-1.05. The values of these two indices are slightly higher in Alamein oil. The index [2-MP]/[9-MP] (MPR*) also exhibits the same trend and could be very useful in cases where the origin of the organic matter could affect the values of MPI 1, MPI 2 and MPR [17]. Indeed, MPR show exceptionally a higher value for Badran crude oil sample (Table 5). This could be explained by the enhanced concentration of 1-MP in Alamein oil, as a result of a higher contribution of organic matter from terrestrial origin [18] as demonstrated earlier. The presence of such compounds abnormally decreases the value of the thermal maturity parameters. As previously reported [22], MPR* could also be very useful when dibenzothiophene compounds are present since some methylated dibenzothiophenes coelute with some MP isomers.

Calculated vitrinite reflectivities (R_c) based on concentration ratios of methylphenanthrenes and phenanthrene (MPI 1) are 0.93 and 0.92 for Alamein and Badran oils, respectively. In a recent study [22] four oil types have been distinguished on the basis of a statistical evaluation of R_c data of crude oils of various origins. The present values of R_c fall into the same distribution range of Type III/II oils which were distiguished in the previous study by a mode occurring at $\%R_c$ 0.90. Crude oils of this type are known to belong to the paraffinic class, presumably derived from mixed Type II/III kerogens with a preponderant terrestrial components [21]. These data do confirm the large terrigenous input into the sediments of both oil samples, and are in agreement with previous results obtained on other lipid components (e.g. n-alkane distribution, high pristane/phytane ratio) [13].

Acknowledgments

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Table 5. Rank parameters based on aromatic hydrocarbon distributions for Alamein and Badran crude oils.

Crude oil	Methylnaphthalene indices				Methylphenanthrene indices				
	MNR	ENR	DNR	TNR	MPI 1	MPI 2	MPR	MPR*	(%)R_c
Alamein	1.52	2.56	3.90	0.80	0.89	1.05	0.99	1.09	0.93
Badran	1.31	2.11	3.52	0.79	0.87	1.03	1.03	1.02	0.92

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