ISSN 0016-7029, Geochemistry International, 2007, Vol. 45, No. 8, pp. 781–797. © Pleiades Publishing, Ltd., 2007.

New Maturation Parameters Based on Naphthalene and Phenanthrene Isomerization and Dealkylation Processes Aimed at Improved Classification of Crude Oils (Southeastern Pannonian Basin, Serbia)[1]

K. Stojanović[a,c], Br. Jovančićević[b,c], Dr. Vitorović[b,c], G. S. Pevneva[d], Ju. A. Golovko[d], and A. K. Golovko[d]

[a] *Department of Medicine, University of Belgrade, Višegradska 26, 11000 Belgrade*
[b] *Department of Chemistry, University of Belgrade, PO Box 158, 11001 Belgrade*
[c] *Center of Chemistry, IChTM, Njegoševa 12, 11000 Belgrade, Serbia and Montenegro*
[d] *Institute of Petroleum Chemistry, pr. Academichesky 3, Tomsk, 634021 Russia*
e-mail: bjovanci@chem.bg.ac.yu; pevneva@ipc.tsc.ru

Received November 15, 2005

Abstract—Aiming at improved classification of crude oils, naphthalene and phenanthrene isomerization and dealkylation processes were considered in detail as a possible basis to select new maturation parameters. Crude oils originating from the Banat depression (Southeastern Pannonian Basin, Serbia) were used as objects of our study. Four new maturation parameters are proposed in this paper. Two of them are based on dimethylnaphthalene (DMN) and trimethylnaphthalene (TMN) isomerization reactions: DNx = (1,3-DMN + 1,6-DMN)/(1,4-DMN + 1,5-DMN) and TNy = (1,3,6-TMN + 1,3,7-TMN)/(1,3,5-TMN + 1,4,6-TMN). The other two are based on demethylation of dimethyl- and trimethylphenanthrenes (DMP and TMP) into corresponding methylphenanthrenes (MP): MDR = ΣMP/ΣDMP and MTR = ΣMP/ΣTMP. The new parameters' advantageous applicability was demonstrated by factor analysis, comparing them with maturation parameters known from literature.

DOI: 10.1134/S0016702907080058

INTRODUCTION

Crude oil maturity has so far been estimated mainly based on parameters calculated from distribution and abundance of either saturated or aromatic hydrocarbons.

The applicability of alkanes in maturity assessment is limited due to the fact that the abundance and distribution of *n*-alkanes and isoprenoid aliphatic alkanes are strongly influenced by other factors such as origin, depositional environment, and biodegradation. Furthermore, it is well known that in terpane and sterane isomerization reactions equilibria are established before the last stages of organic matter catagenesis (Ro = ~0.65% and Ro = ~1.00%, respectively; [1]). Also, a significant effect of minerals on isomerization reactions such as C_{27}-17α(H)-22,29,30-trisnorhopane $\longrightarrow$ C_{27}-18α(H)-22,29,30-trisnorhopane (Tm $\longrightarrow$ Ts) and steranes $\longrightarrow$ diasteranes have been observed [1, 2]. Consequently, maturity classification of crude oils based on terpane and sterane maturation parameters is not quite satisfactory.

Reactions involving aromatic hydrocarbons, in the first place alkyl-naphthalenes and alkyl-phenanthrenes, were lately increasingly used for maturity assessment of crude oils and source rock bitumens. The dependence of abundance and distribution of aromatic hydrocarbons on the maturity of source rock bitumens and crude oils has extensively been studied and confirmed in a great number of papers [3–11]. However, it was shown that abundance and distribution of these hydrocarbons in bitumens and crude oils may also be, to a certain degree, though less compared to saturated hydrocarbons, influenced by origin [5, 6, 12–14], biodegradation [15–18], migration [19], mixing of crude oils of different maturity in reservoirs [20], and mineral catalyst effects in source or reservoir rocks [20–23]. Thus, for example, the reliability of one of the parameters, the methylphenanthrene index 1 (MPI 1), was shown to be insufficient in maturity estimation of bitumens originating from kerogens of dominant algal origin [24–26], as well as crude oils containing high amounts of sulfur [24, 27]. Nevertheless, due to doubtless relevant potential of aromatic hydrocarbon reactions, a permanent interest for this type of compound led to the investigating and defining of new maturation parameters based on distribution and abundance of aromatic hydrocarbons (e.g., [28]).

---

[1] The text was submitted by the authors in English.

One of the most important maturation processes occurring during sedimentary catagenetic evolution is the isomerization of substituted naphthalenes and phenanthrenes containing alkyl groups in α-position, into thermodynamically more stable forms with substituents in β-position [3–5, 7, 8, 20, 29]. Based on ratios between these isomers, most of the so-called naphthalene–phenanthrene maturation parameters were defined. Examination of a great number of crude oils and source rock bitumens, as well as the corresponding geosynthetic reactions, has shown that, in addition to $\alpha \longrightarrow \beta$ isomerization, alkylation–dealkylation processes were also an important factor in maturation changes [5, 11, 13, 20, 30, 31]. It was therefore suggested that parameters based on this type of reaction may also serve for crude oil maturity estimation [11, 32, 33].

In this sense, searching for more reliable maturation parameters, aimed at improved crude oil classification, naphthalene and phenanthrene isomerization, and dealkylation processes, as a possible basis for designing new parameters, were studied in detail in this paper. Their applicability was verified by comparing them with known maturation parameters calculated from the distribution and abundance of aromatic hydrocarbons, with the help of factor analysis (software program SPSS 10.0 for Windows; [34–37]).

Crude oil samples recovered from the Banat depression were used as the objects under study. As to the Banat depression, it constitutes a major part of the Southeastern Pannonian Basin (Serbia). The Banat depression is divided into two parts. The major part of the Banat depression is located on the territory of the Province of Vojvodina (north of the rivers Sava and Danube), while its smaller, southern part is located south of the Danube, near the City of Požarevac, and is called the Drmno depression [38]. Most of these crude oils were not exposed to microorganisms in reservoirs [39, 40]. Minimal biodegradation was observed only with several samples originating from the Velebit and Boka oil fields [41, 42]. These crude oils are characterized by mixed origin: Vojvodina crude oils by a larger contribution of marine type biomass and those from the Drmno depression by biomass of terrestrial origin [40, 43]. According to the depositional environment, the Drmno depression crude oils were found to differ from each other [44]. Similar differences were also observed, to a certain degree, with some crude oils originating from the Banat depression [40].

So far several bulk parameters of these crude oils were determined. Also, *n*- and isoprenoid aliphatic alkanes and polycyclic alkanes of sterane and terpane types were analyzed in detail [39, 41, 43]. The corresponding hopane and sterane parameters suggested the Southeastern Pannonian Basin crude oils to have originated mainly from source rocks of tertiary age. They were of medium to high maturity [39, 40, 45, 46], i.e., the Vojvodina oil field crude oils (e.g., Kikinda and Mokrin-south) of higher maturity compared to crude oils from the Drmno depression (e.g., Bradarac-Maljurevac) [43, 45].

Aiming at improved classification of crude oils, particularly those originating from the Pannonian Basin, the maturity of twenty one crude oil samples from twelve Banat depression oil fields was studied in this paper on the basis of known and new maturation parameters calculated from the abundance and distribution of the components in the aromatic fractions.

SAMPLES AND METHODS

Samples and Geological Setting

The examined crude oil samples originated from the Pannonian Basin. This basin, of an area of approximately 260000 km^2, belongs to the category of hyperthermal basins, characterized by a high geothermal gradient, in some parts up to 70°C/km. Such a high geothermal gradient provided satisfactory heating even of Pliocene sediments [38]. The Pannonian Basin is of complex geological structure. It is not a uniform sedimentary basin. During Neogene and Anthropogene intense tectonic activity, followed by volcanism of variable intensity, resulted in the formation of a number of tectonic depressions, characterized by specific geological and geotectonic development [47]. The oil window in this basin is considered to begin at a depth of 2–3 km and to end at 3.5 to 5 km (corresponding to a vitrinite reflectance of Ro = 0.60–1.30%). Hence, most of the Middle Miocene and Lower Pannon sediments already passed through the oil window phase [48, 49].

The Serbian part of the Pannonian Basin consists of Tertiary Banat, South Backa, Danube–Morava, and Srem subbasins, each of which have an independent tectonic, sedimentary, and geothermal history [50]. The Banat depression, of an area of approximately 13500 km^2, is located in the southeastern part of the Pannonian Basin. Tertiary sediments are at a greatest depth north of Kikinda (over 4500 m). Towards the south and west, the depression is shallower. Successive occurrences of petroleum and gas in the profile of tertiary sediments of the Banat depression, as in the Pannonian Basin, generally indicate the existence of several migration paths and corresponding hydrocarbon accumulations.

Twenty-one samples of crude oils from twelve Banat depression oil fields were investigated in this paper, fourteen samples originating from localities in Vojvodina and seven samples from the Drmno depression localities. These crude oils are produced from reservoir rocks located at depths of 755.0–2304.5 m. All Drmno depression crude oils are found in reservoir rocks of Miocene age, and the crude oils from Vojvodina localities occur in reservoir rocks from Paleozoic, Mesozoic, Miocene, and Pliocene age. The Drmno depression stratigraphy has so far been studied in detail and the source rocks of the corresponding crude oils

Table 1. The investigated crude oil samples

N°	Sample		Oil field	Borehole	Depth (m)	Reservoir temperature (°C)	Lithology	Age
1	VOJVODINA	V1	Kikinda	23	1196–1200	105.0	Sandstone	Pliocene
2		V2	Kikinda	49	1730–1781	/	Sand	Pliocene
3		V3	Kikinda-Varoš	3	1897–1942	108.0	Shale	Paleozoic
4		V4	Velebit	87	753–759	61.4	Sand	Pliocene
5		V5	Velebit	98	752–758	/	Sand	Pliocene
6		V6	Velebit	120	756–758	/	Sand	Miocene
7		V7	Mokrin-south	8	2040–2047	116.0	Conglomerate	Miocene
8		V8	Mokrin-south	11	2040–2045	117.0	Sandstone	Miocene
9		V9	Jermenovci	1	896–899	61.7	Marly sandstone	Miocene
10		V10	Boka	37/2	1196–1206	76.9	Sandstone, limestone	Miocene
11		V11	Karadordevo	10	2557–2572	139.2	Sandstone	Mesozoic
12		V12	Itebej	8	2190–2198	126.6	Aleurolite	Mesozoic
13		V13	Elemir	19	1657–1668	99.0	Sandstone	Miocene
14		V14	Velika Greda-south	20	1006–1010	60.4	Large-grain sandstone, conglomerate	Miocene
15	DRMNO – POŽAREVAC	PO1	Sirakovo	1	1778–1782	101.9	Sandstone, aleurolite, breccia, conglomerate	Miocene (Ottnangian-Carpathian)
16		PO2	Sirakovo	2	1701–1704	98.0	Sandstone, aleurolite, breccia, conglomerate	Miocene (Ottnangian-Carpathian)
17		PO3	Sirakovo	18	1544–1548	92.2	Sandstone, marlstone, aleurolite, limestone	Miocene (Ottnangian-Carpathian)
18		PO4	Sirakovo	20	1440–1444	87.8	Sandstone, marlstone, aleurolite, limestone	Miocene (Ottnangian-Carpathian)
19		PO5	Bradarac-Maljurevac	2	2302–2307	121.9	Crystalline rock	Miocene (Red series)
20		PO6	Bradarac-Maljurevac	4	2156–2170	116.0	Marlstone, sandstone, breccia, conglomerate	Miocene (Red series)
21		PO7	Bradarac-Maljurevac	5	1985–1989	107.0	Sandstone, aleurolite, breccia, conglomerate	Miocene (Baden)

were identified [50–54]. Crude oils from boreholes Bradarac-Maljurevac 2 and 4 originate from Red Formations. By seismic investigation a large fault was discovered between these two boreholes (2 and 4). The boreholes Sirakovo 1, 2, and 18 are located in one zone, i.e., in the deeper, faulty zone, whereas the borehole Sirakovo 20 is situated in another, shallower zone of the Ottnangian-Carpathian sediments. A Badenian oil deposit was found at the depth of 1989–1985 m [46, 52, 53]. Detailed stratigraphic relationships between the Vojvodina Banat depression crude oils have so far not been determined. The locations of their source rocks are still unknown.

The list of the investigated samples, including data on depths, temperature, lithology, and age of the corresponding reservoir rocks, is given in Table 1. The locations of the corresponding oil fields are shown in Fig. 1.

Analytical Methods

Saturated hydrocarbons were isolated from the crude oil samples by column chromatography using silica gel as adsorbent and petroleum ether as eluent. Polycyclic alkanes of triterpane and sterane types in the corresponding saturated hydrocarbon fractions were analyzed by the gas chromatographic-mass spectrometric technique (GC-MSD). Hewlett Packard 5890, Series II gas chromatograph, with a HP-5MS capillary column, using helium as a carrier gas (1 cm^3/min) was coupled with a mass selective detector (Hewlett Packard 5972 MSD, 70 eV). The Single Ion Monitoring (SIM) method was used for the identification of individual components. Terpanes were identified on the basis of m/z 191 and steranes, based on m/z 217 ion fragmentograms.

Naphthalene and phenanthrene isomers were isolated and identified using a specially designed procedure [32, 33, 55], consisting of preliminary elimination

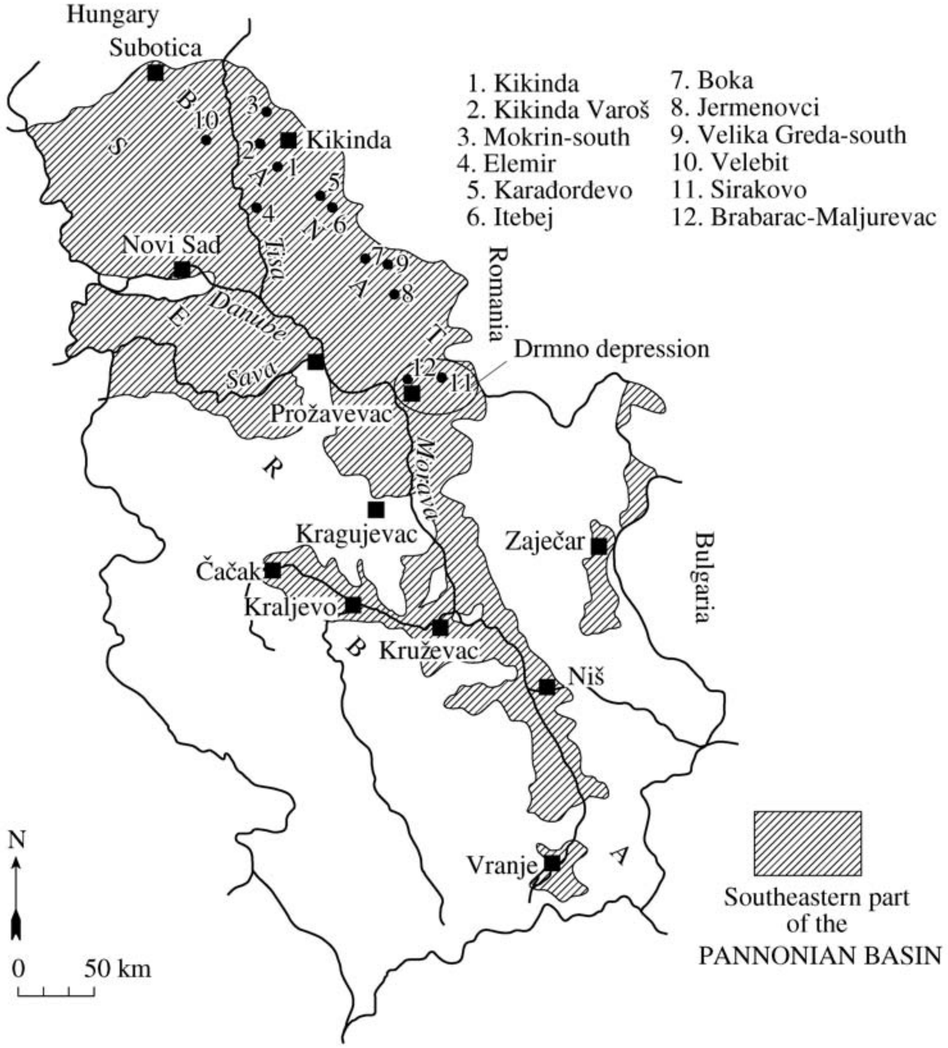

Fig. 1. Location of the examined crude oil fields.

of asphaltenes (precipitation by *n*-heptane), NSO compounds (insolubile in *n*-hexane; separation by Soxhlet extraction), and *n*-alkanes (urea adduction), followed by column chromatography (γ-Al_2O_3; 80 : 1) using *n*-hexane and *n*-hexane/benzene mixture (3 : 1) as eluents for quantitative isolation of di- and tricyclic aromatic hydrocarbons and benzene and benzene/ethanol mixture (1 : 1) for isolation of polycyclic aromatic hydrocarbons with more than three rings and traces of resins. Eluates were collected in 5–10 cm^3 portions whose separation into saturated mono-, di-, and tricyclic aromatic hydrocarbon fractions was achieved by the help of UV spectroscopy (Specord, UV-VIS) and thin layer chromatography (Silufol 254; standard mixture of *n*-hexylbenzene : 1,6-dimethylnaphtalene : phenanthrene:chrysene = 20 : 5 : 3 : 1; mobile phase *n*-hexane: chloroform = 95 : 5; UV lamp, $\lambda = 254$ nm).

Di- and triarenes were analyzed by GC (Model 3700; capillary column Se 54; He carrier gas; FID). The chromatographic maxima were identified by comparing their retention times with retention times of the corresponding standard mixtures of aromatic hydrocarbons or by coinjection of individual standard components. Typical examples of gas chromatograms observed for di- and tricyclic aromatic fractions are shown in Figs. 2 and 3, and identifications of the peaks are reviewed in Tables 2 and 3.

Statistical Methods

The factor analysis was used for checking the applicability of maturation parameters [34–37, 56]. The factor analysis is a statistical method used for reducing a large number of data to a considerably smaller number of factors, representing groups of initial mutual, linearly dependent parameters containing the same amount of information as their constituent parameters. The values of coefficients preceding the parameters (loadings) included in a factor define the significance of

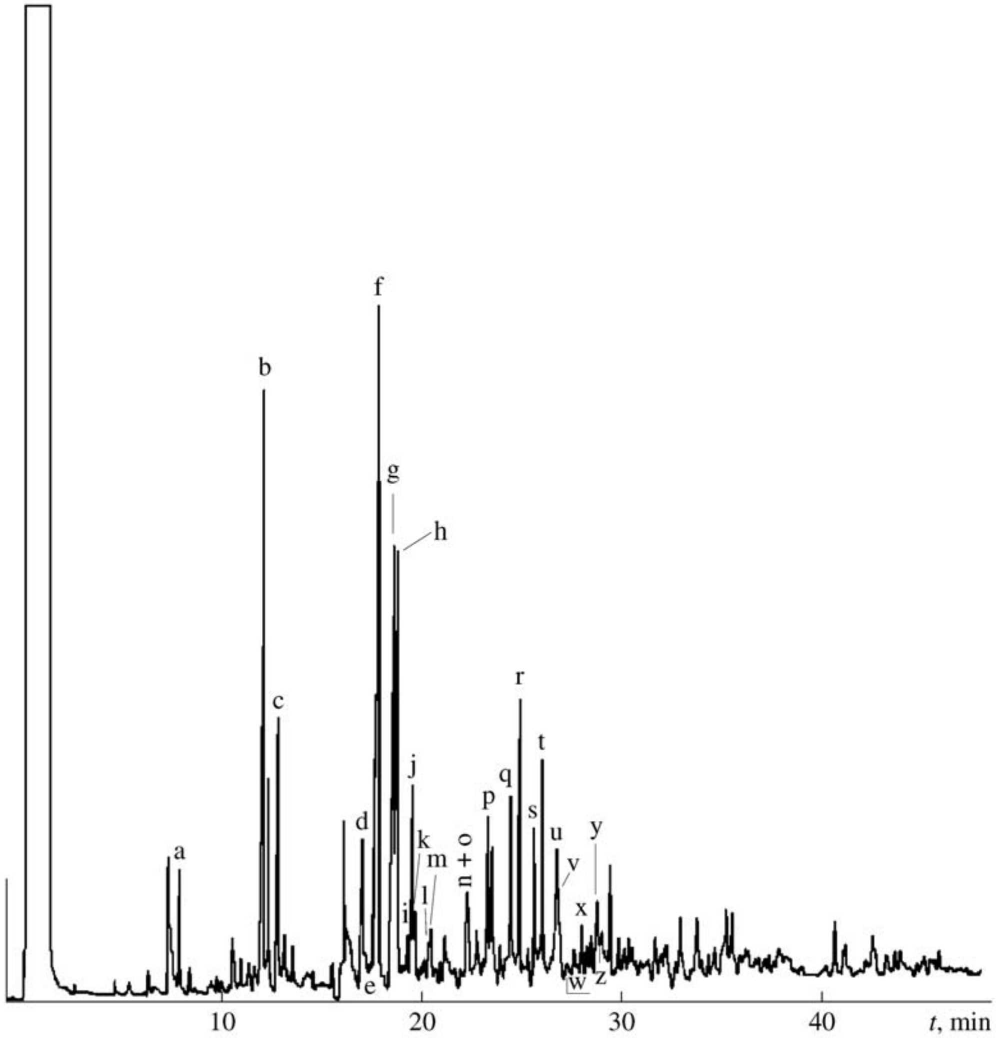

Fig. 2. Gas chromatogram of the dicyclic aromatic fraction of sample PO3, typical of the investigated crude oils (peak identifications are given in Table 2).

a particular parameter for the characterization of analyzed samples, as well as their interrelationship.

RESULTS AND DISCUSSION

Triterpane and Sterane Maturation Parameters

The triterpane maturation parameters C_{30}M/H (explanation Table 4) and C_{31}(22S)/(22S) + (22R) hopanes were found to be within the range of equilibrium values in all investigated crude oil samples (Table 4). Hence, the maturity of their source rocks was presumed to correspond to vitrinite reflectance values of Ro > 0.65%. On the other hand, none of the two sterane parameters, neither the $C_{29}\beta\beta(20R)/\alpha\alpha(20R)$ + $\beta\beta(20R)$ nor the $C_{29}\alpha\alpha(20S)/\alpha\alpha(20R)$ + $\alpha\alpha(20S)$, were found to be within the equilibria range. Based on this observation, the maturity of the source rocks of examined crude oils did not yet reach the value corresponding to vitrinite reflectance Ro = 1.00%. Consequently, according to terpane and sterane parameters, the investigated crude oils were classified within a relatively wide range of maturities. These parameters did not offer a more detailed classification, except that based on the lowest values of sterane parameters; samples V9, V10, V14, and PO6 could have been classified into a group of crude oils of lowest maturity.

Maturation Parameters Based on Di- and Tricyclic Aromatic Hydrocarbons

A number of crude oil maturation parameters has so far been proposed based on the distribution and abundance of di- and tricyclic aromatic hydrocarbons. The values of these parameters observed for the Banat depression crude oils are shown in Table 5 (an explanation of maturation parameter abbreviations is given in the Appendix).

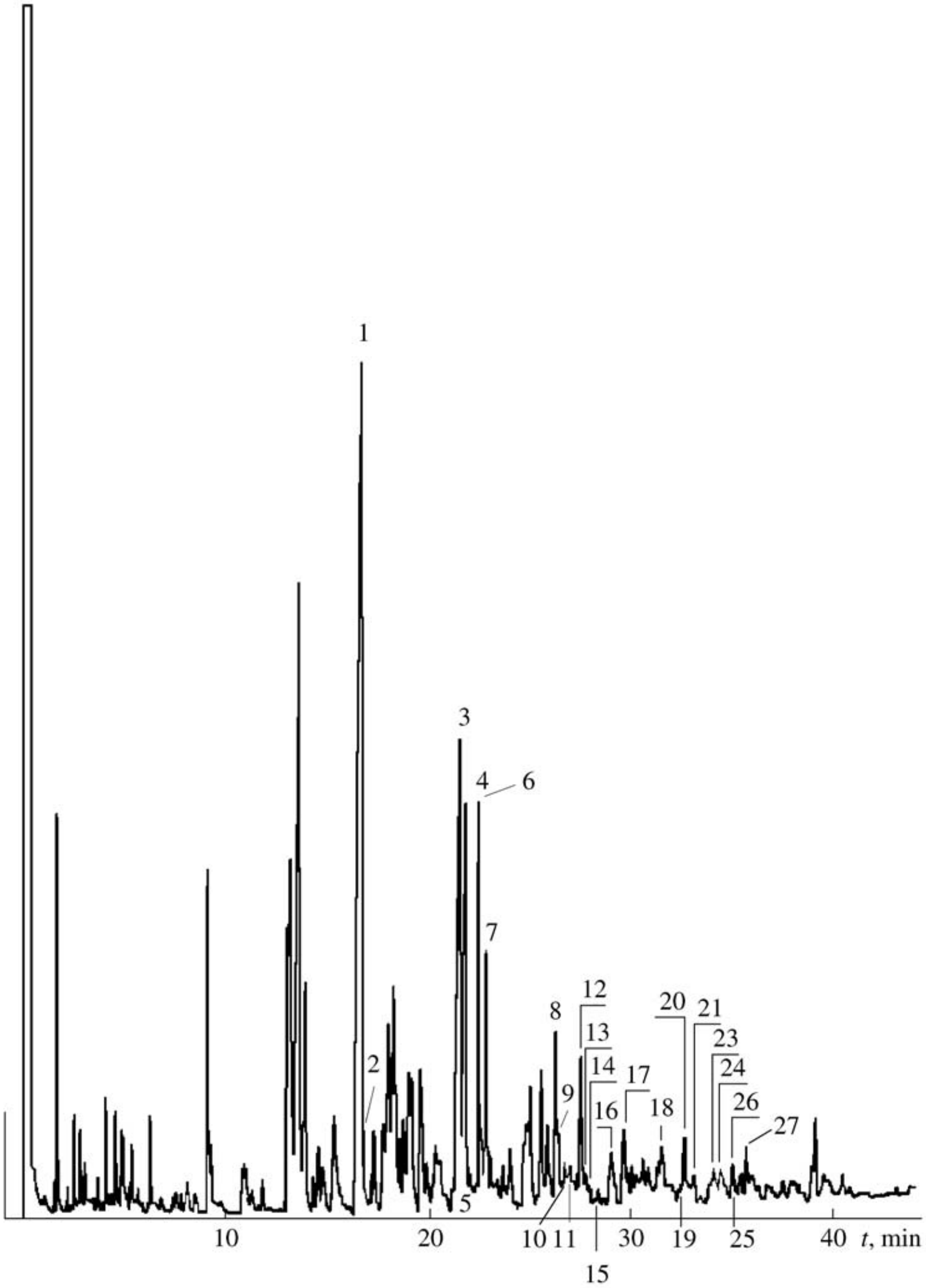

Fig. 3. Gas chromatogram of the tricyclic aromatic fraction of sample PO3, typical of the investigated crude oils (peak identifications are given in Table 3).

In order to select di- and triarene parameters best characterizing the maturity of the investigated crude oils, a factor analysis was carried out involving a large number of parameters. Their choice was aimed at obtaining a maximal value of the Kaiser–Meyer–Olkin measure coefficient of the sampling adequacy (KMO) of the factor analysis. However, care was also taken of methyl-, dimethyl-, and trimethylnaphthalene parameters, as well as corresponding ratios based on the distribution and abundance of methyl- and dimethylphenanthrenes to be equally represented (Table 6). Crude oil reservoir depths were added to the factor analysis of all analyzed maturation parameters, since a proportionality between the corresponding depths and maturities was observed in some earlier papers [28, 33]. Before varimax rotation, the first factor involved the following parameters showing significant loadings ($>|0.6|$): MPI 1, MPI 3, MPR 1, [P], PAI 1, ENR, DNR 2, and α/β DN 1 (Table 6c). By varimax rotation, which according to up-to-date organic geochemical investigations was shown to

Table 2. Identification of peaks from Fig. 2 chromatogram

Symbol	Abbreviations	Compounds
a	N	Naphthalene
b	2-MN	2-Methylnaphthalene
c	1-MN	1- Methylnaphthalene
d	2-EN	2-Ethylnaphthalene
e	1-EN	1-Ethylnaphthalene
f	1,7-+2,6-+2,7-DMN	1,7- + 2,6- + 2,7-Dimethylnaphthalenes
g	1,3-DMN	1,3-Dimethylnaphthalene
h	1,6-DMN	1,6-Dimethylnaphthalene
i	1,4-DMN	1,4-Dimethylnaphthalene
j	2,3-DMN	2,3-Dimethylnaphthalene
k	1,5-DMN	1,5-Dimethylnaphthalene
l	1,2-DMN	1,2-Dimethylnaphthalene
m	1,8-DMN	1,8-Dimethylnaphthalene
n	2-PrN	2-Propylnaphthalene
o	1-PrN	1-Propylnaphthalene
p	/	9,10-Dihydroanthracene
q	1,3,7-TMN	1,3,7-Trimethylnaphthalene
r	1,3,6-TMN	1,3,6-Trimethylnaphthalene
s	1,3,5-+1,4,6-TMN	1,3,5- + 1,4,6-Trimethylnaphthalenes
t	2,3,6-TMN	2,3,6-Trimethylnaphthalene
u	1,2,7+1,6,7-TMN	1,2,7- + 1,6,7-Trimethylnaphthalenes
v	1,2,6-TMN	1,2,6-Trimethylnaphthalene
w	1,2,4-TMN	1,2,4-Trimethylnaphthalene
x	1,2,5-TMN	1,2,5-Trimethylnaphthalene
y	2-BuN	2-Butylnaphthalene
z	1-BuN	1-Butylnaphthalene

Table 3. Identification of peaks from Fig. 3 chromatogram

Symbol	Abbreviations	Compounds
1	P	Phenanthrene
2	A	Anthracene
3	3-MP	3-Methylphenanthrene
4	2-MP	2-Methylphenanthrene
5	2-MA	2-Methylanthracene
6	9-MP	9-Methylphenanthrene
7	1-MP	1-Methylphenanthrene
8	3,6-DMP-+9-EP	3,6-Dimethylphenanthrene + 9-Ethylphenanthrene
9	1-EP	1-Ethylphenanthrene
10	2,6-+3,5-DMP	2,6- + 3,5-Dimethylphenanthrenes
11	2,7-DMP+2-EP	2,7-Dimethylphenanthrene + 2-Ethylphenanthrene
12	2,10-+3,9-+3,10-DMP	2,10- + 3,9- + 3,10-Dimethylphenanthrenes
13	1,3-+1,6-+2,9-DMP	1,3- +1,6- + 2,9-Dimethylphenanthrenes
14	1,7-DMP	1,7-Dimethylphenanthrene
15	1,9-+4,9-DMP	1,9- + 4,9-Dimethylphenanthrenes
16	1,8-DMP	1,8-Dimethylphenanthrene
17	1,2-DMP	1,2-Dimethylphenanthrene
18	EP+*t*-BuP+*iso*-BuP	Ethyl- + Tert.butyl- + Isobutylphenanthrenes
19	2,6,10-TMP	2,6,10-Trimethylphenanthrene
20	1,3,6-TMP	1,3,6-Trimethylphenanthrene
21	1,3,7-+1,3,9-+ 2,7,10-TMP	1,3,7- + 1,3,9- + 2,7,10-Trimethylphenanthrenes
22	2,3,6-TMP	2,3,6-Trimethylphenanthrene
23	1,3,8-+2,3,7-+2,8,10-TMP	1,3,8- + 2,3,7- + 2,8,10-Trimethylphenanthrenes
24	/	Fluorene
25	2,3,10-+3,8,10-TMP	2,3,10- + 3,8,10-Trimethylphenanthrenes
26	/	Retene
27	1,2,3-+1,2,8-+ 1,7,10-TMP	1,2,3- + 1,2,8- + 1,7,10-Trimethylphenanthrenes

be most convenient [35, 56]; factor 1 (Table 6c) was divided into two new factors (Table 6d). Separation of these parameters into two different factors by varimax rotation suggested the two corresponding groups of parameters to be related to different arene processes. Factor 1 involved parameters based on isomerization reactions of methylnaphthalenes and phenanthrenes and factor 2 parameters [P] and PAI 1, also with signif-

Table 4. Maturation parameters calculated from distributions and abundances of terpane and sterane isomers

Sample	C_{30}M/H	C_{31}(S)/(S) + (R)	$C_{29}\beta\beta(R)/\alpha\alpha(R) + \beta\beta(R)$	$C_{29}\alpha\alpha(S)/\alpha\alpha(R) + \alpha\alpha(S)$
V1	0.110	0.590	0.551	0.455
V2	0.126	0.582	0.542	0.439
V3	0.097	0.581	0.569	0.498
V4	0.143	0.591	0.568	0.490
V5	0.104	0.593	0.571	0.489
V6	0.106	0.592	0.570	0.485
V7	0.105	0.593	0.568	0.489
V8	0.099	0.597	0.570	0.509
V9	0.139	0.585	0.394	0.352
V10	0.154	0.569	0.337	0.328
V11	0.115	0.602	0.495	0.472
V12	0.104	0.599	0.556	0.484
V13	0.096	0.581	0.590	0.496
V14	0.113	0.597	0.460	0.394
PO1	0.131	0.605	0.564	0.575
PO2	0.142	0.609	0.540	0.528
PO3	0.126	0.609	0.559	0.462
PO4	0.121	0.615	0.582	0.475
PO5	0.123	0.617	0.605	0.548
PO6	0.142	0.612	0.394	0.446
PO7	0.120	0.607	0.589	0.476
E.V.	0.05–0.15	0.57–0.62	0.67–0.71	0.52–0.55

Note: M – $C_{30}17\beta(H)21\alpha(H)$-moretane; H – $C_{30}17\alpha(H)21\beta(H)$-hopane;
C_{31}(S) – $C_{31}17\alpha(H)21\beta(H)22(S)$-hopane; C_{31}(R) – $C_{31}17\alpha(H)21\beta(H)22(R)$-hopane;
$C_{29}\beta\beta(R)$ – $C_{29}14\beta(H)17\beta(H)20(R)$-sterane; $C_{29}\alpha\alpha(R)$ – $C_{29}14\alpha(H)17\alpha(H)20(R)$-sterane;
$C_{29}\alpha\alpha(S)$ – $C_{29}14\alpha(H)17\alpha(H)20(S)$-sterane; E.V.– equilibrium value [1].

icantly high loadings (>|0.80|), based on methyl-phenanthrene alkylation–dealkylation processes (Table 6d).

Among the parameters having high loadings in factor 1, listed in Table 6, the methylphenanthrene index 3 (MPI 3) has so far most often been used. Based on this parameter, the following classification of crude oils was proposed: high maturity crude oils MPI 3 > 1.00, medium maturity MPI 3 = 0.80–1.00, and immature crude oils MPI 3 > 0.80 [5, 32, 57]. Based on MPI 3 parameter (Table 5), the investigated crude oil samples were classified into the following groups:

—high maturity crude oils (MPI 3 > 1.00)—samples V1, V2, V3, V7, V8, V11, V12, V13, PO1, PO2, PO3, PO4, and PO7;

—medium maturity (MPI 3 = 0.80–1.00)—V4, V5, V6, V14, PO5, and PO6;

—immature crude oils (MPI 3 < 0.80)—samples V9 and V10.

Proposal of New Maturation Parameters Based on Methylnaphthalene Isomerization Reactions

Aiming at more precise classification, particularly of the thirteen crude oil samples of high maturity (MPI 3 > 1.00), several other reactions of crude oil aromatic hydrocarbons were considered in more detail.

Several facts were learned from the literature: (a) isocadalene/cadalene ratio was successfully used in crude oil maturity assessment [8]; (b) parameters based

Table 5. Maturation parameters calculated from distributions and abundances of di- and tricyclic aromatic hydrocarbons

Sample	MPI 3	MPR 1	MPI 1	DMPI 1	DMPI 2	[P]	PAI 1	MNR	DNR 1	ENR	DNR 2	α/β DN 1	TNR 1	TNR 2	TNR 3	DNx	TNy	MDR	MTR
V1	1.17	1.38	0.85	1.19	0.36	16.79	2.05	1.51	0.02	1.87	2.82	0.41	0.27	0.56	3.11	4.25	2.54	1.02	2.94
V2	1.20	1.41	0.87	1.12	0.45	16.41	2.04	1.54	0.03	1.92	2.97	0.53	0.37	0.67	2.17	4.33	2.63	0.91	3.43
V3	1.25	1.43	0.86	0.99	0.43	17.15	1.90	1.57	0.02	1.95	2.44	0.47	0.36	0.61	3.33	4.37	2.65	0.94	2.85
V4	0.83	1.00	0.72	1.25	0.57	12.23	2.49	1.23	0.04	0.85	2.13	0.62	0.59	0.82	2.83	3.23	2.13	0.79	2.29
V5	0.87	1.02	0.75	1.09	0.44	12.73	2.50	1.28	0.03	0.86	2.62	0.55	0.23	0.76	2.89	3.77	2.28	0.85	2.51
V6	0.90	1.07	0.71	1.07	0.44	13.92	2.13	1.25	0.03	0.87	1.84	0.66	0.56	0.84	3.16	3.23	2.09	0.78	2.14
V7	1.41	1.69	0.90	0.63	0.39	23.48	1.79	1.82	0.02	3.80	6.62	0.21	0.25	0.67	3.22	7.19	3.07	1.76	5.68
V8	1.37	1.64	0.87	0.61	0.38	22.14	1.73	1.75	0.02	3.22	3.84	0.30	0.77	0.99	2.48	7.10	3.04	1.75	3.70
V9	0.77	0.83	0.65	1.20	0.47	10.91	2.30	0.80	0.06	0.78	1.61	0.94	0.44	0.76	0.92	2.36	1.66	0.74	1.34
V10	0.80	0.92	0.80	0.87	0.25	8.04	3.54	0.93	0.01	0.82	1.17	0.84	0.42	0.47	2.63	2.48	1.97	0.74	1.62
V11	1.07	1.31	0.79	1.04	0.53	15.89	1.99	1.37	0.02	1.99	1.53	0.89	0.74	0.79	1.21	4.07	2.51	1.22	3.01
V12	1.26	1.45	0.88	1.35	0.38	17.20	1.97	1.63	0.06	1.96	1.28	1.09	0.65	0.76	1.46	4.79	2.67	1.14	2.86
V13	1.19	1.40	0.88	1.43	0.64	16.05	2.14	1.53	0.08	1.91	1.73	0.99	0.59	0.77	2.70	4.31	2.60	1.23	2.79
V14	0.81	0.97	0.69	1.00	0.31	13.36	2.39	1.14	0.08	0.97	1.62	1.11	0.21	0.58	2.51	2.90	2.03	0.86	2.56
PO1	1.27	1.48	0.86	0.92	0.23	23.34	1.87	1.61	0.05	1.67	4.34	0.33	1.18	0.87	1.80	4.38	2.61	1.95	7.26
PO2	1.27	1.23	0.76	0.69	0.51	29.28	1.52	1.65	0.04	2.19	7.11	0.24	1.23	0.90	1.82	6.53	2.73	3.42	5.40
PO3	1.33	1.61	0.87	1.19	0.44	24.74	1.80	2.20	0.03	4.18	9.50	0.20	1.47	0.94	5.80	7.29	3.07	2.43	5.24
PO4	1.66	1.91	1.12	1.02	0.45	19.19	2.17	2.22	0.03	3.11	6.32	0.20	1.55	0.92	4.35	10.21	3.07	1.44	6.06
PO5	0.99	1.11	0.85	1.13	0.49	10.55	2.67	1.43	0.06	2.23	3.74	0.45	1.18	0.85	1.87	2.88	2.33	0.73	1.52
PO6	0.81	0.99	0.67	0.79	0.26	12.53	2.21	1.19	0.04	2.35	2.31	0.42	1.15	0.82	1.33	3.98	2.20	0.84	1.75
PO7	1.14	1.28	0.90	1.02	0.43	13.32	2.39	1.44	0.03	1.84	3.17	0.31	1.48	0.98	3.09	5.39	2.90	0.85	2.35

Note: DNR 2 and α/β DN 1 parameters were altered due to coelution of 1,7-DMN together with 2,6- and 2,7-DMN (cf. Figure 2 and Table 2, peak f). Explanation of abbreviations is given in the Appendix.

Table 6. Factor analysis of di- and triarene maturation parameters known from literature (including the reservoir rock depths)

Factor	Extraction sums of squared loadings before varimax rotation (a)			Varimax rotation sums of squared loadings (b)		
	total	% of variance	cumulative %	total	% of variance	cumulative %
1	*7.178*	*55.215*	*55.215*	*4.392*	*33.787*	*33.787*
2	*1.485*	*11.420*	*66.635*	*3.616*	*27.813*	*61.600*
3	*1.184*	*9.106*	*75.742*	*1.548*	*11.909*	*73.509*
4	*1.150*	*8.849*	*84.591*	*1.441*	*11.081*	*84.591*
5	0.917	7.055	91.645			
6	0.413	3.180	94.825			
7	0.322	2.476	97.301			
8	0.193	1.488	98.790			
9	8.724×10^{-2}	0.671	99.461			
10	3.347×10^{-2}	0.257	99.718			
11	2.531×10^{-2}	0.195	99.913			
12	9.195×10^{-3}	7.073×10^{-2}	99.984			
13	2.120×10^{-3}	1.631×10^{-2}	100.000			

Note: Kaiser–Meyer–Olkin measure of sampling adequacy (KMO) = 0.645
Bartlett's test of sphericity: approx. chi-square = 317.868
Significance = 0.000; Determinant = 4.936×10^{-10}
Sums of squared loading of riguificant factors according to Kaiser's and Catell's rules, which subjected to varimax rotation are marked in italic [35–37, 56].

Parameter	Component matrix before varimax rotation (c)				Varimax rotated component matrix (d)			
	factor				factor			
	1	2	3	4	1	2	3	4
MPI 1	0.762	9.776×10^{-2}	-6.637×10^{-2}	0.597	0.969	4.540×10^{-2}	8.117×10^{-2}	6.164×10^{-2}
MPI 3	0.936	-9.646×10^{-2}	0.108	0.217	0.827	0.510	7.638×10^{-3}	2.069×10^{-2}
MPR 1	0.919	-6.996×10^{-2}	9.853×10^{-2}	0.280	0.858	0.448	1.963×10^{-2}	1.086×10^{-2}
DMPI 2	8.248×10^{-2}	-1.977×10^{-2}	0.727	0.181	0.154	0.164	0.104	–0.712
[P]	0.816	–0.174	0.198	–0.412	0.307	0.897	3.274×10^{-2}	8.011×10^{-2}
PAI 1	–0.655	0.417	–0.394	0.403	–0.181	–0.909	0.184	0.166
MNR	0.970	7.991×10^{-2}	8.495×10^{-2}	0.106	0.782	0.554	0.194	0.101
ENR	0.895	-8.622×10^{-2}	–0.110	-1.684×10^{-2}	0.647	0.568	6.263×10^{-3}	0.282
DNR 2	0.839	0.266	-5.792×10^{-2}	–0.359	0.381	0.687	0.401	0.359
α/β DN 1	–0.724	–0.245	0.298	0.316	–0.335	–0.516	–0.314	–0.544
TNR 1	0.553	1.695×10^{-2}	–0.456	-7.210×10^{-2}	0.376	0.254	5.609×10^{-3}	0.561
TNR 3	0.546	0.758	0.106	9.558×10^{-2}	0.480	0.129	0.801	7.522×10^{-2}
Depth	0.448	–0.732	–0.323	0.222	0.474	0.220	–0.746	0.245

on dimethylnaphthalene isomerization reactions were successfully applied in cases where methylphenanthrene parameters failed [26]; and (c) $\alpha \longrightarrow \beta$ isomerization reactions of naphthalene alkyl groups are occurring in a similar way, regardless of the number of substituents [20].

Based on these observations, two new maturation parameters are proposed:

—the dimethylnaphthalene ratio

DNx = (1,3-DMN + 1,6-DMN)/(1,4-DMN + 1,5-DMN) and

—the trimethylnaphthalene ratio

TNy = (1,3,6-TMN + 1,3,7-TMN)/(1,3,5-TMN + 1,4,6-TMN).

These ratios are based on isomerization of thermodynamically less stable αα-1,4- and 1,5-dimethylnaphthalenes (DMN) into more stable αβ-1,3- and 1,6-dimethylnaphthalenes and isomerization of ααβ-1,3,5-

Table 7. Factor analysis of combined list of di- and triarene maturation parameters known from literature and the newly proposed parameters DNx and TNy (including the reservoir rock depths)

Factor	Extraction sums of squared loadings before varimax rotation (a)			Varimax rotation sums of squared loadings (b)		
	total	% of variance	cumulative %	total	% of variance	cumulative %
1	*8.929*	*59.528*	*59.528*	*5.927*	*39.514*	*39.514*
2	*1.503*	*10.023*	*69.551*	*3.820*	*25.466*	*64.981*
3	*1.185*	*7.901*	*77.452*	*1.550*	*10.331*	*75.311*
4	*1.171*	*7.808*	*85.260*	*1.492*	*9.949*	*85.260*
5	0.920	6.132	91.392			
6	0.429	2.861	94.252			
7	0.326	2.171	96.423			
8	0.204	1.357	97.780			
9	0.156	1.038	98.817			
10	9.299×10^{-2}	0.620	99.437			
11	2.943×10^{-2}	0.196	99.633			
12	2.467×10^{-2}	0.164	99.798			
13	2.124×10^{-2}	0.142	99.939			
14	8.097×10^{-3}	5.398×10^{-2}	99.993			
15	9.784×10^{-4}	6.523×10^{-3}	100.000			

Note: Kaiser–Meyer–Olkin measure of sampling adequacy (KMO) = 0.624
Bartlett’s test of sphericity: approx. chi-square = 393.547
Significance = 0.000; Determinant = 8.618×10^{-13}
Sums of squared loading of riquificant factors according to Kaiser's and Catell's rules, which subjected to varimax rotation are marked in italic [35–37, 56].

Parameter	Component matrix before varimax rotation (c)				Varimax rotated component matrix (d)			
	factor				factor			
	1	2	3	4	1	2	3	4
MPI 1	0.776	8.396×10^{-2}	7.426×10^{-2}	0.579	0.972	-3.005×10^{-3}	5.445×10^{-2}	6.188×10^{-2}
MPI 3	0.943	–0.101	0.148	0.162	0.854	0.467	-1.575×10^{-2}	2.079×10^{-2}
MPR 1	0.927	-7.827×10^{-2}	0.156	0.229	0.883	0.402	-6.807×10^{-3}	9.698×10^{-3}
DMPI 2	8.498×10^{-2}	-2.255×10^{-2}	0.741	-2.185×10^{-2}	0.149	0.167	0.109	–0.704
[P]	0.808	–0.167	8.365×10^{-2}	–0.466	0.356	0.878	1.910×10^{-2}	8.074×10^{-2}
PAI 1	–0.645	0.410	–0.275	0.509	–0.222	–0.897	0.192	0.166
MNR	0.970	7.486×10^{-2}	9.781×10^{-2}	5.951×10^{-2}	0.810	0.514	0.168	0.103
ENR	0.892	-8.847×10^{-2}	–0.122	-1.335×10^{-2}	0.673	0.535	-1.761×10^{-2}	0.283
DNR 2	0.825	0.274	–0.154	–0.354	0.417	0.669	0.386	0.367
α/β DN 1	–0.716	–0.248	0.372	0.243	–0.370	–0.499	–0.294	–0.547
TNR 1	0.545	2.600×10^{-2}	–0.473	9.997×10^{-2}	0.372	0.243	-1.063×10^{-3}	0.570
TNR 3	0.549	0.748	0.126	7.313×10^{-2}	0.508	0.105	0.779	8.050×10^{-2}
Depth	0.446	–0.743	–0.270	0.265	0.458	0.195	–0.768	0.238
DNx	0.930	0.110	2.120×10^{-2}	3.217×10^{-2}	0.753	0.494	0.191	0.176
TNy	0.954	-9.239×10^{-2}	4.979×10^{-2}	0.124	0.827	0.488	-1.459×10^{-2}	0.121

and 1,4,6-trimethylnaphthalenes (TMN) into more stable αββ-1,3,6- and 1,3,7-trimethylnaphthalenes. Some earlier investigations showed the contents of 1,6-DMN and 1,3,6-TMN may depend on the crude oil origin [8, 20]. The effect of genetic factors on the contents of these two isomers was, therefore, separately considered

Table 8. Classification of the investigated crude oils according to maturity, based on MPI 3, MPR 1, MNR, DNx and TNy parameters

Group	Maturity	MPI 3	MPR 1	MNR	DNx	TNy
I	High (V7, V8, PO 3 and PO 4)	>1.30	>1.50	>1.65	>7.00	>2.90
II	Medium to high (V1, V2,V3, V11, V12, V13, PO 1, PO 2 and PO 7)	1.00–1.30	1.20–1.50	1.30–1.65	4.00–7.00	2.50–2.90
III	Medium (V4, V5, V6, V14, PO5 and PO6)	0.80–1.00	0.95–1.20	1.00–1.30	2.50–4.00	2.00–2.50
IV	Low (V9 and V10)	<0.80	<0.95	<1.00	<2.50	<2.00

by correlation with sterane and terpane source parameters (Table, Appendix). The results showed that, in the case of Banat depression crude oils, genetic factors had no effect on the contents of 1,6-DMN and 1,3,6-TMN, suggesting their possible unlimited usage for maturation parameters calculation.

The values of the two new parameters, calculated for the 21 crude oil samples are given in Table 5. Their applicability was checked by factor analysis (Table 7). Parameters DNx and TNy were added to the list of selected literature parameters (Table 6) and the factor analysis was repeated (Table 7). Before rotation, as well as after varimax rotation, the newly proposed parameters, characterized by high loadings (>|0.70|), were involved in the most important factor, factor 1. These two parameters were the only representatives of di- and trimethylnaphthalene parameters to have been found in factor 1 both before and after varimax rotation (Table 7c and 7d). Moreover, it is of greatest importance that DNx and TNy parameters raised the significance of factor 1 (% of variance; Tables 6 and 7a and 7b).

Parameters DNx and TNy were thus shown to be a good tool which enabled subclassification of the 13 high maturity crude oil samples into two new categories. Consequently, based on these two newly proposed maturation parameters, the investigated crude oils were classified into four groups (Table 8).

Finally, DNx and TNy also contributed to establishing boundary values for MNR and MPR 1 parameters (Table 8), as well as to a more precise subdivision of parameter MPI 3 values: medium to highly mature crude oils MPI 3 = 1.00–1.30, and high maturity crude oils MPI 3 > 1.30 (Table 8).

Proposal of New Maturation Parameters Based on Dealkylation Reactions of Methylphenanthrenes

In several earlier papers, crude oils and sedimentary bitumens have already been classified according to maturity parameters based on methylphenanthrene alkylation–dealkylation reactions. Namely, some organic geochemical investigations [5, 11, 13, 32, 33], as well as geosynthetic modelling studies [31], have shown that during catagenetic evolution, depending on temperature and proton-donor type clay minerals, alkylation of phenanthrenes into methylphenanthrenes may have occurred, and also their dealkylation, particularly at higher degrees of maturity. Therefore, for the sake of comparison, two parameters based on alkylation–dealkylation, i.e., [P] and PAI 1 (Table 5), were first used in this paper for maturity estimation of the Banat depression crude oils. Their significance was confirmed by factor analysis (Tables 6 and 7c and 7d). The fact that loadings observed for parameter [P] in factors 1 and 2 were positive, like those for MNR, MPI 3, MPR 1, and that the one of parameter PAI 1 was negative, indicated that methylphenanthrene dealkylation may also have occurred (Tables 6, 7c and 7d).

Hence, a rationale for designing new aromatic hydrocarbon alkylation–dealkylation maturation parameters was found in the fact that, in addition to isomerization of α- into more stable β-methylphenanthrenes, dealkylation of methylphenanthrenes into phenanthrene also represented one of the main maturation processes in the investigated crude oils (factors 1 and 2; Tables 6 and 7, c and d). Therefore, two additional new maturation parameters are proposed in this paper based on demethylation of trimethyl- and dimethylphenanthrenes into corresponding methylphenanthrenes (Table 5):

—the ratio between the contents of methyl- and dimethylphenanthrenes in tricyclic aromatic fraction MDR = ΣMP/ΣDMP and

—the ratio between the contents of methyl- and trimethylphenanthrenes in tricyclic aromatic fraction MTR = ΣMP/ΣTMP.

The applicability of MDR and MTR was checked by factor analysis. For this purpose the new parameters were added to the list of best known literature parameters (Table 9). Before varimax rotation, MDR and MTR were ranked into factor 1 (Table 9c). After varimax rotation, they were transferred into factor 2, though with significantly high loadings, ≥|0.7|, together with [P] and PAI 1, reflecting important methylphenanthrene dealkylation processes occurring in the catagenetic stage (Table 9d). Importantly, the newly proposed parameters contributed to higher factor 2 significance: % of variance approached the corresponding factor 1 value (Table 9b), suggesting that aromatic hydrocarbons' dealkylation processes were of significance in maturity assessment of the investigated crude oils.

Table 9. Factor analysis of combined list of di- and triarene maturation parameters known from literature and the newly proposed parameters MDR and MTR (including the reservoir rock depths)

Factor	Extraction sums of squared loadings before varimax rotation (a)			Varimax rotation sums of squared loadings (b)		
	total	% of variance	cumulative %	total	% of variance	cumulative %
1	*8.386*	*55.908*	*55.908*	*4.910*	*32.733*	*32.733*
2	*1.561*	*10.410*	*66.318*	*4.825*	*32.169*	*64.902*
3	*1.439*	*9.593*	*75.911*	*1.492*	*9.944*	*74.846*
4	*1.184*	*7.893*	*83.804*	*1.344*	*8.958*	*83.804*
5	0.985	6.565	90.369			
6	0.543	3.621	93.990			
7	0.357	2.378	96.368			
8	0.273	1.817	98.185			
9	0.115	0.763	98.948			
10	8.833×10^{-2}	0.589	99.537			
11	3.691×10^{-2}	0.246	99.783			
12	2.669×10^{-2}	0.178	99.961			
13	2.481×10^{-3}	1.654×10^{-2}	99.978			
14	1.913×10^{-3}	1.275×10^{-2}	99.990			
15	1.426×10^{-3}	9.506×10^{-3}	100.000			

Note: Kaiser–Meyer–Olkin measure of sampling adequacy (KMO) = 0.650
Bartlett's test of sphericity: approx. chi-square = 427.538
Significance = 0.000; Determinant = 7.823×10^{-14}
Sums of squared loading of riquificant factors according to Kaiser's and Catell's rules, which subjected to varimax rotation are marked in italic [35–37, 56].

Parameter	Component matrix before varimax rotation (c)				Varimax rotated component matrix (d)			
	factor				factor			
	1	2	3	4	1	2	3	4
MPI 1	0.718	0.517	0.356	5.075×10^{-2}	0.952	6.010×10^{-2}	4.416×10^{-2}	3.339×10^{-2}
MPI 3	0.926	0.116	0.230	0.144	0.826	0.508	-4.783×10^{-2}	-3.251×10^{-2}
MPR 1	0.898	0.199	0.267	0.146	0.869	0.424	-3.392×10^{-2}	-3.906×10^{-2}
DMPI 2	6.084×10^{-2}	2.812×10^{-2}	7.768×10^{-2}	0.775	0.149	8.975×10^{-2}	8.132×10^{-2}	–0.758
[P]	0.871	–0.415	–0.173	0.107	0.313	0.934	-2.169×10^{-2}	2.318×10^{-2}
PAI 1	–0.682	0.531	-4.117×10^{-2}	–0.305	–0.225	–0.824	0.239	0.235
MNR	0.956	0.191	5.723×10^{-2}	0.108	0.811	0.538	0.130	3.622×10^{-2}
ENR	0.871	5.349×10^{-2}	0.156	-9.958×10^{-2}	0.704	0.505	-6.513×10^{-2}	0.205
DNR 2	0.863	-9.961×10^{-4}	–0.380	–0.117	0.431	0.718	0.339	0.295
α/β DN 1	–0.721	–0.104	0.262	0.344	–0.425	–0.486	–0.256	–0.485
TNR 1	0.549	5.088×10^{-2}	3.626×10^{-2}	–0.438	0.398	0.284	-4.166×10^{-2}	0.506
TNR 3	0.516	0.644	–0.441	0.131	0.536	0.128	0.766	4.861×10^{-2}
Depth	0.419	–0.255	0.770	–0.263	0.471	0.150	–0.788	0.191
MDR	0.756	–0.479	–0.300	6.203×10^{-3}	0.135	0.926	2.369×10^{-2}	0.120
MTR	0.853	–0.152	–0.178	-4.635×10^{-2}	0.434	0.743	0.102	0.187

Moreover, high loadings values for phenanthrene dealkylation parameters [P], PAI 1, MDR, and MTR were suggesting that, during maturation dealkylation, reactions of all methylphenanthrene isomers occurred simultaneously, regardless of the number of methyl groups in the phenanthrene nucleus. According to maturity based on phenanthrene content in the tricyclic aromatic fraction and the newly proposed MDR and

Table 10. Classification of the investigated crude oils according to maturity, based on [P], MDR, and MTR parameters

Group	Maturity	[P]	MDR	MTR
I	High (V7, V8, PO 1, PO 2, PO 3 and PO 4)	>18.00	>1.30	>3.50
II	Medium to high (V1, V2, V3, V11, V12 and V13)	14.00–18.00	0.90–1.30	2.60–3.50
III	Medium (V4, V5, V6, V14, PO 6 and PO 7)	12.00–14.00	0.75–0.90	1.70–2.60
IV	Low (V9, V10 and PO 5)	<12.00	<0.75	<1.70

MTR parameters, the investigated crude oils were classified as shown in Table 10.

Concerning the crude oils originating from the Vojvodina part of the Banat depression, no difference was observed between the classification based on isomerization parameters (Table 8) and that one based on [P], MDR, and MTR parameters (Table 10). On the other hand, on the basis of the same parameters, crude oils originating from Sirakovo and Bradarac-Maljurevac oil fields (Drmno depression) were found to be different, the Sirakovo crude oils being characterized by higher maturity (Table 10). Similar differences were observed using naphthalene and phenanthrene isomerization reactions (Table 8).

Several other observations concerning the classification of the Drmno depression crude oils based on dealkylation parameters (Table 10) are also of interest. Namely, all Sirakovo samples, i.e., PO 1, PO 2, PO 3, and PO 4, were classified into Group I crude oils. Hence, compared to classification based on naphthalene and phenanthrene isomerization parameters, no difference was observed with samples PO 3 and PO 4, while samples PO 1 and PO 2 were transferred from Group II into Group I crude oils, suggesting a somewhat more intense dealkylation reactions with these two samples compared to isomerization reactions (Tables 8 and 10).

Bradarac-Maljurevac crude oil samples suffered greater changes by classification based on dealkylation parameters: PO 7 was transferred from Group II into Group III, and PO 5 from Group III into Group IV. The only sample which remained in the same Group III by both isomerization and dealkylation parameter classifications was the sample PO 6. Hence, in contrast to samples PO 1 and PO 2, less intensive dealkylation compared to isomerization processes was suggested in crude oils PO 5 and PO 7 (Tables 8 and 10). Lower intensity of dealkylation reactions observed with Bradarac-Maljurevac crude oils compared to Sirakovo crude oils suggested different source rocks of these two groups of crude oils, or that these oils originated from the same source rock but were expelled at different times and at a different stage of maturity. The Bradarac-Maljurevac crude oils probably originate from sediments of lower stage of thermal maturity. This observation is in agreement with geological experience [50, 52–54]. It may be supposed that differences in intensities of alkylphenanthrene isomerization and dealkylation processes observed with individual Drmno depression crude oil samples are mainly due to significant heterogeneity of the depositional environment of source rocks [44, 46, 51–53].

CONCLUSIONS

This paper is aimed at improving the maturity classification of crude oils, particularly the classification resulting from using sterane and terpane maturation parameters alone. For this purpose, the potentials of naphthalene and phenanthrene isomers', reactions occurring in crude oil aromatic fractions, were analyzed in more detail. Crude oils originating from the Banat depression (Southeastern Pannonian Basin) were used as objects understudy. Altogether four new parameters are proposed.

Two of them are based on dimethyl- and trimethylnaphthalene isomerization reactions:

DNx = (1,3-DMN + 1,6-DMN)/(1,4-DMN + 1,5-DMN), and

TNy = (1,3,6-TMN + 1,3,7-TMN)/(1,3,5-TMN + 1,4,6-TMN).

Their advantageous improved applicability was confirmed by factor analysis. Based on these two new maturation parameters, the Banat depression crude oils were classified into four groups, instead of into only two groups using sterane and terpane parameters:

Crude oils of	DNx	TNy
High thermal maturity	>7.00	>2.90
Medium to high thermal maturity	4.00–7.00	2.50–2.90
Medium thermal maturity	2.50–4.00	2.00–2.50
Low maturity	<2.50	<2.00

Furthermore, these two parameters enabled the establishing of boundary values for parameters MNR (2-MN/1-MN) and MPR 1 (2-MP/1-MP), known from literature:

Crude oils of	MNR	MPR 1
High maturity	>1.65	>1.50
Medium to high maturity	1.30–1.65	1.20–1.50
Medium maturity	1.00–1.30	0.95–1.20
Low maturity	<1.00	<0.95

Finally, they contributed to establishing more precise boundary values for parameter MPI 3, i.e., in the case of considerably mature crude oils: crude oils of high thermal maturity (MPI 3 > 1.30) and medium to high maturity crude oils (MPI 3 = 1.00–1.30).

The other two newly proposed maturation parameters are based on demethylation of dimethyl- and trimethylphenanthrenes into corresponding methylphenanthrenes: MDR = ΣMP/ΣDMP and MTR = ΣMP/ΣTMP.

Their advantageous applicability was also confirmed by factor analysis. These parameters, together with parameter [P], representing the concentration of phenanthrene in the tricyclic aromatic fraction and also based on dealkylation of methylphenanthrene isomers, were successfully used for maturity assessment of the examined crude oils. Based on these two new maturation parameters, the Banat depression crude oils were also classified into four groups:

Crude oils of	MDR	MTR
high thermal maturity	>1.30	>3.50
medium to high thermal maturity	0.90–1.30	2.60–3.50
medium thermal maturity	0.75–0.90	1.70–2.60
low maturity	<0.75	<1.70

With crude oils originating from Vojvodina localities, no differences were observed between maturity classifications based on isomerization or dealkylation parameters, in contrast to Drmno depression crude oil classifications, which demonstrated certain discordance. Namely, lower intensity of dealkylation reactions observed with Bradarac-Maljurevac crude oils clearly suggested their lower maturity compared to Sirakovo crude oils. Differences in the intensity of alkylphenanthrenes, isomerization, and dealkylation transformations observed with some Drmno depression crude oil samples are probably due to significant differences in their depositional environments of source rocks.

In general, a more precise maturity ranking of crude oils may lead to a new interpretation of the structural development of subbasins and may thus give an impetus to the petroleum exploration in that region.

ACKNOWLEDGMENTS

We thank the Alexander von Humboldt-Stiftung for supporting this research. We also thank Dr. Hermann Wehner (Federal Institute for Geosciences and Natural Resources) for his help with the GC-MSD analyses. This work was supported in part by the Research Fund of the Republic of Serbia.

APPENDIX

MNR = 2-MN/1-MN [4]

DNR 1 = 1,8-DMN/SDMN [58]

DNR 2 = (2,6- + 2,7-DMN)/1,5-DMN [4]

α/βDN 1 = (1,4- + 1,5- + 1,8-DMN)/(2,3- + 2,6- + 2,7-DMN) [29]

TNR 1 = 2,3,6-TMN/(1,3,5- + 1,4,6-TMN) [7]

TNR 2 = (1,3,7- + 2,3,6-TMN)/(1,3,5- + 1,3,6- + 1,4,6-TMN) [24]

TNR 3 = 1,3,6-TMN/1,2,5-TMN [6]

ENR = 2-EN/1-EN [4]

MPR 1 = 2-MP/1-MP [4]

MPI 1 = 1,5 × (2- + 3-MP)/(P + 1- + 9-MP) [3]

MPI 3 = (2- + 3-MP)/(1- + 9-MP) [5, 57]

PAI 1 = (1- + 2- + 3- + 9-MP)/P [59]

[P], content of phenanthrene in tricyclic aromatic fraction, (%) [33]

DMPI 1 = 4 × (2,6- + 2,7- + 3,5- + 3,6-DMP + 1- + 2- + 9-EP)/(P + 1,3- + 1,6- + 1,7- + 2,5- + 2,9- + 2,10- + 3,9- + 3,10-DMP) [3]

DMPI 2 = (2,6- + 2,7- + 3,5-DMP)/(1,3- + 1,6- + 2,5- + 2,9- + 2,10- + 3,9- + 3,10-DMP) [4]

MN—methylnaphthalene; DMN—dimethylnaphthalene;

TMN—trimethylnaphthalene; EN—ethylnaphthalene;

P—phenanthrene; MP—methylphenanthrene;

DMP—dimethylphenanthrene; EP—ethylphenanthrene.

Table. Correlation of the contents of 1,6-DMN and 1,3,6-TMN with sterane and terpane source parameters [60

Correlation coefficient – r	1,6-DMN	1,3,6-TMN
%$C_{27}14\alpha(H)17\alpha(H)20(R)$-sterane	–0.024	0.438
%$C_{28}14\alpha(H)17\alpha(H)20(R)$-sterane	–0.014	–0.476
%$C_{29}14\alpha(H)17\alpha(H)20(R)$-sterane	0.033	0.369
Oleanane × 100/C_{30}hopane	–0.209	–0.126
Gammacerane × 100/C_{30}hopane	–0.020	0.495

REFERENCES

1. K. E. Peters and J. M. Moldowan, *Biomarker Guide* (Prentice Hall, Englewood Cliffs, 1993).
2. W. K. Seifert and J. M. Moldowan, "Applications of Steranes, Terpanes and Mono-Aromatics to the Maturation, Migration and Source of Crude Oils," Geochim. Cosmochim. Acta **42**, 77–95 (1978).
3. M. Radke, D. H. Welte, and H. Willsch, "Geochemical Study on a Well in the Western Canada Basin: Relation of the Aromatic Distribution Pattern to Maturity of Organic Matter," Geochim. Cosmochim. Acta **46**, 1–10 (1982).
4. M. Radke, H. Willsch, D. Leythaeuser, and M. Teichmuller, "Aromatic Components of Coal: Relation of Distribution Pattern to Rank," Geochim. Cosmochim. Acta **46**, 1831–1848 (1982).
5. M. Radke, "Organic Geochemistry of Aromatic Hydrocarbons," in *Advances in Petroleum Geochemistry,*

Ed. by J. Brooks and D. Welte (Academic, London, 1987), pp. 141–205.

6. M. G. Strachan, R. Alexander, and R. I. Kagi, "Trimethylnapthalenes in Crude Oils and Sediments: Effects of Source and Maturity," Geochim. Cosmochim. Acta **52**, 1255–1264 (1988).
7. R. Alexander, R. I. Kagi, S. J. Rowland, et al., "The Effects of Thermal Maturity on Distributions of Dimethylnaphthalenes and Trimethyl-Naphthalenes in Some Ancient Sediments and Petroleums," Geochim. Cosmochim. Acta **49**, 385–395 (1985).
8. R. Alexander, R. I. Kagi, R. K. Singh, and I. B. Sosrowidjojo, "The Effect of Maturity on the Relative Abundances of Cadalene and Isocadalene in Sediments from the Gippsland Basin, Australia," Org. Geochem. **21**, 115–120 (1994).
9. A. Shimoyama, H. Masayosi, and N. Shinya, "Naphthalenes in Neogene Sediments of the Shinjo Basin, Japan," Geochem. J. **34**, 333–340 (2000).
10. D. Botor, M. Kotarba, and P. Kosakowski, "Petroleum Generation in the Carboniferous Strata of the Lublin Trough (Poland): An Integrated Geochemical and Numerical Modelling Approach," Org. Geochem. **33**, 461–476 (2002).
11. D.-J. H. Simons, F. Kenig, and C. J. Schroder-Adams, "An Organic Geochemical Study of Cenomanian–Turonian Sediments from the Western Interior Seaway, Canada," Org. Geochem. **34**, 1177–1198 (2003).
12. W. Püttman and H. Villar, "Occurrence and Geochemical Significance of 1.2,5.6-Tetramethylnaphthalene," Geochim. Cosmochim. Acta **51**, 3023–3029 (1987).
13. R. K. Singh, R. Alexander, and R. I. Kagi, "Identification and Occurrence of Norcadalenes and Related Compounds in Crude Oils and Sediments," Org. Geochem. **21**, 249–256 (1994).
14. A. Golovko and G. Pevneva, "Oil Families of West Siberia in Accordance with Alkylnaphthalenes Composition," in *Abstracts of 21st International Meeting on Organic Geochemistry, Krakow, September 8–12, 2003* (GEOSPHERA, 2003), pp. 73–74.
15. J. K. Volkman, "Biodegradation of Aromatic Hydrocarbons in Crude Oils from the Barrow Sub-Basin of Western Australia," Org. Geochem. **6**, 619–632 (1984).
16. S. J. Fisher, R. Alexander, and R. I. Kagi, "Biodegradation of Aromatic Hydrocarbons in Sediments Adjacent to an Off-Shore Petroleum Development and Production Platform," Polycyc. Arom. Comp. **9**, 257–264 (1995).
17. S. J. Fisher, R. Alexander, and R. I. Kagi, "Biodegradation of Alkylnaphthalenes in Sediment Adjacent to an Off-Shore Petroleum Production Platform," Polycyc. Arom. Comp **11**, 35–42 (1996).
18. K. Grice, S. J. Fisher, R. Trolio, et al., "Changes in the Molecular Composition of a Condensate with Increasing Biodegradation in Intertidal Coastal Sediments," in *Abstracts of 19th International Meeting on Organic Geochemistry, Istanbul, September 6–10, 1999* (TÜBITAK, Istanbul, 1999), pp. 359–360.
19. A. Golovko and V. Ivanov, "Changes in Triarene Composition on the Oil Filtration through Various Minerals," in *Abstracts of 19th International Meeting on Organic Geochemistry, Istanbul, September 6–10, 1999* (TÜBITAK, Istanbul, 1999), pp. 585–586.
20. B. G. K. van Aarssen, T. P. Bastow, R. Alexander, and R. I. Kagi, "Distributions of Methylated Naphthalenes in Crude Oils: Indicators of Maturity, Biodegradation and Mixing," Org. Geochem. **30**, 1213–1227 (1999).
21. R. Alexander, R. I. Kagi, and A. V. Larcher, "Clay Catalysis of Aromatic Hydrogen-Exchange Reactions," Geochim. Cosmochim. Acta **46**, 219–222 (1982).
22. R. Alexander, R. I. Kagi, A. V. Larcher, and G. W. Woodhouse, "Aromatic Hydrogen Exchange in Petroleum Source Rocks," in *Advances in Organic Geochemistry 1981*, Ed. by M. Bjoroy et al. (Wiley, New York, 1983), pp. 69–71.
23. A. G. Requejo, R. Sassen, T. McDonald, et el., "Polynuclear Aromatic Hydrocarbons (PAH) as Indicators of the Source and Maturity of Marine Crude Oils," Org. Geochem. **24**, 1017–1033 (1996).
24. M. Radke, H. Willsch, and D. H. Welte, "Maturity Parameters Based on Aromatic Hydrocarbons: Influence of the Organic Matter Type," Org. Geochem. **10**, 51–63 (1986).
25. A. G. Requejo, "Maturation of Petroleum Source Rocks-II. Quantitative Changes in Extractable Hydrocarbon Content and Composition Associated with Hydrocarbon Generation," Org. Geochem. **21**, 91–105 (1994).
26. S. R. Yawanarajah and M. A. Kruge, "Lacustrine Shales and Oil Shales from Stellarton Basin, Nova Scotia, Canada: Organofacies Variations and Use of Polyaromatic Hydrocarbons as Maturity Indicators," Org. Geochem. **21**, 153–170 (1994).
27. F. H. Abdullah and J. Connan, "Geochemical Study of Some Cretaceous Rocks from Kuwait: Comparison with Oils from Cretaceous and Jurassic Reservoirs," Org. Geochem. **33**, 125–148 (2002).
28. A. Wilhelms, N. Telnæs, A. Steen, and J. Augustson, "A Quantitative Study of Aromatic Hydrocarbons in a Natural Maturity Shale Sequence—The 3-Methyl-Phenanthrene/Retene Ratio, a Pragmatic Maturity Parameter," Org. Geochem. **29**, 97–105 (1998).
29. A. K. Golovko, Doctoral Dissertation in Geology and Mineralogy, University of Tomsk (1997).
30. M. Radke and D. H. Welte, "The Methylphenanthrene Index (MPI): A Maturity Parameter Based on Aromatic Hydrocarbons," in *Advances in Organic Geochemistry 1981*, Ed. by M. Bjoroy et al. (Wiley, New York, 1983), pp. 504–512.
31. J. W. Smith, S. C. George, and B. D. Batts, "The Geosynthesis of Alkylaromatics," Org. Geochem. **23**, 71–80 (1995).
32. V. Ivanov and A. K. Golovko, "Phenanthrene Hydrocarbons in USSR Crude Oils," Sib. Chem. J., No. 1, 94–102 (1992).
33. K. Stojanović, B. Jovančićević, G. S. Pevneva, et al. "Maturity Assessment of Oils from the Sakhalin Oil Fields in Russia: Phenanthrene Content as a Tool," Org. Geochem. **32**, 721–731 (2001).
34. M. D. Belonin, V. N. Golubeva, and G. T. Skublov, *Principal Component Analysis in Geology* (Nauka, Moscow, 1982) [in Russian].
35. C. Reimann, P. Filmoser, and R. G. Garrett, "Factor Analysis Applied to Regional Geochemical Data: Prob-

lems and Possibilities," Appl. Geochem. **17** (3), 85–206 (2002).

36. http://trochim.human.cornell.edu/tutorial/flynn/factor.htm
37. http://www.statsoftinc.com/textbook/stfacan.html
38. M. Ercegovac, in *Petroleum geology* (Belgrade, RGF and DIT NIS-Naftagas, 2002), pp. 380–397 [in Serbian].
39. M. Šaban, S. B. Jovančićević, S. Saračević, et al. "Correlative Geochemical Study of Crude Oils from Southeastern Part of the Pannonian Basin," Org. Geochem. **13**, 325–333 (1988).
40. B. Jovančićević, P. Polić, and D. Vitorović, "Organic Geochemical Investigation of Crude Oils. The Southeastern Part of the Pannonian Basin in Yugoslavia," J. Serb. Chem. Soc. **63**, 397–418 (1998).
41. M. Šaban, S. B.Jovančićević, T. Glumičić, and S. Saračević, "Organic Geochemical Study of the "W" Oil–Gas Field in the Yugoslav Part of the Pannonian Basin," Org. Geochem. **16**, 477–488 (1990).
42. B. JoJovančićevićj, Tasić, P. Polić, et al. "GC–MS in Oil Correlation Studies—Effects of Biodegradation on Sterane and Terpane Maturation Parameters," J. Serb. Chem. Soc. **61**, 817–821 (1996).
43. M. Šaban, S. B. Jovančićević, T. Glumičić, and N. Dogović, "Oil–Oil Correlation Based on Gas Chromatographic–Mass Spectrometric Analysis of Polycyclic Biomarkers," Rapid Communications in Mass Spectrometry **4**, 505–509 (1990).
44. K. Stojanović, B. Jovančićević, J. A. Golovko, et al., "New Di- and Trimethylnaphthalene Parameters for the Evaluating the Thermal Maturity of Oils from South-Eastern Part of Pannonian Basin (Serbia)," in *Proceedings of 5th International Conference on Oil and Gas Chemistry, Tomsk, Russia, September 22–26 2003* (2003), pp. 23–26 [in Russian].
45. B. Jovančićević, M. Šaban, T. Glumičić, et al., "Correlation of Some Southeast Pannonian Basin Oils Based on Carbon Isotopes, Compositions and Hydrocarbon Biomarkers," J. Serb. Chem. Soc. **57**, 391–405 (1992).
46. B. Jovančićević, H. Wehner, G. Scheeder, et al., "An Organic Geochemical Correlation Study of Some Drmno Depression Crude Oils (Southern Part of the Pannonian Basin, Yugoslavia)," J. Serb. Chem. Soc. **66**, 297–308 (2001).
47. F. Horváth, "Towards a Mechanical Models for the Formation of the Pannonian Basin," Tectonophysics **226**, 333–357 (1993).
48. C. S. Sajgó, Z. A. Horváth, and J. Lefler, "An Organic Maturation Study of the Hod-I Borehole (Pannonian Basin)," in *The Pannonian Basin—A Study in Basin Evolution*, Ed. by L. Royden and F. Horvath (Tulsa–Oklahoma–Budapest, AAPG Memoir, 1988), pp. 297–309.
49. F. Horváth, "Phases in Compression during the Evolution of the Pannonian Basin and Its Bearing on Hydrocarbon Exploration," Marine Petrol. Geol. **12**, 837–844 (1995).
50. M. Ercegovac, A. Kostić, H. Karg, et al. "Temperature and Burial History Modelling of the Drmno and Markovac Depressions, SE Pannonian Basin, Serbia," Petrol. Geol. **26**, 5–27 (2003).
51. M. Ercegovac and A. Kostić, "The Thermal Maturity of Kerogen and Geothermics of Neogene Sediments in the Drmno Depression (Serbia)," Ann. Geol. Peninsule Balkanique **57**, 331–356 (1993).
52. M. Ercegovac and A. Kostić, "The Kerogen Maturity of the Neogene Sediments in the Drmno Depression (Kostolac, Serbia)," J. Serb. Chem. Soc. **61**, 1063–1069 (1996).
53. M. Ercegovac, A. Grubić, I. Doković, et al. "Contribution to Better Understanding of Geological and Geochemical Properties Characterizing Drmno Depression (Serbia) from the Aspect of Oil–Gas Potential," Ann. Geol. Peninsule Balkanique **57**, 373–393 (1993).
54. M. Ercegovac, M. Jeremić, and S. Dajić, "Miocene Sedimentary Organic Facies and Palynofacies in Drmno Depression (Serbia)," Ann. Geol. Peninsule Balkanique **61**, 143–165 (1997).
55. V. Ivanov, O. S. Andrienko, and A. K. Golovko, "Triarene Isolation from Crude Oils for Geochemical Investigation," Geokhimiya, No. 3, 91–94 (1991).
56. K. G. Jöreskog, J. E. Klovan, and R. A. Reyment, *Methods in Geomathematics I, Geological Factor Analysis* (Elsevier, Oxford, 1976).
57. M. L. Angelin, A. Collignan, J. Bellocq, et al., "Investigation of Polycyclic Aromatic Hydrocarbons in Source Rock Bitumens and Petroleums by High Pressure Liquid Chromatography," C. R. Acad. Sci., Ser. II **296**, 705–708 (1983).
58. R. Alexander, R. I. Kagi, and P. N. Sheppard, "1.8-Dimethylnapthalene as Indicator of Petroleum Maturity," Nature **308**, 442–443 (1984).
59. R. Ishiwatari and K. Fukushima, "Generation of Unsaturated and Aromatic Hydrocarbons by Thermal Alteration of Young Kerogen," Geochim. Cosmochim. Acta **43**, 1343–1349.
60. K. Stojanović, *New Approaches in the Investigation of Crude Oil Maturity on the Basis of Polycyclic Saturated and Aromatic Hydrocarbon Distributions,"* Dr. Sci. Thesis (University of Belgrade, 2004) [in Serbian].