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BIOMARKERS OF NAFTALAN OIL

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Keywords: Naftalan oil, geochemistry, hydrocarbon composition, biomarkers, gas chromatography-mass spectrometry *Summary.* The results of a study using chromatography-mass spectrometry of Naftalan oil: medicinal (I-II horizon), fuel (III-IV horizon) and used for medicinal purposes during a year in the Naftalan health center in order to determine hydrocarbon and biomarker compositions are presented. Terpanes (191), steranes (m/z 217), hopanes (m/z 191) and adamantanoids (m/z 135, 136, 149, 163) were identified for the first time in Naftalan oil. It was noted that medicinal oil contains approximately 4 times more biomarkers than fuel oil (7.6%; 1.6%, respectively). As a result of a comparative analysis of biomarker indicators of medicinal and fuel Naftalan oil, carried out on a biodegradation scale, it was shown that medicinal Naftalan oil belongs to the biodegraded oil type B-1, stage I-II, with a moderate degree of biodegradation, and fuel Naftalan oil belongs to the chemical type A2, which is typical for oils with a low degree of biodegradation – stage I. Based on the decrease of biomarkers in the composition of Naftalan oil, used throughout the year for treatment, a conclusion was made about their possible participation in the balneological process. Judging by the geochemical parameters, medicinal and fuel oil has the same genesis.

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Introduction

Studying biomarkers in oils is very important for understanding their genesis and geochemical history, for increasing reliability of prognosis of oiland-gas bearing capacity because the complex structures of biomarkers give the detailed information concerning their origin. There is practically no information about biomarkers in Naftalan oil.

Individuality and uniqueness of the Naftalan oil field are explained (Мехтиев и Ахмедбейли, 1969; Шихмамедова и др., 2014) by its confinement to the deep fracture zone. The Naftalan structure is situated within the Arpa-Samur fracture zone, which at all times from Paleozoic till now, was the zone of active display of tectonic movements, conductor of magmatic melts, ore bearing solutions and seismicity. In the formation of the specific shape of oil the participation of the underlying fluids is possible, both as a result of interaction with the organic matter during its fossilization or at the stage of its transformation into the oil, and at the interaction of the mantle emanations with the already formed oil. At the same time, emanation of fluids into the paleobasin and formation of specific conditions of fermentation

of initial organic matter at certain stages of sedimentogenesis, which in principle can explain the presence of different-type oils within the same field, seem to be quite probable.

Numerous studies of Naftalan oil have been conducted for many years, but there are still no clear understandings about the difference in composition and properties of naphthenic oil and medicinal Naftalan oil, and moreover, there is no difference in composition and properties of Naftalan oil from different horizons: medicinal heavy oil – in upper horizons of the Upper Maykop and fuel light oil – in lower horizons of the Upper and Lower Maykop.

Objects and methods of research

The aim of this work was to study the biomarker composition of Naftalan oil:

1. Medicinal Naftalan oil from oil base I-II horizon, filter 151-586 m;

2. Fuel Naftalan oil from petroleum base III-IV horizon 1 well;

3. A year used medicinal oil from petroleum base of Naftalan city;

HC composition and biomarkers investigations were made by chromatography-mass spectrometry (GC-MS) on Perkin-Elmer Clarus 680 instrument having interface with high-efficiency mass-selective detector Clarus SQ8T. Hydrocarbon chromatograms were obtained using total ion current (TIC). The chromatograph was equipped with a quartz capillary column of 100 m length, 0.25 mm diameter and impregnated with ZB-1 phase. The carrier gas is helium, with a flow rate of 1ml/min. Evaporator temperature 300°C; programmed temperature ramp from 80 to 290°C at a rate of 4°C/min followed by an isotherm for 70 min. Ionizing source voltage - 70 eV, source temperature - 250°C. Methylene chloride was used as a solvent.

Discussion of results

Hydrocarbon composition of samples of Naftalan oil was determined by the method of chromatography-mass spectrometry (Бабаев и др., 2017; Бабаев и др., 2015; Бабаев и др., 2018а). As we can see (Fig.1, Table 1), medical and fuel naphthalene have essential differences in hydrocarbon composition, namely \sum amount of alkane HC in fuel oil is 23%, whereas in medicinalutic oil their amount is only 3.5%; amount of naphthenic HC in fuel oil is ~59.4%, whereas in medicinal oil it is 83.69%.

Values of Pr=4.94; Ph=2.11; Pr/Ph=2.34 have been calculated for the sample of Naftalan fuel oil (2). According to the literature data, if Pr/Ph = 1.08 - 2.3, it corresponds to sapropel-humus genesis, i.e. mixed genesis.

As for Naftalan oil used for medicinal purposes, its content of alkane HC according to GC-MS data is ~9.1%, naphthenic HC - ~76.79% and aromatic HC - ~14.11%.

Terpanes, steranes, hopanes and adamantanes were identified in all oil samples. Here are given mass spectra plots for calculation of terpanes, hopanes (m/z 191), steranes (m/z 217) and adamantoids (m/z 135, 136, 149, 163) in the samples of Naftalan oil (Fig. 2-4).



Fig. 1. Mass chromatogram of medicinal (a), fuel (b) and Naftalan oil used during the year for medical purposes (c)

Hydrocarbon composition of medicinal and fuel Naftalan oil

Σ Naphtenes isopr Arenes i-alk n-alk Σ Σ Naftalan alkaenoid % % naphten aren mono bi tri tetra penta mono bi tri % nes 1) medi-3.53 3.53 44.08 35.3 4.31 83.69 2.33 4.67 5.11 12.11 cinal * 2) fuel ** 6.81 16,12 7.05 22.93 41.7 17.14 0.53 59.37 3.7 1.76 12.02 17.48 --3) used 1 9.1 49.91 9.1 26.57 0.12 0.19 76.79 4.13 3.45 6.53 14.11 year *Dif-0.67; **Dif-0.22



Fig. 2. Chromatography-mass spectrum section of hopanes (m/z 191) in Naftalan medicinal (a), fuel (b) and 1 year used (c) oil

Sample	1 - medicinal, %	2 - fuel, %	3- used,%
Ts	4.09	4.21	5.00
Tm	4.02	3.46	3.92
H ₂₈ 17αH, 18αH,21βH bisnorhopane	0.77	1.02	0.67
H ₂₉ Nor- 25- hopane	1.96	1.83	1.33
Adiantane	14.84	10.85	14.69
Diahopane H ₃₀	2.2	2.04	1.76
Moretane H ₂₉	0.92	1.11	0.68
Oleanane	7.47	5.64	7.44
Hopane H ₃₀	19.19	24.52	19.89
Moretane H ₃₀	3.06	3.03	2.78
Homohopane Hh ₃₁	15.63	15.78	14.93
Bis homohopane H ₃₂	10.14	10.34	9.96
Tris homohopane Hh ₃₃	9.45	7.79	7.67
Tetrakis homohopane Hh ₃₄	4.8	5.67	6.00
Pentakis homohopane Hh ₃₅	3.35	2.73	3.29

Hopane content (m/z 191) in Naftalan oil

Table 2

Geochemical indicators			
Ts / Tm	1.01	1.22	1.28
Hh35/(Hh31-Hh35)	0.08	0.06	
Homohopane index	0.08	0.00	0.08
Hh ₃₄ /Hh ₃₅	1.43	2.08	1.82
H_{29}/H_{30}	0.77	0.44	0.74
17β ,21 α -moretanes			
$C_{29} + C_{30} / 17\alpha, 21\beta$ -hopanes	0.12	0.12	0.1
$C_{29} + C_{30}$			

To estimate the degree of catagenetic transformation of oils a number of ratios is used: Ts/Tm; 17β , 21α -moretanes H₂₉ +H₃₀ / 17α , 21β -hopanes H₂₉ +H₃₀. The Ts/Tm ratio increases with increasing maturity and is 1 in the main oil formation zone and ~ 5-10 – in the later stages of catagenesis. It is advisable to use this indicator to assess the degree of maturity of oils for oils with approximately the same level of biodegradation. So, for 1 – Ts/Tm = 1.01, for 2 – Ts/Tm = 1.22.

The hopanes consist of three stereoisomeric series, viz: 17α (H), 21β (H), 17β (H), 21α (H), 17β (H), 21β (H)-hopanes. The compounds in the $\beta\alpha$ series are called moretanes. The designations alpha (α) and beta (β) indicate that the hydrogen atoms are below or above the ring plane. The ratio of 17β , 21α moretanes C₂₉ +C30 / 17α , 21β -hopanes H₂₉ +H₃₀ decreases with increasing thermal maturity and reaches 0,05 (equilibrium level) in heavily transformed oils. For Naftalan oil sample 1 this coefficient is 0.16 whereas for sample 2 – 0.09 (Table 2) (Ten Haven et al., 1992). It should be noted that due to the high degree of biodegradation of the studied oils, the calculated maturity parameters probably do not correspond to real values.

To determine the genotype of OM it is necessary to use the obtained indices and relations in combination with other geological indices and geology of the region. The relative distribution of Hh_{31} - Hh_{35} homohopanes is used as an indicator of the oxidation-reduction environment in sedimentogenesis and diagenesis. The ratio of Hh_{35} / $(Hh_{31} - Hh_{35})$ homohopanes is called the homohopane index. The index describes the aeration of the sedimentation basin, like Pr/Ph, but of a different chemical nature.

Relatively high concentrations of homohopane Hh_{35} indicate marine conditions of sedimentogenesis and reductive conditions of diagenesis (Nazir, Fazeelat, 2014). Relatively low concentrations of Hh_{35} indicate suboxidative or weakly reducing conditions. In our case, homohopane index for Naftalan medicinal oil is 0.08 and 0.06 – for fuel oil. As a result of secondary alteration (oxidation-biodegradation) the homohopane index of Naftalan oils should differ from actual values and probably increase.

The ratio of C_{29} normethylhopane (adianthane) to hopane is used to establish the facial-geochemical conditions for the accumulation of organic matter. It is believed that in oils formed in terrigenouscarbonate deposits the adiantane/hopane ratio is lower than in oils from halogen-carbonate deposits. In marine anaerobic environments, the ratio of the concentrations of hopanes H₂₉ and H₃₀ is, as a rule, below 0.5, and in non-marine organic matter last ones are greater than 0.8. In oil from OM-rich carbonate-evaporite rocks H_{29}/H_{30} is close to 1 (Clark, Philip, 1989). In medicinal oil from the Naftalan field (sample 1), H₂₉/H₃₀ is 0.77, and in fuel oil (sample 2) it is 0.44 (Table 2), which at first glance indicates a non-marine source of OM for oil sample 1 and marine anaerobic conditions for the accumulation of OM for sample 2. However, the secondary processes that altered the primary composition of Naftalan oils do not allow us to come to an **unambiguous conclusion** about the sources of their OM.

The distribution of C_{27} , C_{28} , and C_{29} sterane hydrocarbons is considered as an indicator of the type of organic matter (OM). The predominance of the C_{29} homologue indicates a large contribution of terrestrial vegetation to the original organic matter, whereas the dominance of C_{27} steranes indicates a significant contribution of zooplankton and algal (Clark, Philip, 1989). In the studied samples of Naftalan oils slightly prevail of C_{27} steranes (Fig. 3, Table 3). This is not consistent with the H_{29}/H_{30} hopane and Hh_{35} / (Hh₃₁ - Hh₃₅) neohopane indices due to an imbalance in the biomarkers of biodegraded oils.



Fig 3. Plot of the chromatography-mass spectrum of steranes (m/z 217) in Naftalan medicinal (a), fuel (b) and a year used (c) oil

Table 3

Table 4

Stearanes content (m/z 217) in Naftalan oil

Steranes %	1. Medicinal	2. Fuel
Diasterane	19.41	15.47
Sterane 27	22.31	22.79
Sterane 28	17.14	16.63
Sterane 29	21.6	20.55
Sterane 21+22	5.37	5.94
St ₂₇ : St ₂₈ : St ₂₉	22:17:22	23:17:21

Sterols in sample 3 of Naftalan oil used during the year

Steranes %	Naftalan oil 3
Diasterane	18.64
Sterane 27	21.92
Sterane 28	18.16
Sterane 29	22.36
Diasterane/reg.sterane 29	0.83

Comparison of the steranes distribution in original medicinal oil and in a year used for treatment medicinal oil shows that after medical treatment content of steranes in the oil almost unchanged (Tables 3 and 4).

Terpanes in Naftalan oils are represented mainly by tricyclic C₁₉-C₂₀ (from 20.81 to 28.52) and pentacyclic triternenoids (18 α (H) oleanane (5-7% RH). This indicates the presence of continental and higher vegetation in the initial OM. The 18 α (H) oleanane in the oil clearly indicates the Cenozoic age of the source rocks. Judging by the comparative star diagrams of the geochemical parameters of medicinal and fuel Naftalan (Fig.4), both samples generally have the same biomarker-geochemical features.

When considering the ratio of steranes $C_{27}:C_{28}:C_{29}$ for medicinal and fuel Naftalan oil (Table 3), almost equal values of steranes C_{27} and C_{29} (phytoplankton and terrestrial plants) were noted with a lower value of sterane C_{28} (zooplankton), which allows us to judge that we are dealing with genetically similar oils generated by OM of identical rocks.



Fig. 4. Comparative diagram of medicinal and fuel Naftalan according to biomarker-geochemical parameters



Fig. 5. Comparative diagram of different wells of the Guneshli field according to biomarker-geochemical parameters

For samples from the Guneshli deposit, all sterane ratios decrease sequentially from horizon samples: IX \rightarrow X \rightarrow hiatus suite. As can be seen (Fig. 5), the greatest difference in the diagram is observed in the ratios of C₂₇/C₂₉ steranes. When considering the ratio of steranes C₂₇:C₂₈:C₂₉, it was noted that the IX horizon is characterized by a predominance of C₂₇, C₂₈ steranes, and the X horizon and hiatus formation are characterized by a predominance of C₂₉. The presence of C₂₇ sterane indicates the predominance of: phytoplankton, C₂₈ – zooplankton, C₂₉ – terrestrial plants – in the genesis of oil. It can be assumed that all oil samples from the Gunashli field are genetically of the same type, formed mainly in marine-type sediments, in which sedimentation and diagenesis occurred in a reducing environment (Бабаев и др., 2018b).

Identification of adamantoids in samples of Naftalan oil was carried out by chromatographymass spectrometry by m/z 135 – alkyladamantanes, m/z 149 – dialkyladamantanes and m/z 163 – trimethyladamantanes according to NIST.

Fig. 6 (a,b,c) shows sections of chromatography-mass spectrum of alkyladamantanes for medicinal, fuel and used during the year Naftalan oil.



Fig. 6. Chromato-mass spectrum section of alkyladamantanes (m/z 135) in Naftalan medicinal (a), fuel (b) and a year used (c) oil

Table 5 shows the total adamantoid content in % in samples of Naftalan oil. GC/MS data show that dimethyl-substituted homologues (C_{12} dialkyladamantane) have the highest content among alkyladamantanes, and the relative concentration of unsubstituted adamantane is the lowest.

Based on the data in Tables 4-5 for the content of adamantantoids in medicinal oil and oil used during a year, it is shown that the content of dialkyl adamantane decreases by 7% during treatment. This suggests that the effect of medicinal Naftalan oil, along with hopanes and tricyclic terpanes, is also associated with dialkyladamantane.

In Table 6 total quantitative content of biomarkers (%) in samples of medicinal (sample 1), fuel (sample 2) and used (sample 3) Naftalan oil is presented. As it can be seen, the content of hopanes has changed to the greater extent after treatment procedures, namely in sample 3 there are no oleanane, diahopane H_{31} , moretane H_{30} , and the quantity of hopane H_{30} has decreased in 3 times (Table 2). At the same time, the amount of adiantane, diahopane H_{30} and moretane H_{29} increased in sample 3.

In our earlier work, we established that one of the distinctive features of medicinal Naftalan oil is the presence of a significant amount of hydrosaturated cyclic hydrocarbons with decahydronaphthalenes in their composition (m/z–95) ~59.68...60.12%, in contrast to fuel oil, where the amount of hydrosaturated cyclic hydrocarbons is ~ 5.82...11.21% (Бабаев и др., 2017; Бабаев и др., 2015).

ICP / MS method for trace metals and noble metals content in Naftalan have shown that, in quantitative terms, their content exceeds their amount in naphtenic oils of Absheron (Нанаджанова и др., 2016). The natural nanodispersed Naftalan oil was studied (Гулиев и др., 2017). According to dynamic light scattering data, the intensity of particles with a diameter in the range from 100 to 1000 nm was revealed in medicinal Naftalan oil. The fuel oil sample contained particles with a diameter of 50 nm and below. The diffusion coefficients for medicinal oil samples were calculated to be greater than for fuel oil, which obviously also contributes to the balneological effect. As for the used Naftalan oil, its tendency to aggregate particles with a diameter from 100 to 8000 nm was noted, and particles above 1000 nm are stable up to 50°C (Martynova et al., 2022). Comparative studies of Naftalan oil samples have shown that dynamic light scattering data can provide a distinctive fingerprint of the used medicinal oil.

By serial dilutions of Naftalan followed by inoculation onto a culture of buccal epithelial cells using a micronucleus test, the toxicity dose of native Naftalan was established and its non-toxicity was shown in decimal dilutions $(10^{-2}, 10^{-5}, 10^{-8})$ of physiological solution (Гулиев и др., 2022).

Judging by the data obtained, we can conclude that in the process of Naftalan treatment the amount of all biomarkers is significantly reduced, but to a greater extent – triterpanes, hopanes and adamantanes, which makes it possible to assume their participation in the healing process.

Table 5

Table 6

Sample Naftalan oil Adamantanes, %	1. Medicinal oil, %	2. Fuel oil, %	3.Used a year oil, %
C11 (alkyladamantanes)	12.9 15.01		16.41
C12 (dialkyladamantane)	65.29	72.04	58.23
C ₁₃ (trialkyladamantane)	10.82	11.8	17.95

Content of adamantoids in Naftalan oil

The comparative content of biomarkers in Naftalan oil

Naftalan oils	Triterpanes	Hopanes	Steranes	Adamantanes	Σ% in oil
sample 1	1.280	0.470	0.160	5.70	7.60
sample 2	0.250	0.040	1.07	0.020	1.60
sample 3	0.057	0.026	0.200	0.140	0.423

Judging by the data obtained, we can conclude that in the process of Naftalan treatment the amount of all biomarkers is significantly reduced, but to a greater extent – triterpanes, hopanes and adamantanes, which makes it possible to assume their participation in the healing process.

Conclusion

For the first time identification of terpanes (191), steranes (m/z 217), hopanes (m/z 191) and adamantanoids (m/z 135, 136, 149, 163) in Naftalan oil was carried out.

Medicinal and fuel oils from the Naftalan field are biodegraded to varying degrees. This greatly complicates their reliable facial-geochemical conditions of OM accumulation, correlation, genetic typing and assessment of oils maturity based on the content and ratio of terpanes, steranes, and hopanes. At the same time, it can be confidently stated that, along with marine zooand phytoplankton, a significant amount of terrestrial plants accumulated in the paleobasin. This is con-

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firmed by the high contents of oleanane in oils. In both fuel and medicinal oils, oleanane is detected in high concentration (5% and 7% respectively). At the same time, this biomarker proves the Paleogene–Lower Miocene age of the studied oils.

Steranes C_{27} dominate among steranes both in fuel and in medicinal oil. The content of adamantoids in both oils (medicinal and fuel oils) is approximately the same, the prevailing content of dialkyladamantanes – C_{12} is the same as in the naphthenic oils of Absheron.

Consideration of the ratio of steranes in medicinal and fuel oil allows us to judge that we are dealing with genetically related oils formed by the organic matter of identical rocks.

Judging by the data obtained, we can conclude that during the treatment process the amount of all biomarkers, but to a greater extent – triterpanes, hopanes and adamantanes, significantly decreases in Naftalan oil, which makes it possible to assume their healing effect.

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БИОМАРКЕРЫ НАФТАЛАНСКОЙ НЕФТИ

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Резюме. Представлены результаты исследования нафталанской нефти: лечебной (I-II горизонт), топливной (III-IV горизонт) и использованной в лечебных целях в течение года в оздоровительном центре Нафталана методом хромато-масс-спектрометрии с целью определения углеводородного и биомаркерного составов. Впервые в нафталанской нефти была проведена идентификация терпанов (191), стеранов (m/z 217), гопанов (m/z 191) и адамантаноидов (m/z 135, 136, 149, 163). Отмечено, что в лечебной нефти примерно в 4 раза больше биомаркеров, чем в топливной нефти (7.6%; 1.6% соответственно). В результате сравнительного анализа биомаркерных показателей лечебной и топливной нафталанской нефти, проведенного по шкале биодеградации, было показано, что лечебная нефть Нафталана относится к биодеградированной нефти типа Б-1, стадия I-II, с умеренной степенью биодеградации, а топливная нафталанская нефть относится к химическому типу А-2, который характерен для нефтей слабой степени биодеградации – стадии I. На это указывает отсутствие н-алканов и изопреноидов, пристана, фитана, а также завышенные значения многих геохимических параметров. Согласно проведенным расчетам, соотношение Олеанан/Гопан(30) и Моретан/Гопан(30) для лечебной нафталанской нефти, соответствует биодеградированной нефти типа Б-1. В нефтях, находящихся на этой стадии, стераны не изменены. Что касается топливной нефти, то на ее биодеградацию указывает отсутствие в составе н-алканов С17, С18. Содержание изопреноидов (Pr, Ph) превосходит значение н-алканов, что свойственно для нефтей типа А-2. Соотношения Олеанан/Гопан(30) и Моретан/Гопан(30) для топливной нефти также имеют такие же значения, как и для биодеградированной нефти типа A-2. Показано, что в процессе лечения углеводородный состав нефти не претерпел существенных изменений, зато уменьшилось суммарное количество биомаркеров, что дает возможность предположить их участие в бальнеологическом процессе. Судя по геохимическим параметрам, лечебная и топливная нефть имеют единый генезис.

Ключевые слова: нафталанская нефть, геохимия, углеводородный состав, биомаркеры, хромато-масс-спектрометрия

NAFTALAN NEFTINDƏ BIOMARKERLƏR

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Xülasə. Karbohidrogen və biomarker tərkibinin müəyyən edilməsi üçün xromatoqrafiya-mass spektrometriyasından istifadə etməklə müalicəvi (I-II horizont), yanacaq (III-IV horizont) və Naftalan sağlamlıq mərkəzində 1 il ərzində müalicəvi məqsədlər üçün istifadə olunan Naftalan neftinin tədqiqatının nəticələri təqdim olunur. Naftalan neftində ilk dəfə olaraq terpanlar (191), steranlar (m/z 217), hopanlar (m/z 191) və adamantanoidlər (m/z 135, 136, 149, 163) müəyyən edilmişdir. Qeyd edilib ki, dərman neftinin tərkibində yanacaqdan təxminən 4 dəfə çox biomarker var (müvafiq olaraq 7.6%; 1.6%). Biodeqradasiya miqyasında aparılan müalicəvi və yanacaq Naftalan neftinin biomarker göstəricilərinin müqayisəli təhlili nəticəsində məlum olmuşdur ki, müalicəvi Naftalan nefti B-1 tipli, I-II mərhələli biodeqradasiyaya uğramış neftə aiddir. Yanacaq Naftalan nefti isə biodeqradasiya dərəcəsinə əsasən A-2 kimyəvi növünə aiddir ki, bu da zəif biodeqradasiyaya məruz qalmış olan neftlər üçün xarakterikdir - I mərhələ. Bu, nalkanların və izoprenoidlərin, pristan, fitanın olmaması, həmçinin bir çox geokimyəvi parametrlərin həddindən artıq yüksək qiymətləri ilə göstərilir. Hesablamalara görə, müalicəvi Naftalan nefti üçün oleanane/hopane(30) və moretane/hopane(30) nisbəti B-1 tipli biodeqradasiya olunmuş neftə uyğundur. Bu mərhələdə neftlərdə steranlar dəyişmir. Yanacaq neftinin biodeqradasiyası onun tərkibində C17 və C18 n-alkanların olmaması ilə göstərilir. İzoprenoidlərin (Pr, Ph) tərkibi A2 tipli neftlər üçün xarakterik olan nalkanların dəyərini üstələyir. Yanacaq neftinin oleanane/hopane(30) və moretane/hopane(30) nisbətləri də A-2 tipli biodeqradasiyaya uğramış neftlərə uyğundur. Göstərilmişdir ki, interpretasiya zamanı neftin karbohidrogen tərkibi əhəmiyyətli dəyişikliklərə məruz qalmamış, lakin biomarkerlərin ümumi sayı azalmışdır ki, bu da onların balneoloji prosesdə iştirakını güman etməyə imkan verir. Geokimyəvi parametrlərə görə müalicəvi və yanacaq neftləri eyni mənşəyə malikdir.

Açar sözlər: Naftalan nefti, geokimya, karbohidrogen tərkibi, biomarkerlər, xromato-mass spektrometriya