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Composition and Properties of the Unique Oil from Azerbaijan's Naftalan Oilfield

V. A. Adigozalova[a]*, U. F. Hashimova[b], and L. P. Polyakova[c]**

[a] *Azerbaijan State Academy of Physical Culture and Sports, pr. Fatali Khana Khoiskogo 98, Baku, AZ1072 Azerbaijan*
**e-mail: vkar22@yandex.ru*

[b] *Karaev Institute of Physiology, National Academy of Sciences of Azerbaijan, Sharifzade 78, Baku, AZ 1100 Azerbaijan*
***e-mail: ulduz.hashimova@science.az*

[c] *Obninsk Institute for Nuclear Power Engineering, Branch of National Research Nuclear University MEPhI," Campus 1, Obninsk, Kaluga oblast, 249040 Russia*

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Abstract—Azerbaijan's Naftalan oil is unique in the world because of its medicinal properties. The physicochemical characteristics and chemical composition of the oils from various levels of the top department of the Naftalan oilfield were studied with the view of identifying the features of its biological action. The objectives pursued by this study were as follows: to determine the physicochemical properties, the component composition, and the hydrocarbon group content of the oil from the operating wells of three mining levels (1st, marly, and 2nd, sandy) of the top department of the Maykop Suite of the Naftalan oilfield and to examine and evaluate the oil reservoir homogeneity in terms of the physicochemical parameters and chemical composition of the Naftalan oil from individual mining levels.

Keywords: Naftalan oil, physicochemical properties, component composition, different levels, oilfield, hydrocarbon group content

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The Naftalan oilfield situated near the city of Ganja in the Azerbaijan Republic is the world's only oilfield whose oil contains biologically active substances responsible for its healing properties. Protection and preservation of this unique natural wealth constitute one of the most important tasks of applied ecology.

For several centuries the Naftalan oil has been used by local people for curing various health problems. Recognized by academic medicine in 1898, it came into use as effective natural source of biologically active substances for both balneological and pharmaceutical chemistry applications.

Numerous medical and chemical studies on the state of the Naftalan provided a wealth of information now available in the literature.

The Naftalan oil is used for treating various diseases, with its unique healing effect being determined by the peculiar chemical nature which distinguishes it from the oil intended for industrial purposes. By now, effective ways of treatment using Naftalan oil and its components and numerous recommendations for various medical applications have been proposed.

However, the available literature indicates that, though long been used as a therapeutic agent, Naftalan oil practically lacks scientifically developed technical documentation governing its production and delivery to consumers under mandatory control of its main physicochemical parameters, essential for medical applications. Also, use of the Naftalan medicinal oil is poorly controlled and wasteful to a certain extent.

This is largely due to insufficient information on the dependence of the properties and composition of the Naftalan oil on the geological conditions of its occurrence.

The need to develop the scientific basis for environmental monitoring of the medicinal oil and to solve practical issues associated with its standardize-

tion makes topical studying the physicochemical properties and chemical composition of Naftalan oil from various mining levels.

Herein, we studied the physicochemical properties and chemical composition of the oil from different levels of the top department of the Naftalan oilfield with the view of identifying the features of its biological action. To this end, the following tasks were set:

– to determine the physicochemical properties, the component composition, and the hydrocarbon group content of the oil from the operating wells of three mining levels (1st, marly, and 2nd, sandy) in the top department of the Maykop Suite of the Naftalan oilfield and

– to examine and evaluate the oil reservoir homogeneity in terms of the physicochemical parameters and chemical composition of the Naftalan oil from individual mining levels.

The evaluation criteria chosen for the medicinal Naftalan oil were based on the physicochemical properties of the conventionally traditionally used heavy oil (density ρ_{20}^4 0.927–0.960 g/cm^3) that also passed special clinical trials in the native form as early as the 1930s.

According to the criteria set, only the top department of the geological section of the deposits in the main oil-bearing strata of the Naftalan oilfield of the Maykop Suite is saturated with medicinal oil. This is in contrast to the light oil intended for industrial purposes, occurring in the lower department, whose properties differ from those of the medicinal oil.

Over the twentieth century, a scientific rationale was provided for the practical application of Naftalan oil regarded as a valuable natural agent for treating a number of diseases, including those of the musculoskeletal system, skin, central and peripheral nervous systems, some gynecological, allergic, surgical, and other diseases, as well as for using in veterinary medicine [1–3].

Also, Naftalan oil has become the subject of extensive chemical research aimed at identifying the main sources of its therapeutic effect. Another area of focus were the geological aspects of the problem, essential for elucidating the peculiar conditions of the formation and occurrence of oil deposits within the Naftalan oilfield.

It has been accepted that, by the end of the Maykop Age, medicinal and fuel oils had formed and concentrated respectively in the top and lower departments of the geological section of the deposits in the main oil-bearing stratum of the Naftalan oilfield of the Maykop Suite [4]. However, by contrast to the historical knowledge of the medicinal oil, information about the oil from the Naftalan oilfield, intended for industrial purposes (its reserves were discovered in 1936), became known relatively recently [5].

Formed in the clay rocks stratum, the medicinal oil underwent slight vertical and lateral migration, resulting in its distribution within the following levels: 1st (Miocene), marly (Oligocene-Lower Miocene), and 2nd, sandy (Oligocene) levels. Part of this oil reservoir in the layers of the Akchagyl Stage (Pliocene) was derived from the main Maykop reservoir as a consequence of more substantial migration.

Fuel oil accumulations coincided with level nos. 3–7 (Oligocene) of the oilfield. The respective oil densities initially determined for these levels were 0.917–0.925 and 0.850–0.912 g/cm^3 for level nos. 3–4 and nos. 4–7 [4, 5].

Drilling the stratigraphic test wells and the exploration wells showed that the Naftalan oilfield is essentially a submeridionally extending brachyanticlinal fold of 5 km length and 1.5 km width, with the hinge plunged in both directions. In the periclinal parts of the Naftalan structure the pitch angles are no greater than 10°, in the southeastern branch they increase to 18°, and in the northwestern branch, vary within 4°–17°. The therapeutic oil levels occur at depths ranging from 100 to 700 m; their oil productive acreage varies within 120–241 ha, and the effective thickness, from 2.5 m to 5.9 m.

The medicinal oil initially in place was estimated at 2950 thousand tons, and the recoverable reserves (for a reserve usage coefficient of 0.1), at 480 thousand tons of which 268 thousand tons is accounted for by economically recoverable reserves [4, 6].

The oilfield is highly fragmented by numerous longitudinal and transverse normal and reverse faults. The oilfield fragmentation by rupture faults is responsible for existence of a certain relationship between the two parts, enabling periodical throw of industrial and medical oils into selected production wells of mixed levels [7].

In accordance with the program of studying the oils from individual levels and areas of the oilfield [8], samples of the Naftalan oil from 30 operating and

Table 1. Physicochemical characteristics of the Naftalan oil

Well no./ Level no. (number of samples)	Nos. of wells with oils of close quality	Perforation interval, m	Mass fraction of emulsion water, %	Parameters of dehydrated oil					
				density at 20°C, g/cm^3	acid value, mg KOH/g	kinematic viscosity at 100°C, mm^2/s	flash point, °C	freezing point, °C	distillation onset point, °C
73/1(8)	54.82	198–151	45–71	0.9443–0.9609	2.88–3.75	9.762–19.09	118–126	−7 to −11	238–258
20/1(5)	2.27	239	30–55	0.9360–0.9407	1.76–2.11	7.323–8.100	103–109	−20 to −24	225–239
88/M(6)	51, 78, 89, 79	from bottomhole	35–58	0.9330–0.9427	1.52–1.70	8.292–8.760	107–109	−20 to −23	230–248
28/2(4)	62.38.29	403–366	30–37	0.9300–0.9397	1.49–1.91	7.189–7.476	101–107	−21 to −25	220–242
90/2(6)	85.40	487–480	50–60	0.9332–0.9380	–	7.891–7.963	100–102	−24 to −28	212–240
66/2(4)	68.74.92	567–536	25–45	0.9240–0.9332	1.05–1.86	5.431–7.121	86–101	−24 to −36	204–236
86/2(4)	91	529–510	17–38	0.9205–0.9297	0.60–1.39	5.322–5.978	91–103	−28 to −31	212–242
39/2(7)	87	604–586	2.0–12	0.9207–0.9230	1.32–1.93	5.371–5.555	86–90	−28 to −35	182–205
33/2(6)	61.47.53	598–581 583–515	0.6–24	0.9176–0.9214	0.68–1.00	5.090–5.471	79–86	−37 to −42	180–210

suspended wells (with mixed level wells excluded) were analyzed. These wells account for ca. 70% of the total producing well stock exploiting the 1st, marly, and 2nd, sandy, levels of the oilfield.

Examination of the Naftalan oil properties and composition was primarily focused on the indicators that were identified as the most characteristic of the therapeutic oil according to the available literature [9].

The oil sampling and preparation for analysis, as well as the determination of the physicochemical properties and fractional composition followed the unified techniques developed for oil [8, 10]. With the view of eliminating the influence of seasonal factors on the Naftalan oil quality indicators, only data on the samples taken in the autumn period of the year were factored into comparative assessments of the oil composition.

The chemical composition of the Naftalan oil was determined with the use of a complex of physicochemical methods of separation and concentration: demulsification by distillation with a solvent [11], extraction in the system of selective solvents [10], adsorption column [12] and thin-layer chromatography [13], and vacuum fractionation [14]. Paraffins were isolated by complexing with urea [15]; the content of carboxylic acids was determined by modified sorbent-based chromatography [16, 13].

Table 1 lists the physicochemical parameters determined for the oils from wells of the three mining levels of the Naftalan oilfield. Each parameter is characterized by a minimum value and a maximum value indicating the limits within which the properties of the oil well production in the oilfield changed over a 10-year period. Also given are the perforation intervals and the location numbers of the wells within each level.

Our study revealed that the Naftalan oil becomes lighter (its density decreased) downward in the oilfield cross section (in going from the 1st to the 2nd, sandy, level), as indicated by the corresponding changes in the physicochemical properties and component composition. The decrease in density of the oil (from

Table 2. Component composition of the Naftalan oil

Well no. (number of samples)	Mass fraction, %, of indicated component				
	paraffins	carboxylic acids	asphaltenes	Silica gel resins	fractions boiling up to 300°C
73 (8)	Lacking	2.1–3.2	0.50–0.55	14.3–15.6	5.2–13.0
20 (5)	Traces	1.9–2.1	0.41–0.49	13.0–14.1	15.2–19.0
88 (6)	"	1.0–1.2	0.33–0.37	12.9–3.4	17.0–20.5
28 (4)	"	0.9–1.3	0.25–0.32	12.6–13.6	17.0–21.0
90 (4)	"	0.9–1.1	0.25–0.30	12.7–13.2	15.0–21.0
66 (6)	0.12–0.22	0.7–0.9	0.22–0.29	12.3–12.5	17.5–24.5
86 (4)	0.13–0.45	0.7–1.1	0.20–0.21	12.0–13.0	22.0–26.5
39 (7)	0.25–0.30	–	0.15–0.20	10.7–11.4	24.5–28.5
33 (6)	0.27–0.40	0.3–0.6	0.11–0.15	10.4–10.9	24.6–30.5

0.9360–0.9609 to 0.9176–0.9397 g/cm^3) is paralleled by decreases in the distillation onset temperature (from 212–258 to 180–205°C), in the oil freezing point [from (−20)–(–25) to (−30)–(–40°C)], and in the oil flash temperature (from 100–126 to 70–90°C), as well as by decreases in the viscosity (from 7.323–19.09 to 5.090–7.963 mm^2/s) and the acid value (from 1.52–3.75 to 0.60–1.93 mg KOH/g). Deep-lying oil does not form highly dispersed emulsions with associated formation water. The mass fraction of the emulsion water (minimum values) in the oil varies from 45 to 0.6% downward in the oilfield cross section.

The physicochemical parameters of the oil were estimated for both vertical and areal distribution of the oil reservoir [17]. A decrease in the Naftalan oil density with increasing its bedding depth was revealed, as well as the domination of lighter oil in the roof area of the fold structure, and of heavier oil, in the edge area within each level.

The oil from selected 1st level wells (in the water-oil contact zone at a depth of 150–200 m), which contains up to 71% emulsion water, exhibited the highest density (0.9609 g/cm^3), as well as a maximum kinematic viscosity (19.09 mm^2/s) and a maximum acid value (3.75 mg KOH/g).

These findings suggest that the oil from these wells shows evidence for oxidation. Its metamorphization under natural condition is attributable to the following factors: atmospheric exposure, close proximity of the oil reservoir to the surface, and occurrence of tectonic disturbances in the oilfield, as well as activation of biochemical processes due to prolonged contact with formation waters.

Examination of the physicochemical parameters of the oils from the three mining levels revealed certain vertical and horizontal differentiation of the oil in the top department of the Naftalan oilfield, associated with the specific geological parameters of the oil reservoir.

Further examinations were focused on the component composition of the oils from the three mining levels. Specifically, the contents of the fractions boiling up to 300°C, as well as of asphaltenes, silica gel resins, paraffins, and carboxylic acids in the oils from the operating wells were determined. This allowed estimating the concentrations of those oil components whose changes could affect to varying degrees the physicochemical parameters of the oil, presented in Table 1.

The use of the component composition data allowed elucidating how the ratio of individual groups of substances in the oil varies with the oil bedding depth (see Table 2).

Component composition of the Naftalan oil. Table 2 shows that, downward in the oilfield cross section, the mass fraction of the fuel fractions boiling up to 300°C increases (from 13.0–22.0 to 24.5–30.5%), solid paraffin hydrocarbons appear (up to 0.45%), and the naphthenic acids concentration sharply decreases (from 2.1–3.2 to 0.3–0.6%). The acids

exhibited maximal concentrations in the 1st level oils from the water-oil contact zone.

Examination of the fractional composition of the low-boiling oil from individual levels showed the following. By contrast to the light oil occurring at ultimate depths (500–600 m), the representative oils from medium depths (200–500 m) lack naphtha fractions; the near-surface heavy oils from the oil-water contact zone (150–200 m) contain negligible amounts of even paraffin fractions; tops were detected in deep oil from the 2nd sandy level solely.

Information on the presence of paraffins in the Naftalan oil is of great significance as a possible initial parameter in the search for medicinal oil analogs, as follows from the available literature. Also, data on the paraffin content in medicinal oil are far from unambiguous.

We carried out a comparative study of the potential content of normal and isomeric paraffin hydrocarbons in samples of the Naftalan oil from the 1st, marly, and 2nd sandy levels. For preliminary assessment we used the most convenient method of urea complexation under the following experimental conditions: oil : urea ratio 1 : 0.5, solvent petroleum ether (40–70% fraction), activator ethanol (10% on the solvents basis), stirring for 1.5 h at 25–30°C, filtration through a glass filter.

Table 2 shows that 0.12–0.45% solid paraffinic hydrocarbons (melting point = 50–53°C and n_D^{20} = 1.4592) was isolated from the oil of individual wells of the 2nd sandy level. In the oils from the marly and 1st levels paraffinic hydrocarbons were not detected by this method.

The ability to react with urea [15] serves for assessing the oil content of above all straight-chain aliphatic structures. As to branched paraffinic hydrocarbons, they typically do not readily react with urea, forming a complex only when their molecule contains ≥9 carbon atoms in the unbranched part of the chain and ≥18 carbon atoms in linear side chain of the cycloparaffin part [18].

We considered it possible that the solid paraffin hydrocarbons isolated might contain compounds with different structures, as demonstrated [19]. Therefore, for evaluating the presence of *n*-paraffinic hydrocarbons, the resulting concentrate of the light oil from well no. 33 was subjected to separation on zeolite molecular sieves (calcium form, pore size 5 Å) by the procedure from [20]. Thereby, 0.08% *n*-paraffinic and 0.26% isoparaffinic hydrocarbons on the oil basis were extracted from the concentrate. Thus, isostructures account for up to 75% of all the solid paraffinic hydrocarbons extracted from the light Naftalan oil.

Table 1 shows that the oil samples from different Naftalan oilfield levels differ sharply in the acid values representing the total content of oxygen-containing components. A literature search showed that studies dedicated to these compounds in the Naftalan oil are few if any, with the sole finding reported (even in the early stages of medicinal oil studies) concerning high concentrations of carboxylic acids in selected samples [21].

More recently, animal experiments revealed an inhibitory effect produced by naphthenic acids of the Naftalan oil on blood-forming organs [22]. Thus, accurate information on the naphthenic acids content is required for assessing the suitability of the Naftalan oils with different properties for therapeutic purposes.

The average acid values of young (Pliocene) oils bedding at up to 1-km depths reach 4 mg KOH/g [23]. As shown in [24], up to 90–95% of the total oxygen-containing components in naphthenic oils may be accounted for by cyclic (naphthenic) acids, whose total concentration in oil can reach 3%.

We determined the total content of carboxylic acids in the Naftalan oil from different levels by chromatography on a modified sorbent. The available literature on acids extraction from oils [20] describes specifically this method as giving the most correct results, by contrast to alkaline extraction at room temperature and boiling providing underestimated results.

For isolation of the naphthenic acids concentrate on a chromatographic column by the procedure described in [16] we used K_2SiO_3 as the sorbent modifier, following best practice guidance on decelerating side reactions catalyzed by the commonly used alkali [25]. The resulting carboxylic acids concentrate (see Table 2 for data on individual wells) was subjected to further fractionation in order to be analyzed for the potential content of naphthenic acids.

The concentrate was additionally purified on a chromatographic column as well, and this was followed by evaluation of the presence of naphthenic acids by thin layer chromatography using the procedure from [13, 26]. The concentrate was passed

Table 3. Potential content and physicochemical parameters of the naphthenic acids in the Naftalan oil

Sample name (well/level no.)	Content, mass %, on indicated basis		Characteristic		
	oil	carboxylic acids	acid value (mg KOH/g)	molecular weight	n_D^{20}
54/1	2.24	70.0	114	491	1.5226
20/marly	0.73	57.6	120	470	1.5200
33/2	0.15	49.7	115	487	1.5069

through a column packed with silica gel L 100/160 activated for 6 h at 180°C. This allowed isolation of 40–50 fractions, 10 mL each, which were eluted with a mixture of selective solvents (benzene : diethyl ether 9 : 1 and 1 : 1; ether; ether : chloroform 1 : 1; chloroform; alcohol–benzene 1 : 1).

For detecting naphthenic acids, samples of each fraction were analyzed by thin-layer chromatography on Silufol plates in the benzene:ether eluent system. Fractions containing compounds with R_f = 0.45–0.35 established for naphthenic acids using standard samples were pooled.

The removal of compounds of other classes (in particular, phenols) from the acids concentrate isolated was monitored by the absence of the absorption peak of the OH group (3300–3600 cm^{-1}) in the IR spectra.

Next, the physicochemical properties of the purified naphthenic acids were examined; their molecular weight was determined by the cryoscopic method, and the acid value was measured by potentiometric titration.

Table 3 presents the data on the content of naphthenic acids in the oils from the three mining levels. It is seen that the distribution of naphthenic acids in the oils from the individual levels of the Naftalan oilfield is similar to that revealed for the total carboxylic acids, i.e., their concentration in the oil decreases downward in the oilfield cross-section.

The acids isolated from the samples examined had close physicochemical characteristics. These are high-molecular-weight acids which, according to their acid values, had similar saponification values. However, their proportions in the carboxylic acids of the oils from different levels are different, being at a maximum (70%) in the oil sample from the 1st level well located in the zone of accumulation of formation waters, and at a minimum, in the oil from the deeply lying 2nd sandy level [27].

Our data on the potential content of naphthenic acids in the Naftalan oils are consistent with those on the industrial oils from the Lower Kura depression oilfields. As shown in [28], in the latter the content of naphthenic acids also tends to decrease with plunging of the similar levels within individual folded lines. Increased content of naphthenic acids was revealed in the oils near the oil-water contact.

Examination of the hydrocarbon group content of the Naftalan oil pursued a twofold objective: to identify the pattern of distribution of individual hydrocarbon groups in the oil in relation to the oil bedding depth and to determine the structural-group characteristics of the samples from each mining level, having the most different properties [29].

In the former case, the results of the chromatographic analysis were used to determine the total content of saturated, mono-, bi-, and polycyclic aromatic hydrocarbons and asphalt-resinous components in the oils from individual mining levels. In the latter case, the chromatographic data were compared for the samples of the representative oil (p_4^{20} = 0.930–0.950 g/cm^3) oil, the most common in the oilfield, heavy oil (p_4^{20} > 0.950 g/cm^3), and lightweight oil (p_4^{20} < 0.930 g/cm^3).

The hydrocarbon group content of the oil and of its individual bp fractions was determined by gradient elution liquid chromatography with refractometric detection. We analyzed the oils from the 1st (well nos. 54 and 73), marly (well nos. 20 and 51), and 2nd sandy (well nos. 33 and 92) levels. The physicochemical characteristics of the oil samples are given in Table 1.

Both the oil samples proper and the fractions boiling up to 350°C, isolated therefrom, were subjected to chromatographic separation. The content of such fractions in the heavy Naftalan oil (24%) is half that in the lightweight oil (49%).

For the analysis we used an L 60´50 column with an adapter, packed with silica gel L 100/250. The

successively used eluents were petroleum ether (40–70°C fractions), 5–25% solution of benzene in ether, benzene, alcohol-benzene (1 : 1), and acetone. The eluent flow rate was 1 mL/min.

The gradient elution process allowed isolation of 50–60 chromatographic fractions of equal volumes from each oil sample. After the solvent was distilled off in a CO_2 stream, the fractions were weighed, and the concentration (C, %) and the refractive index (n_D^{20}) were calculated.

Based on the chromatographic data, the total content of the saturated, mono-, bi-, and polyaromatic hydrocarbons and of asphalt-resinous substances in the oils and in their fractions was determined by the procedure described in [12]. The distribution of individual hydrocarbon groups in the oil samples was analyzed graphically, in the C and n_D^{20} coordinates.

Table 4 lists the data obtained.

It is seen that the oils from all three levels of the Naftalan oilfield are highly resinous paraffinic-naphthenic base oils. The transformation of the hydrocarbon group content as a consequence of vertical differentiation of the oil exhibits a clear trend, specifically, a decrease in the proportion of aromatic and asphalt-resinous substances due to an increase in the proportion of saturated hydrocarbons (to 14.4%) with increasing depth of bedding.

The chromatographic analysis showed that the heavy and lightweight oils differ from the representative oil in both qualitative and quantitative compositions. Specifically, a difference in the contents of high-molecular-weight polycyclic structures was revealed; also, the lightweight oil was found to contain alkane hydrocarbons.

The heavy oil exhibited a maximum content of high-molecular-weight polycyclic naphthenic structures, and the light oil contained noticeable amounts of paraffinic structures, uncharacteristic for the medicinal oil.

High concentration of hybrid naphthenic-aromatic compounds in the heavy Naftalan oil deserves mentioning. The content of chromatographic fractions that can concentrate these hydrocarbons was estimated at 8.0%, 5.2%, and 1.2% for the oils examined.

The results of the chromatographic separation indicate unequal sorption activities for the same types of hydrocarbon groups of the oils compared (different numbers of moieties on the curves within the same ranges), which indirectly evidences the presence of substances with sharply differing structures.

Table 4. Hydrocarbon group content in the oil fraction boiling up to 350°C

Hydrocarbon group content	Hydrocarbon content, %	
	heavy oil	lightweight oil
Saturated	70.9	76.9
Aromatic	–	–
Monocyclic	8.5	6.7
Monocyclic	8.4	7.6
Polycyclic	5.1	2.0
Intermediate	3.0	3.0
Resinous substances	4.1	3.8

For example, the numbers of fractions isolated in the area of monocyclic aromatic compounds were 5, 8, and 11 for the heavy, representative, and lightweight oils, respectively. The different sorption activities exhibited by aromatic hydrocarbons in the same chromatographic system is attributable, in particular, to the structural features of the aromatic hydrocarbons.

The analysis of the distillate products of the oils (fraction boiling up to 350°C) revealed identical distributions of hydrocarbon groups in the heavy and lightweight oils, with the basis (>70%) formed by naphthenic hydrocarbons and with other groups occurring in gradually decreasing concentrations (Table 4).

However, comparison of the data on the content of the same groups revealed some differences. Specifically, the light oil exhibited an increased content of naphthenic structures, and the heavy oil, of aromatic components.

Physiological experiments revealed toxicity of the low-boiling part of the Naftalan oil. Because of the lack of perfect analogy between the compositions of this part in the samples, enhanced toxicity of the lightweight oil is presumably attributable not only to its high content. Specifically, account should also be taken of the qualitative composition, in particular, of the presence (up to 50%) of the components lacking in the heavy oil.

Our studies showed that the change in the physicochemical properties of the heavy and

lightweight Naftalan oils as compared with those of the representative oil is due to changes in the component composition, including that of its hydrocarbon part.

The revealed features of the composition of the heavy oil (high concentrations of asphalt-resinous substances and of naphthenic and hybrid naphthenic-aromatic hydrocarbons, low content of saturated components, negligible amount of paraffin and of light components boiling up to 300°C) and of the lightweight oil (high content of saturated hydrocarbons, presence of paraffins, and significant concentrations of light fractions boiling p to 300°C) indicate that these oils underwent different chemical transformations compared to the representative oil.

The available results of chemical and biological analyses of the therapeutic Naftalan oil allowed expanding its application areas and drawing attention to the Naftalan oil regarded as an issue of great significance.

Practical application of the Naftalan oil required giving serious consideration to the use of this medicinal agent and full attention to each patient by medical doctors.

The indications and contraindications to the therapeutic use of the Naftalan oil and its preparations came around as a result of hard work by many scientists.

All available data, the results of critical assessment of research and observations and of objective analysis of cases of negative results from treatment with the Naftalan oil, and, eventually, of the experimental findings were put together and thus constituted ample evidence concerning the applicability of the Naftalan oil in medicine.

Much credit in development of indications for medicinal use of the Naftalan oil, as well as of combined Naftalan oil preparations, deresined Naftalan oil, and a number of fractions and components of this oil and medicinal mastic, which worked well in practice must go to the teams from Narimanov Azerbaijan State Medical Institute, Kirov Azerbaijan Research Institute of Balneology and Physical Treatment Methods, and Azerbaijan State University, as well as from a number of Azerbaijan's medical research institutes.

Successful medical and veterinary application of numerous preparations derived from the Naftalan oil allowed recommending them for practical use.

The development of these medicinal agents resulted from the work done over the years by the staff of the Naftalan oil pilot plant laboratory in Baku and of a number of research institutes and higher educational institutions, as well as of chemico-pharmaceutical plants not only in Azerbaijan but also in other cities, in particular, in Moscow, Leningrad (now St. Petersburg), Tbilisi, Rostov-on-Don.

Given below are the details concerning mainly the Naftalan oil derivatives without additives of substances of a different nature.

Deresined Naftalan is obtained from Naftalan oil via refining by the acid-contact method. To further remove small amounts of resins and a part of naphthenic acids from hydrocarbons and to isolate the so-called White Naftalan, the resulting product (Deresined Naftalan) is passed through a column packed with an activated clay adsorbent.

White Naftalan can be fractionated by the percolation method into the so-called Series A, B, C, and D White Naftalans differing from one another in physicochemical properties.

Series A White Naftalan is comprised of low-molecular-weight naphthenic hydrocarbons with densities of 0.9055 g/cm^3 and viscosities of 16.71 mm^2/s. This preparation is recommended for use in ophthalmic practice, in treatment of laryngeal tuberculosis, and during surgeries (always sterile).

Higher-molecular-weight hydrocarbons with an average density of 0.908 g/cm^3 and viscosity of 28.28 mm^2/s make up Series B White Naftalan; 8–10 drops 3 times a day of this preparation is recommended for treating gastric and duodenal ulcers.

Series C White Naftalan is a mixture of high-molecular-weight naphthenic and low-molecular-weight aromatic hydrocarbons. The average density of the hydrocarbons in this preparation is 0.9132 g/cm^3 and viscosity, 36.15 mm^2/s; it is effective in treatment of patients with atonic colon and chronic constipation.

A mixture of low-molecular-weight aromatic hydrocarbons with an average density of 0.9344 g/cm^3 makes up the composition of Series D White Naftalan recommended for external use (skin lubrication) and for applications as the basis for a number of combination preparations.

Also, Series E Deresined Naftalan, which is a mixture of aromatic hydrocarbons of relatively high

molecular weight, having a density of 0.9166 g/cm^{3}and a viscosity of 52.7 mm^2/s, is recommended for treatment of rheumatic diseases of joints and muscles, some gynecological and skin diseases, and wounds, pyorrhea, and chronic tonsillitis.

In some cases, the so-called White Naftalan Oil (density of 0.909 g/cm^3), obtained from the native Naftalan oil by treating with 98% sulfuric acid at a temperature of 30°C, is the recommended basis for the preparation of Naftalan ointment and white medicinal mastic.

Good effect in treating some diseases of the gastrointestinal tract, cystitis, and urethritis, as well as of nonpurulent wounds and some other diseases is provided by a sum of naphthenic hydrocarbons with a density of 0.905 g/cm^3, obtained by deresinification and the sulfonation of the native Naftalan oil.

Thus, the Naftalan oil is a very complex substance affecting the body as a whole.

The Naftalan oil is not a universal remedy; it is recommended as an effective balneological and medical preparation for treating some diseases but is contraindicated in cases of some other diseases. Even when the use of the Naftalan oil or of its preparations is clearly indicated, each individual case should be carefully approached, with giving due consideration to the factors characterizing the state of a patient's body.

Specific treatment methods, as well as the duration and frequency of the treatment procedures should be objectively evaluated with taking into account the specific conditions of the Naftalan oil treatment under resort and non-resort conditions.

Physiologists and clinicians believe that treatment with the Naftalan oil requires strict systematic laboratory control (blood and urine tests, etc.) and analysis of various physiological indicators characterizing the activity of the nervous system and internal organs of a patient's body as a whole. This will make it possible to eliminate the undesired effect of the Naftalan oil treatment at the very beginning and to ensure its effectiveness only where it is indicated. Medical doctors, physiologists, pathophysiologists, biochemists, and also organic chemists and physical chemists engaged in studying the petroleum chemistry problems, as well as pharmaceutical chemists are faced with the problem of finding more efficient ways to use the Naftalan oil.

CONFLICT OF INTEREST

No conflict of interest was declared by the authors.

REFERENCES

1. Kuliev, A.Kh., *Naftalan i metodika ego lechebnogo primeneniya* (Naftalan and Methods of Its Therapeutic Use), Baku: Azerneshr, 1936.
2. Guliev, S.A., *Unikal'naya lechebnaya naftalanskaya neft'* (Unique Therapeutic Naftalan Oil), Baku: Azerneshr, 1981.
3. Aliev, N.D., Tagdisi, D.G., and Mamedov, I.D., *Mekhanizm terapevticheskogo deistviya naftalana* (The Mechanism of Therapeutic Action of Naftalan), Baku: Azerneshr, 1983.
4. Mekhtiev, Sh.M. and Akhmedbeili, F.S., *Naftalan* (Naftalan), Baku: Azerneshr, 1959, pp. 56, 100–101.
5. Ali-zade, A.A. and Zeinally, M.I., *Materialy nauchno-prakticheskoi konferentsii po izucheniyu lechebnykh faktorov kurorta Naftalan* (Materials of the Sci.-Practical Conf. on the Study of Therapeutic Factors of the Resort Naftalan), 1963, pp. 11–14.
6. Zeinally, M.I., *Azerbaidzh. Neft. Khoz.,* 1973, no. 12, pp. 11–14.
7. Kadyrov, A.A. and Imanov, K.A., *Sb. trudov Azerb. Nauchno-Issled. Inst. kurortologii i fizicheskikh metodov lecheniya* (Coll. of Works of the Azerbaijan Research Inst. of Balneology and Physical Treatment Methods), Baku, 1963, issue 9, pp. 136–137.
8. Kaminskii, E.F., Demidenko, V.A., and Doroginskaya, V.A., *Khim. Tekhnol. Topliv Masel*, 1986, no. 12, pp. 4–6.
9. Kadyrov, A.A., Polyakova, L.P., Matushkina, E.I., and Kalisher, G.R., *Trudy pyatoi respublikanskoi nauchnoi konferentsii po naftalanu* (Proc. Fifth Republican Sci. Conf. on Naphthalan), Baku, 1982, pp. 25–29.
10. *Neft' i nefteprodukty: Sbornik Gosudarstvennykh standartov* (Oil and Petroleum Products: Collection of State Standards), Moscow: Izd. Standartov, 1977.
11. Kuliev, A.M., Buzova, N.G., Levshina, A.M., and Muradov, A.M., Azerb. Neft. Khoz., 1977, no. 2, p. 55.
12. Bogomolov, A.I., Temyanko, B.M., and Khotyntseva, L.I., *Sovremennye metody issledovaniya neftei* (Modern Methods of Oil Research), Leningrad, 1984, pp. 93, 130, 251, 292.
13. Frolov, E.B., Vanyukova, N.A., and Sanin, N.A., *Neftekhimiya,* 1986, no. 4, p. 482.
14. Kuliev, A.M., Levshina, A.M., and Shepeleva, T.V., *Dokl. Akad. Naul Azerb. SSR*, 1980, no. 10, pp. 50–53.
15. Rudakova, N.Ya., Timoshina, A.V., and Drogobychek, G.K., *Neft. Gaz. Prom–st',* 1986, no. 4, p. 48.
16. Amat, M., Arpino, P., Orrit, J., et al., *Analusis*, 1980, vol. 8, pp. 170–176.

17. Kuliev, A.M., Levshina, A.M., Kadyrov, A.A., and Polyakova, L.P., *Azerb. Neft. Khoz*., 1988, no. 6, pp. 56–61.
18. Proskuryakova, V.A. and Drabkina, A.E., *Khimiya nefti i gaza* (Chemistry of Oil and Gas), Leningrad: Khimiya, 1981, pp. 90, 100, 149.
19. Musaev, I.A., Kurashova, E.Kh., Simanyuk, R.N., Polyakova, A.A., Ermakova, L.S., Smirnova, M.B., and Sanin, N.A., *Neftekhimiya*, 1985, p. 315.
20. Brunnock, J.V., *Anal. Chem*., 1966, vol. 38, no. 12, p. 1648.
21. Krasuskii, K.A., *Trudy Azerb. Filiala Akad. Nauk SSSR., Ser. Geol.* (Proc. Azerbaijan Branch of the USSR Academy of Sciences, Ser. Geol.), Baku, 1935, issue 18, pp. 95–99.
22. Kuliev, A.M. and Levshina, A.M., *Gazokondensaty i neft'* (Gas Condensates and Oil), Ashkhabad: Ylym, 1968, p. 330.
23. Kam'yanov, V.F., Aksenov, V.F., and Titov, V.I., *Geteroatomnye komponenty neftei* (Heteroatomic Components of Oils), Novosibirsk: Nauka, Siberian Department, 1983, pp. 88, 98.
24. Nametkin, N.S., Egorov, G.M., Nametkin, N.S., Egorova, G.M., and Khamaev, V.Kh., *Naftenovye kisloty i produkty ikh khimicheskoi obrabotki* (Naphthenic Acids and Products of Their Chemical Treatment), Moscow: Khimiya, 1982, p. 10.
25. Stakhina, L.D., *Izuchenie sostava i svoistv komponentov neftei Nizhnevartovskogo svoda* (Study of the Composition and Properties of the Components of the Oils of the Nizhnevartovsk Arch), Tomsk, 1984, pp. 95–105.
26. Frolov, E.B., Vanyukova, N.A., Mikaya, M.N., Frolov, E.B., Vanyukova, N.A., Mikaya, A.I., and Sanin, P.I., *Neftekhimiya,* 1985, no. 3, p. 364.
27. Kadyrov, A.A., Polyakova, L.P., and Krasilova, L.M., *Sbornik trudov Azerb. Nauchno-Issled. Inst. Medreabilitatsii i prirodnykh lechebnykh faktorov* (Coll. of Works of the Azerbaijan Research Inst. of Medical Rehabilitation and Natural Healing Factors), 1987, issue 18, pp. 133–137.
28. Gadzhi-Kasumov, A.S., Dzhavadova, R.A., and Alimuradov, Sh.E., *Neft' i gaz* (Oil and Gas), Baku: Azerb. Nauchno-Issled. Inst im. Azizbekova, 1977, no. 5, p. 40.
29. Polyakova, L.P. and Movsumzade, E.M., *Bashkir. Khim. Zh*., 1996, vol. 3, no. 4, pp. 44–47.