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Investigation of Surakhani light crude oil compounds as a case study using modern spectroscopic techniques

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Abstract

The complex application of modern analysis methods (FT-IR, NMR, GC–MS and UV/Vis) allowed us to study in detail the composition of the crude Surakhani light oil with a complex composition. An accurate and comprehensive study of the composition of crude oils makes it easier to find the necessary field of application for them. For this purpose, the studied crude oil was separated into two fractions, such as paraffinic–naphthenic and aromatic (groups 1st, 2nd, 3rd and tar), by absorption column chromatography. The results show that Surakhani light oil is a paraffin–naphthene-based oil that contains 74% of paraffin–naphthene, 11.15% of aromatic hydrocarbons and 14.8% of gases. It has been shown that the aromatic group of compounds is mainly composed of mono- and bicyclic compounds and has alkyl chains with different lengths and branches (with the presence of methylene and methine groups). Based on the parameters of the structural group, it was found that the portion of H atoms in the aromatic nucleus and alkyl chain was 4.4–20.1% and 79.9–95.6%, respectively. The degree of aromaticity of the separated aromatic group is approximately 50%, which proves that these compounds are alkylated. The structure of the isolated paraffin–naphthene fraction has also been investigated by spectroscopic techniques, and it has been determined that this fraction is composed of iso- and cycloalkanes with alkyl chains of different lengths. As it is seen from the obtained results, unlike the other oils existing on the Absheron Peninsula, Surakhani light oil consists of one- and two-ring naphthene and isostructured paraffinic hydrocarbons. The composition of this petroleum mainly consists of isosubstituted alkyl cycloalkanes and relict, viz. biologically active hydrocarbons such as sterane and hopane used in medicine. It seems that the methodology developed for the petroleum industry can be used in other fields such as medicine.

Graphical abstract
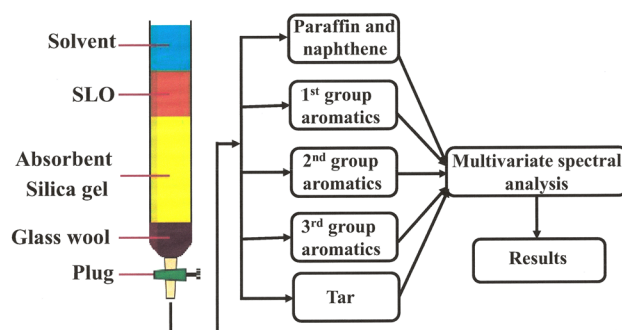
Abbreviations

EPR	Electron paramagnetic resonance
f_a	Degree of aromaticity
FT-IR	Fourier transform infrared
GC–MS	Gas chromatography–mass spectrometry
HPC	High-performance liquid chromatography
J	Isoparaffin index
NMR	Nuclear magnetic resonance
UV–Vis	Ultraviolet–visible spectroscopy
SARA	Saturate, aromatic, resin and asphaltene
SLO	Surakhani light oil

Extended author information available on the last page of the article

Introduction

The optimal application of hydrocarbon resources is significant in countries with rich oil and gas resources. For several years, scientists in the Republic of Azerbaijan and around the world, dealing with petrochemical and oil refining issues, have been looking for effective methods in this direction by studying the combined compounds of oil extracted from various fields at the molecular level (Samedova et al. 2009; Guseynova et al. 2010; Yolchueva et al. 2015). Existing fractionation techniques and geochemical methodologies in this direction are time-consuming to prepare samples for and take a long time to evaluate compositions employing (Permanyer et al. 2002; Ryder et al. 2002). Highly sensitive spectroscopic equipments (FT-IR, NMR, EPR, GC–MS and UV/Vis) are required in this discipline due to the necessity for quick and easy techniques. On the other hand, the electron spectra of oil and oil derivatives are complicated due to their complex chemical components. Because of this, eliminating the specified problem while also thoroughly analyzing the complicated compositions will be made possible by the concurrent deployment of more sensitive analytical methodologies for the study of oils. However, due to the lack of complex applications of spectroscopy and luminescence techniques, a comprehensive study of the composition and characteristics of the structural group of oil and petroleum products (Steffens et al. 2011; Alan 2005; Ezekiel and Adeniyi 2007; Guzmán-Osorio et al. 2021) has not been conducted. Therefore, only a limited number of physical and chemical properties and structures of oils have been studied, which confines their application fields.

We have recently studied the physicochemical properties, structural group composition and photochemical transformation processes of Balakhani crude oil and its components with the help of highly sensitive devices (Yolchuyeva et al. 2020). It was determined that the fractions separated from the Balakhani oil are rich in aromatic compounds with a lower oxidizing ability and higher luminescence capability. The photooxidation process takes a relatively long time in these aromatic groups derived from Balakhani oil. This property increases their luminescence and allows them to use as petroleum luminophores.

It is known that (Tissot and Welte 1984) the oil consists mainly of aromatic hydrocarbons, paraffin–naphthene and olefin. However, the amount of these chemical compositions of crude oils from different producing regions (even within a particular formation, depending on the extraction solubility) can vary tremendously (Yolchuyeva et al. 2021). Due to the complex nature of crude oil, it is impossible to determine the individual molecular components. Hence, its composition should be studied in separate fractions. Crude oil is divided into saturated, aromatic, tar and asphaltene parts by fractionation called the SARA group. Although high-performance liquid chromatography was first used to study the composition of these fractions, its high cost and time consumption led to the search for alternatives (Yolchuyeva et al. 2020; Hammami et al. 1998). In this regard, some components of crude oil have been extensively studied at the molecular level using various vibrational spectroscopy methods (Andreas et al. 2005; Gang et al. 2018). According to the group structure, the oils extracted on the Absheron Peninsula are mainly aromatic, naphthenic and paraffin-based oils. Due to the variety of oils depending on the location and depth of extraction, before precise and targeted guidance to downstream (e.g., oil refining and petrochemical industries), the study of structural group composition, spectral–luminescence properties and chemical conversion processes due to external influences (including light, heat, etc.) as well as drawing the appropriate application plans for the intended purpose is crucial. For example, petroleum luminophores have been produced and used for several years from aromatic base oils and oil refining products extracted in Azerbaijan. For this purpose, the composition of the oil is first studied using vibrational spectroscopy methods. These materials are used in various sectors such as automotive industries and space technologies. In addition, the preparation process is easier and more cost-effective than synthetic luminophores (Mamedov et al. 2000, 1999; Jafarova 2004a, b; Salmanova et al. 2009).

The Republic of Azerbaijan is known for its unique oil (Naftalan, Surakhani, etc.), rich in naphthenic hydrocarbons. Academician Y.H. Mammadaliyev consistently separated water, asphaltene–tar compounds, petroleum acids and aromatic hydrocarbons from therapeutic Naftalan oil, which is used for the treatment of a number of diseases in the last century. It was determined that its therapeutic effect is due to the presence of short-side-chain multi-ring naphthenic hydrocarbons (Abbasov et al. 2007, 2014). Currently, under the supervision of academician V.M. Abbasov, is being conducted research dedicated to studying the composition of this oil and expanding its scope. It was found that the reason for the biological activity of Naftalan oil is the compounds with bridged structures and short-side-chain multiring naphthenic hydrocarbon types with low boiling points. Taking into consideration the similarity of petroleum from the genetic viewpoint extracted on the Absheron Peninsula, it is quite important to study in detail the chemical composition of these petroleum from practical and theoretical points of view.

Among these crude oils, the study of the structures of biomolecules of Surakhani light oil (SLO) by determining its structural group composition with low density and the molecular weight is of particular importance. The aim of

this study is to investigate the composition of SLO, which was separated by liquid adsorption chromatography, with the help of new high-sensitivity spectroscopy (FT-IR, NMR, EPR, GC–MS) and luminescence (UV/Vis) devices and to suggest a fruitful application.

Research methods

The SLO located on the Absheron Peninsula of the Republic of Azerbaijan has been selected as a case study. This oil is light in color and its boiling point is 260 °C. Surakhani oil is obtained from a depth of 465 m. The physical and chemical properties of this crude oil are given in Table 1.

In order to study the structure and composition of Surakhani light oil by spectroscopy and luminescence methods and also to determine the hydrocarbon content, first hydrocarbons were separated according to the relevant method based on the refractive index by liquid adsorption chromatography (GOST 11244-76). The composition and

physicochemical parameters of the separated hydrocarbon groups are given in Table 2.

Gases released from SLO have been analyzed by gas chromatography and it was determined that its composition consists of methane—1.185%, ethane—32.652%, propane—48.187%, i-butane—14.994%, n-butane—2.454%, 2-methyl butane—0.0665%, 2,2-dimethyl propane—0.075%, i-pentane—0.379% and n-pentane—0.0075%.

For comparison, the composition of hydrocarbon groups of separated oils by liquid adsorption chromatography in our previous studies is shown in Table 3 (Yolchuyeva et al. 2021; Hammami et al.). Unlike these oils, the content of aromatics in SLO is scarce (about 3% according to the results of spectral analysis). Even unlike other studied oils, which are separated under the same conditions, there is no conventionally called 4th group aromatics. Unlike the crude oils available in our country, this crude oil is similar to the kerosene fraction due to its low density and

Table 1 Physicochemical parameters of Surakhani oil

Oil	Physicochemical properties							
Well no	Density (at 20 °C, kg/m^3)	Flash point °C	Kinematic viscosity, (at 40 °C, mm^2/s)	Sulfur, w%	Freezing point °C	Acid value, mg KOH/g	Tarw%	Molecular weight
75,348	798,9	+40	1.22	0.03	−60	0.35	0.95	157.4

Table 2 Composition and physicochemical parameters of SLO

Well no	Components	Content in petroleum, %	Refractive index, n_d^{20}	Viscosity, 40 °C mm^2/s	Density, 20 °C kg/m^3	Molecular weight
75,348	Paraffin–naphtha	74	1.4463	16	810.5	167
	1st group aromatics	3.9	1.5134	28.1	820.5	187
	2nd group aromatics	5.0	1.5558	31.3	855.3	236
	3rd group aromatics	1.3	1.5860	33.6	886.7	315
	Tar	0.95	–	–	960.1	510
	Gases	14.85	–	–	–	–

Table 3 Comparison of hydrocarbon content of crude oils

No	Crude oil	Component content of crude oils, %					
		Paraffin–naphtha	1st group aromatics	2nd group aromatics	3rd group aromatics	4th group aromatics	Tar
1	Surakhani light oil	74	3.9	5.0	1.3	0	0.95
2	Heavy Surakhani oil (Abbasov et al. 2015a, b)	75.42	5.87	3.68	6.23	4.7	4.1
3	Balakhani oil [8,9]	66	6	6.46	3.19	9.48	8.87
4	Heavy Balakhani oil (Yolchuyeva et al. 2016; Jafarova 2021)	52.04	8.1	7.1	8.6	13	11

aromatic hydrocarbon content and can be used directly as fuel (Aleksandrova 2004; Abbasov et al. 2015a, b).

By means of liquid adsorption chromatography, the amount of individual aromatic compounds in the separated aromatic group hydrocarbons of Surakhani light oil (SLO) and the maximum absorption bands of each of them were calculated in accordance with the relevant methodology (Baklanova et al. 2017) based on optical densities in the UV spectra.

IR spectra have been recorded on a Zn–Se crystal in the wavenumber range of 600–4000 cm^{-1} in an Alpha Fourier IR spectrophotometer manufactured by Bruker.

PMR spectra have been recorded on a 300.18 MHz Fourier spectrometer. Deuterated benzene (C_6D_6) has been used as the solvent. Based on the obtained ^1H NMR spectra and elemental analysis, the relative distribution of protons in different structural groups has been calculated.

The composition of the SLO has been determined by gas chromatography–mass spectrometry (Thermo Electron GMS Trace DSO system).

The electron absorption spectra of analyzed samples were recorded at room temperature on a JENWAY-6850 UV/visible spectrophotometer using a quartz cuvette ($d = 1$ cm) at a spectral range of 190–1000 nm and using hexane as a solvent.

Luminescent excitation and photoluminescence spectra of this crude oil and its components were recorded and studied in 1-cm-wide rectangular quartz cuvettes at room temperature in the wavelength range of 190–1100 nm in the "Cary Eclipse" spectrofluorimeter. Hexane is used as a solvent.

Results and discussion

Since the composition of oil and oil products is a complex system consisting of various hydrocarbon mixtures, the use of spectral devices separately creates certain limitations in the detailed study of these compositions, which is a drawback of the method. As it is known, the composition of oil consists of mono- and polycyclic aromatic hydrocarbons with values of ionization potentials that are quite close to each other, so their absorption spectra overlap each other and cause the formation of a whole absorption band, which makes it difficult to study these hydrocarbons separately. Therefore, along with the UV/Vis spectral method, the application of the luminescent method, which has a relatively higher sensitivity, allows a more accurate determination of the type of aromatic hydrocarbons of this type according to the luminescence and excitation maxima. On the other hand, since it is not possible to study saturated hydrocarbons with ionization potential greater than 9–10 eV with UV/Vis spectroscopic and luminescence methods, NMR, IR and GC–MS spectroscopic

methods were used to study crude oil and its hydrocarbon composition. Infrared, ultraviolet, nuclear magnetic resonance spectroscopies and mass spectrometry techniques used in the analysis of crude oil reflect its complete molecular composition and are widely used as an alternative to ASTM and IP tests in the characterization and classification of oil and oil products (James 2002). Each of these devices has its own role and function in the investigation of complex structures. Their complex application, which is one of the main advantages of these methods, makes an effective contribution to the comprehensive study of such complex structures. The analysis methods (FT-IR, NMR, GC-MS and UV/Vis) used for the detailed study of the content of the SLO, which we took as the research object and the results obtained by applying them are focused on in the article.

Fourier transform infrared analysis

FT-IR spectroscopy is an easy and inexpensive experimental analysis method used to study the structural group composition of oil and oil products. The structures of SLO and its separated components were studied by IR spectroscopy, and the spectra of the crude oil and its paraffinic–naphthenic hydrocarbon components are shown in Fig. 1a and b. As can be seen from the IR spectrum of SLO, it contains alkyl-substituted aromatic hydrocarbons. Absorption areas 1612–1620 cm^{-1} and 3010–3046 cm^{-1} are characteristic for aromatic hydrocarbons in this spectrum. However, the 10–12 cm^{-1} shift of the absorption maxima to high and low frequencies indicates the presence of mono-, di- and trisubstituted aromatic rings in the compounds. In order to determine the types of the aromatic compound substituents, the absorption area 700–900 cm^{-1} was investigated and it was determined that the aromatic group hydrocarbons of the studied oil contain mono- (628, 650, 698, 702, 703 cm^{-1}), 1,2 di- (738, 741, 745, 746 cm^{-1}), 1,3 di- (780, 872 cm^{-1}), 1,2,3 tri (779, 780 cm^{-1}), 1,2,4 tri- (809, 811, 871 − 875, 879 cm^{-1}) alkyl-substituted aromatic hydrocarbons. In the IR spectrum of paraffinic–naphthenic hydrocarbons (Fig. 1b), the absorption band of pendulum oscillation (728 cm^{-1}) of C–H bonds of the CH_2 groups in the alkyl chain is present. The absorption bands at 1375 cm^{-1} and 1457 cm^{-1} refer to the symmetrical deformation vibrations of the CH_3 and deformation vibrations of the CH_2 groups, respectively. The presence of the intensive bands at 2920 cm^{-1} and 2857 cm^{-1} refers to valence vibrations of the C–H bond of the methylene groups in the $(CH_2)_n$ chain. The absorption bands at 968 cm^{-1} and 1035 cm^{-1} are considered as evidence for the deformation vibrations of the C–H bond of CH_2 groups in the naphthenic ring. The absorption bands
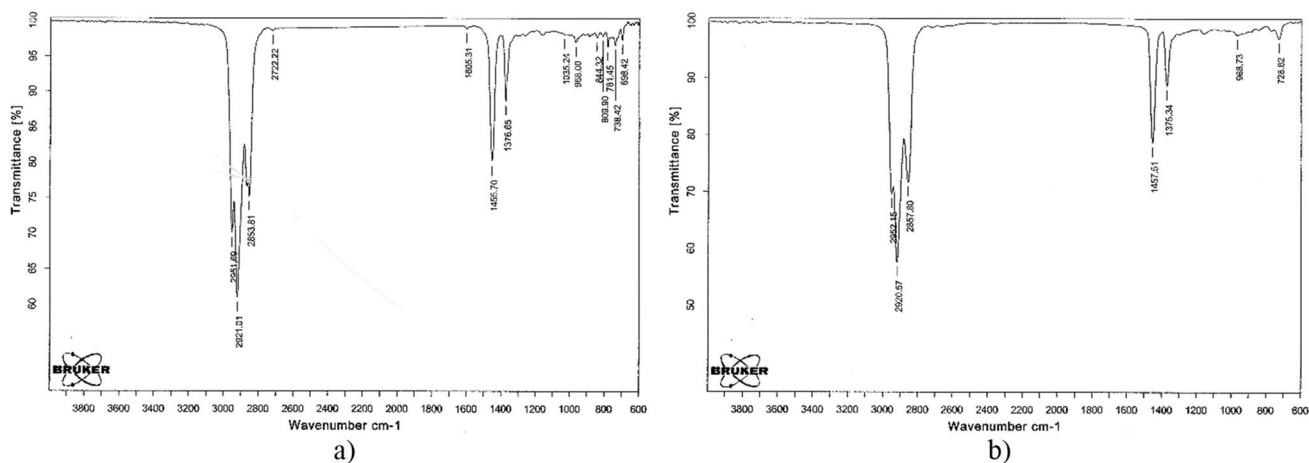
Fig. 1 IR spectra of SLO (**a**) and its naphthene–paraffin hydrocarbon fraction (**b**)

Table 4 Absorption bands presented in SLO and its separated group components

Wavenumber, cm^{-1}						Assignment
SLO	Paraffin–naphtha	1st group aromatics	2nd group aromatics	3rd group aromatics	Tar	
2853	2857	2858	2858	2854	2856 2922	Symmetric and asymmetric stretching vibrations of C–H bonds of CH$_3$ and CH$_2$ groups
2921	2920	2922	2922	2920		
2951	2952					
1376	728	1375	1375	1374	959	Bending vibrations of C–H bonds of CH$_3$ and CH$_2$ groups
1455	1375	1453	1453	1457	1038	
	1457					
968	968	956	955	967, 1031	959	Bending vibrations of C–H bonds of CH$_2$ group in naphthenic ring
1035		1031			1038	
1605	no peak	1602	1602	1602	1600	Stretching vibrations of benzene ring C–C bonds
698		701	744	745	703	Bending vibrations of benzene ring C–H bonds
738		745	780	810	741	
781	No peak	779	810	875		
809		811	872			
844		871				
No peak	No peak	3010. 3044	3012	No peak	No peak	Stretching vibrations of benzene ring=CH groups
			3046			
No peak	No peak	1164, 1264	1031	1163	1071	Stretching vibrations of C–O bonds
			1164		1124	
			1266		1272	
No peak	No peak	1737	1740	1738	1728	Stretching vibrations of C=O bonds

presented in the IR spectra of SLO and its separated group components are given in Table 4.

Nuclear magnetic resonance analysis

Nuclear magnetic resonance analysis has the unique advantage of providing information on functional groups in the analysis of crude oil. SLO and its aromatic and saturated hydrocarbon components separated by adsorption were also studied using the ^{1}H NMR spectroscopy method. ^{1}H NMR spectra of the crude oil and the third group aromatics separated from it are given in Fig. 2a and b, respectively. In the ^{1}H NMR spectrum of SLO, along with the chemical shift signals at $\delta = 0.88$ and 1.28 ppm of CH$_3$ and CH$_2$ groups of
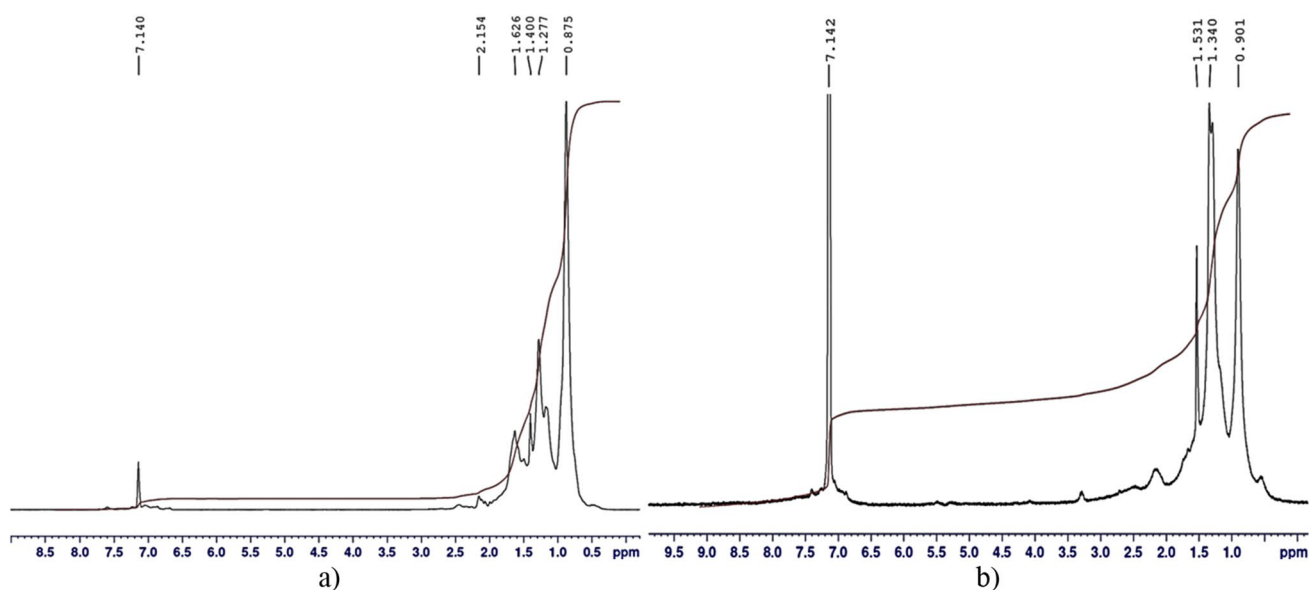
Fig. 2 ^{1}H NMR spectra of SLO (**a**) and the 3rd group of aromatic fraction (**b**) separated from it

the alkyl chain, a chemical shift signal at 1.45–2.23 ppm of the methine group is also observed (Fig. 2a). Methine group chemical shift signals are also observed in paraffin–naphthene and aromatic group components separated from SLO. This once again confirms that the alkyl chain has an isostructure. In addition, as can be seen from the ^{1}H NMR spectrum of the separated third group of aromatic components of SLO, along with chemical shift signals of protons of the aromatic nucleus, chemical shift signals of protons of the alkyl CH_3 and CH_2 groups are also observed (Fig. 2b). The chemical shift signals presented in ^{1}H NMR spectra of SLO and its separated group components are given in Table 5.

The distribution of hydrogen atoms in the structural groups of SLO and its separated components was calculated according to the relevant methodology (Edwards CJ 2011;

Clutter et al. 1972) based on the results of ^{1}H NMR spectra and element analysis. Obtained results are given in Table 6. As can be seen from the table, the share of hydrogen atoms in alkyl (H_β) and terminal methyl groups (H_γ), which are not in direct contact with aromatic nuclei, is dominant in SLO and is generally more than 72%. The share of protons in naphthenic structures ($\delta = 1.4$–2.0 ppm) is 21.7%, and the distribution of methine, methylene and methyl groups ($\delta = 2.0$–2.9 ppm) in α-position relative to aromatic nuclei is 2.8%. In the paraffinic–naphthenic structure, the relative proportion of the hydrogen atoms in the alkyl chain and the hydrogen atoms in the terminal methyl groups is approximately the same (42 and 43%, respectively) due to the high branching of the alkyl chain.

Table 5 A chemical shift in ^{1}H NMR spectra of SLO and its separated group components

Region, ppm						Structure assignment
SLO	Paraffin–naphthene	1rd group aromatics	2nd group aromatics	3rd group aromatics	Tar	
0.61–1.03	0.63–1.03	0.77–1.01	0.72–1.00	0.67–1.04,	0.68–1.04	Paraffinic hydrogens of CH_3 groups
1.03–1.45	1.03–1.45	1.01–1.39	1.00–1.38	1.04–1.48,	1.03–1.51	Paraffinic hydrogens of CH_2 groups
1.45–2.02	1.45–2.23	1.39–1.83	1.38–1.82	1.48–1.99,	1.51–1.98	Naphthenic hydrogens of CH_2 and CHgroups
2.02–3.13	2.23–2.79	1.83–3.20	1.82–3.31	1.99–3.34,	1.98–3.65	Paraffinic hydrogens of CH, CH_2 and CH_3 groups are attached to the α-position of the aromatic nucleus
6.65–7.67	6.85–7.41	6.61–7.90	6.70–8.62	6.79–8.14,	6.68–8.70	Hydrogens in aromatics rings
No peak	No peak	No peak	No peak	4.81–5.67	4.15–5.58	Olefinic hydrogens

Table 6 Structural group parameters of SLO and its separated components

Hydrocarbon	Relative distribution of hydrogen atoms in different structural groups, %						Aromaticity degree	Isoparaffin index
	H_{Ar}	H_{doy}	H_α	H^*_β		H_γ	J	f_a
SLO	0.9	99.1	2.8	(21.7)	29.3	43.3	~0.03	1.3
Paraffin–naphtha	trace	~100	0.5	(14.9)	41.6	43.0	trace	0.96
1st group aromatics	20.1	79.9	28.4	(10.0)	23.7	17.8	0.52	0.50
2nd group aromatics	17.9	82.1	31.6	(10.1)	24.8	15.6	0.49	0.87
3rd group aromatics	18.7	81.3	4.1	(9.1)	23.9	14.2	0.50	0.83
Tar	4.4	95.6	9.9	(10.4)	47.8	27.5	0.20	0.38

H_{ar} hydrogen of aromatics, H_α hydrogen of alkyl in the α-position with respect to the aromatic ring, H_β hydrogen atoms of the alkyl chain that is not in direct contact with the aromatic nuclei, H_γ the number of H atoms in the terminal methyl groups. J isoparaffin index (branching index)

*In parentheses, the amount of hydrogen atoms of naphthenic structures is given
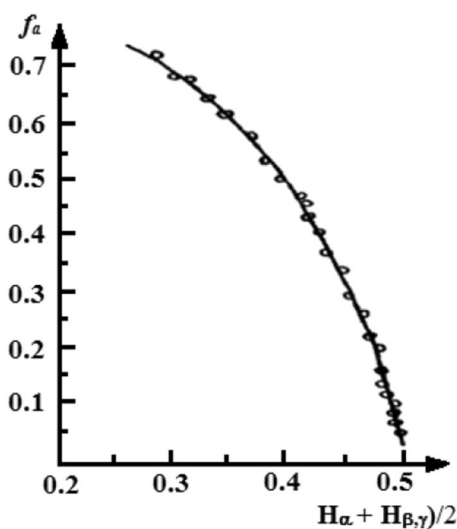
Fig. 3 Dependence of the oil aromaticity degree on the value of $(H_\alpha + H_{\beta,\gamma})/2$

One of the important characteristics of oil fractions is their degree of aromaticity (f_a). Various methods are used to determine this parameter (spectrophotometric, X-ray, NMR, etc.). The simplest of these is the graphical method (Clutter et al. 1972). This method is based on the dependence of the degree of aromaticity on the ratio $(H_\alpha + H_{\beta,\gamma})/2$ calculated by ^{1}H NMR spectroscopy (Fig. 3). Thus, the degree of aromaticity of Surakhani oil and its separated hydrocarbon samples was determined by this method. One of the advantages of this method is that the analysis does not take much time and obtained results are quite accurate ($f = 0.5\%$). As can be seen from the table, the degree of aromaticity of SLO is very low, about 3%. In addition, the aromaticity of these groups is 49–52% due to the presence of substituted aromatic compounds. Moreover, as can be seen from the distribution of hydrogen atoms in Table 6, in the aromatic compounds separated from SLO the amount of H atoms in the aromatic ring and alkyl chain is 4.4–20.1% and 79.9–95.6%, respectively.

The proportions of alkyl groups (CH_3 and CH_2) were also determined in order to further study the saturated fragments in the molecules of the fractions. It should be noted that this proportion ($J = CH_3/CH_2$) is the main parameter that characterizes the degree of branching of aliphatic chains and it is called the isoparaffin index. As given in Table 6, Surakhani crude oil and its paraffin–naphthene hydrocarbon components separated by adsorption are characterized by a high isoparaffin index (J) (1.3 and 0.96, respectively). Such high values of the isoparaffin index prove that branched alkanes predominate in the oil of the studied well. The degree of branching of alkyl fragments in the aromatic group components and in the tar separated from SLO is not high and varies in the interval of 0.4–0.9. The distribution of terminal methyl groups (H_γ) in the composition of these hydrocarbons is high (17–28%). The distribution of unsubstituted hydrogen atoms in the nuclei of these separated aromatic hydrocarbons is ~18–20%. The composition of the residual tar component is richer with almost saturated structures. In other words, ~96% of hydrogen atoms are from the saturated fragments of this component. Therefore, the amount of protons in the aromatic rings is not very high (~4%).

Gas chromatography–mass spectrometry analysis

GC–MS is an important analytical method for determining the organic component content of complex oil. The composition of the separated naphthene–paraffin hydrocarbon fraction of SLO was studied by gas chromatography–mass spectrometry, and the GC–MS spectrum of this fraction is given in Fig. 4. The particular naphthenic and paraffinic hydrocarbons, which dominate in this fraction, are selected and given in Table 7. As can be seen from the table, the oil under study is dominated by branched alkanes (butane,

Fig. 4 Gas chromatography–
mass spectrometry spectrum
of the naphthene–paraffin
hydrocarbons
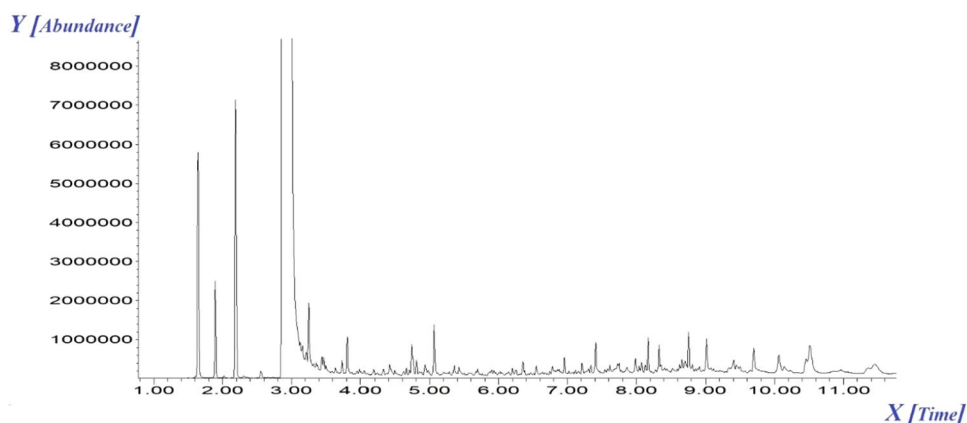
2,2,3,3-tetramethyl, heptane, 3-ethyl-2-methyl, hexadecane, 2,6,10,14-tetramethyl, etc.) and naphthenic hydrocarbons (cyclohexane, 1,1,2,3-tetramethyl, cyclohexane, 1,2-dimethyl-3-pentyl-4-propyl, bicyclo[3.1.1]heptane, 2,6,6-trimethyl, bicyclo[3.1.1]heptane, 2,6,6-trimethyl, cyclotridecane, etc.), the side chains of which consist of alkyl radicals of different lengths. As can be seen, the length of substituted alkyl radicals of naphthenic hydrocarbons is relatively short. Short substituted side chains of cyclohydrocarbons lead to their high bioactivity.

Besides spiro-structured *cis,trans*-1,6-dimethylspiro[4.5] decane (0.172%) given in the table, there were also found spiro[2.4]hepta-4,6-diene (0.088%), *trans,cis*-1,8-dimethylspiro[4.5]decane (0.099%), *cis,cis*-2,9-dimethylspiro[5.5] undecane (0.051%) compounds in the SLO paraffin–naphthene fraction.

As a result of the GS–MS analysis of methane–naphthene fraction, it was also found that the composition of this fraction consist of particular importance bioactive components (Kalaiarasan and John 2011; Halehatty et al. 2009), such as acetic acid derivatives—3.870% (methoxyacetic acid 2-tetradecyl ester, methoxyacetic acid heptadecyl ester, methoxyacetic acid tridecyl ester, trifluoroacetic acid *n*-octadecyl ester, bromoacetic acid hexadecyl ester, acetic acid octadecyl ester, bromoacetic acid octadecyl ester, methoxyacetic acid 3-tridecyl ester, acetic acid 3,7,11,15-tetramethyl-hexadecyl ester, trifluoroacetic acid *n*-octadecyl ester, 2-methoxyacetic acid 1-ethylundecyl ester), oxalic acid derivatives—0.791% (isobutylheptyloxalate, oxalic acid decyl propyl ester, oxalic acid isobutyl heptadecyl ester, oxalic acid cyclohexylmethyl isohexyl ester, oxalic acid isobutyl hexadecyl ester, oxalic acid bis(6-ethyloct-3-yl) ester, oxalic acid isobutyl tetradecyl ester, oxalic acid isobutyl hexadecyl ester, oxalic acid isobutyl hexadecyl ester), sulfuric acid derivatives—1.632% (sulfurous acid butyl octadecyl ester, sulfurous acid butyl heptadecyl ester, sulfurous acid butyl tetradecyl ester,

sulfurous acid octadecyl 2-propyl ester, sulfurous acid butyl tridecyl ester, sulfurous acid 2-propyl tridecyl ester, sulfurous acid, octadecyl 2-propyl ester), carbonic acid derivatives—0.154% (carbonic acid, isobutyl octadecyl ester, carbonic acid ethyl octadecyl ester) and small amounts of aldehydes and alcohols. Most of the oxygen-containing compounds in the paraffin–naphthene component of SLO are listed in Table 7. Esters are predominant and their amount reaches 5.874%.

Along with the oxygenated compounds present in the naphthenic–paraffin hydrocarbon fraction, icozane—$C_{20}H_{42}$ (0.844%), octacozane—$C_{28}H_{58}$ (0.202%); 1-docozane—$C_{22}H_{46}$ (0.062%); nonadecane—9-methyl ($C_{20}H_{42}$); nonadecane—7-methyl ($C_{20}H_{42}$); heptadecane, 2,6,10,14-tetramethyl ($C_{21}H_{44}$); hexadecane, 2,6,10,14-tetramethyl ($C_{20}H_{42}$); heptadecane ($C_{17}H_{36}$), etc., bioactive substances with therapeutic properties are also available (Table 7).

The existence of compounds with particular structures and importance in the composition of the SLO paraffin–naphthene component increase their therapeutic role. Therapeutic properties of some compounds with bioactive, antimicrobial and metabolic properties in the composition of the methane–naphthene fraction have been found, while others are being studied.

In addition to the compounds listed in the table, heteroatomic cyclic compounds such as phthalane, stigmastane and cholestane, steranes and the cyclic compound 28-Nor-17α(H)-hopane were also found in the SLO. In most cases, the concentration of steranes in oils is usually equal to the concentration of hopanes (0.015%) and in some cases higher. In oil, hopanes and steranes are relevant compounds that confirm their organic origin, such that these compounds are one of the main hydrocarbons in oil, which contain the structure of primary natural biomolecules and the spatial displacement of individual atoms. They are used in catagenic transformation and possible genetic correlations.

Table 7 Naphthene–paraffin hydrocarbon content of SLO

#	Ret. time	Compound name	#	Ret. time	Compound name
1	1.842	Decane, 2,2,3-trimethyl-	44	7.061	Bicyclo[3.1.1]heptane, 2,6,6-trimethyl
2	1.894	Hexane	45	7.118	Cyclohexane, 2-butyl-1,1,3-trimethyl
3	2.020	Cyclopentane, methyl-	46	7.158	*cis*,*trans*-1,6-Dimethylspiro[4.5]decane
4	2.306	Butane, 2,2,3,3-tetramethyl-	47	7.215	Cyclohexane, (2-methylpropyl)-
5	2.558	Cyclohexane, methyl-	48	7.307	Nonadecane, 9-methyl-
6	2.735	Cyclopentane, 1,2,3-trimethyl-	49	7.415	Dodecane, 2,6,11-trimethyl
7	3.743	Cyclohexane, ethyl-	50	7.547	Cyclopentane, 1-pentyl-2-propyl-
8	3.502	Cyclohexane, 1,1,3-trimethyl-	51	7.587	Cyclohexane, 1-isopropyl-1-methyl
9	3.874	1,3,5-Cycloheptatriene	52	7.684	Cyclopentane, 1-pentyl-2-propyl-
10	3.994	1-Ethyl-4-methylcyclohexane	53	7.702	Octane, 3,5-dimethyl
11	4.011	Cyclohexane, 1-ethyl-4-methyl-,	54	7.702	7-Oxabicyclo [4.1.0] heptane, 1,5-dimethyl
12	4.188	1-Ethyl-4-methylcyclohexane	55	7.753	Hexadecane, 2,6,10,14-tetramethyl
13	4.423	Cyclohexane, propyl-	56	7.925	Cyclohexane, 1,1,2,3-tetramethyl
14	4.497	Heptane, 3-ethyl-2-methyl-	57	8.045	Tridecane, 2-methyl-
15	4.623	Undecane, 5,6-dimethyl-	58	8.079	Methoxy acetic acid, 3-tridecyl ester
16	4.623	Oxalic acid, isobutyl heptadecyl ester	59	8.177	Hexadecane, 2,6,10,14-tetramethyl-
17	4.852	Cyclohexane, 1-methyl-4-(1-methylethyl)	60	8.285	Cyclopentane, 1,1,3-trimethyl
18	5.287	Decane, 4-methyl-	61	8.331	Tetradecane
19	5.424	Cyclohexane, (2-methylpropyl)-	62	8.417	Cyclohexane, 1,5-diisopropyl-2,3-dimethyl
20	5.567	Cyclopentane, hexyl-	63	8.714	Cyclohexane, octyl-
21	5.699	Naphthalene, decahydro-	64	8.760	Heptadecane, 2,6,10,14-tetramethyl
22	5.905	Cyclohexane, 1-ethyl-2-methyl-, cis	65	8.817	Tetradecane, 3-methyl-
23	5.905	Oxalic acid, cyclohexyl methyl isohexyl ester	66	8.817	Sulfurous acid, butyl tridecyl ester
24	5.962	Cyclohexane, 1-ethyl-2-propyl-	67	9.012	Pentadecane
25	6.048	Cycloheptane, methyl-	68	9.115	17-Pentatriacontene
26	6.111	Cyclohexene,1-(2-methylpropyl)-	69	9.206	Cyclohexane, 1,2-dimethyl-3-pentyl-4-propyl
27	6.202	Naphthalene, decahydro-2-methyl-	70	9.338	Tetradecane, 6,9-dimethyl-
28	6.294	Bicyclo[3.1.1]heptane, 2,6,6-trimethyl	71	9.498	Tridecane, 2-methyl-
29	6.323	Cyclopentane, butyl-	72	9.647	17-Pentatriacontene
30	6.357	Cyclohexane, pentyl-	73	9.699	Hexadecane
31	6.380	Cyclododecane	74	9.830	Bicyclo[3.1.1]heptan-3-one, 6,6-dimethyl-2-(2-methylpropyl)-
32	6.431	Cyclopentane, 1-butyl-2-propyl-	75	10.065	Pentadecane, 2,6,10-trimethyl-
33	6.511	Cyclohexane, 1,2,3-trimethyl-, (1.alpha.,2.alpha.,3.beta.)-	76	10.145	Undecane, 4-cyclohexyl-
34	6.609	Undecane, 3-methyl-	77	10.460	Heptadecane
35	6.677	*cis*,*trans*-1,6-Dimethylspiro[4.5]decane	78	10.511	Pentadecane, 2,6,10,14-tetramethyl
36	6.786	Decalin, anti-1-methyl-, cis	79	10.963	Cyclopropane, 1-(1,2-dimethylpropyl)-1-methyl-2-nonyl-
37	6.815	Cyclopentane, 1,1,3-trimethyl-	80	11.364	Octadecane
38	6.815	Undecane, 2,6,10-trimethyl	81	11.455	Hexadecane, 2,6,10,14-tetramethyl-
39	6.855	Azulene	82	11.721	Carbonic acid,ethyl octadecyl este
40	6.878	Cyclohexane, 1-methyl-2-pentyl-	83	11.747	Carbonic acid, isobutyl octadecyl ester
41	6.906	Cyclopentane, 2-isopropyl-1,3-dimethyl	84	12.479	Nonadecane
42	6.958	Undecane, 2,6-dimethyl-	85	12.497	Sulfurous acid, octadecyl 2-propyl ester
43	7.061	8-Oxabicyclo [5.1.0] octane	86	13.967	Methoxy acetic acid, heptadecyl ester

Table 8 Visual fluorescence of light Surakhani oil and its aromatic group components

Well no.	SLO and its separated components	Colors of luminescence
75,348	SLO	Light yellow
	1st group aromatics	–
	2nd group aromatics	–
	3rd group aromatics	Faint purple
	Tar	Pale yellow

Ultraviolet and luminescent analysis of SLO and its separated fractions

Ultraviolet spectroscopy is a low-cost technique used for studying petroleum products such as the aromatic content in petroleum fractions. As a qualitative analysis, the composition of SLO and its separated components was examined under the influence of UV rays (mercury lamp: PRK-4; filters: UBS-1, UBS-5). In this case, the composition of the oil was determined based on the color of the luminescence of the oil solution stain absorbed on a paper filter. Hexane was used as the solvent. The results of visual observations are shown in Table 8.

As it is known from the literature (Krylov and Mosyagin 2010; Jafarova 2004a, b), mono- and bicyclic aromatic hydrocarbons have colorless fluorescence. However, Table 8 shows that white–violet fluorescence is observed in the group 3rd aromatic hydrocarbons. This is caused by the presence of substituted naphthalene and small amounts of phenanthrene in that group of aromatic hydrocarbons.

Solutions of different concentrations of SLO and its separated aromatic group components were prepared, and their UV absorbance spectra were recorded and are shown in Fig. 5. As it is known, the characteristic UV absorbance peaks of aromatic compounds differ from each other according to their number of benzene rings and the structure of different alkyl-substituted derivatives. Therefore, it is possible to determine the core structure of the aromatic hydrocarbon compounds based on the spectra of the groups (Table 10). As can be seen from the UV spectra, SLO consists mainly of mono- and bicyclic aromatic hydrocarbons and their alkyl-substituted derivatives. Based on the UV spectra of the separated aromatic group components, the amount of aromatic hydrocarbons was calculated and is given in Table 9.

As can be seen from the UV spectra, the separated aromatic hydrocarbon groups are mainly composed of benzene (200 nm), naphthalene (226 nm) and a small amount of phenanthrene (250 nm) hydrocarbons and their alkyl derivatives (Fig. 5b–d). In the UV spectrum of the first and second groups of aromatic compounds, the absorption peaks of di- and trisubstituted radicals of aromatic hydrocarbons were recorded at 273 and 315 nm. Unlike the other two groups, 3rd group contains small amounts (approximately 0.05%) of phenanthrene and its alkyl derivatives in the 256 nm absorption band. Characteristic ultraviolet absorptions of alkyl-substituted aromatic compounds presented in the separated aromatic group components are given in Table 10.

The luminescence excitation and luminescence spectra of these compounds separated from SLO have also been studied in order to further clarify the type of alkyl-substituted aromatic hydrocarbons in the separated aromatic group components. The luminescence excitation spectrum of this oil covers a spectral range of 190–800 nm and consists of a large number of overlapping maxima. Two intense excitation maxima were recorded in the spectrum: $\lambda_{exc.max.} = 250$ and 302 nm. In the luminescence spectra recorded according to the excitation maxima for the substituted aromatic hydrocarbons, these areas were found to belong to the alkyl substituents of benzene (≤ 315 nm) and naphthalene (315–425 nm) hydrocarbons (Fig. 6). It is clear from the figure that the intense emission maximum in the luminescence spectrum is 359 nm.

The luminescence excitation and luminescence spectra of each of the aromatic group components separated from SLO were also plotted. Intense 342 nm luminescence peaks belonging to naphthalene and its methyl derivatives are recorded when the first group of aromatic components is excited by monochromatic light at a $\lambda_{exc.max} = 327$ nm maximum belonging to naphthalene hydrocarbons (Fig. 7a). In contrast to the 1st group aromatic components, a maximum of 314 nm of intense excitation and a maximum of 245 nm of weak excitation were observed in the 2nd group. The luminescence of these wavelength maximums at 356 nm indicates that this excitation belongs to naphthalene (Fig. 7b).

During the excitation of the 2nd group aromatic at 245, 314, 327 and 364 nm, it could be seen that it consists mainly of mono- and bicyclic arenes. When the substance is excited to the maximum corresponding to mono- ($\lambda_{exc.max.} = 245$ nm) and trisubstituted ($\lambda_{exc.max.} = 314$ nm) alkylbenzenes and naphthalene hydrocarbons, luminescence bands of intensive maxima are recorded.

Much like the 1st and 2nd aromatic group components, the 3rd group aromatic component consists of mono-, di- and trisubstituted alkylbenzenes and naphthalene hydrocarbons. However, the slight shift (190–460 nm) of the long wavelength boundary of the absorption spectrum toward the low-energy spectral field relative to the other components indicates the presence of alkyl substituents with weaker C–C and C–H bonds in this component. Along with it, luminescence at 511 and 563 nm wavelengths in the luminescence spectrum indicates the presence of small amounts of phenanthrene in this compound. According to studies in luminescence spectra, mono- ($\lambda_{exc.max.} = 240$ nm) and bicyclic ($\lambda_{exc.max.} = 250, 262, 297$ nm) aromatic hydrocarbons predominate in this component, which confirms the data
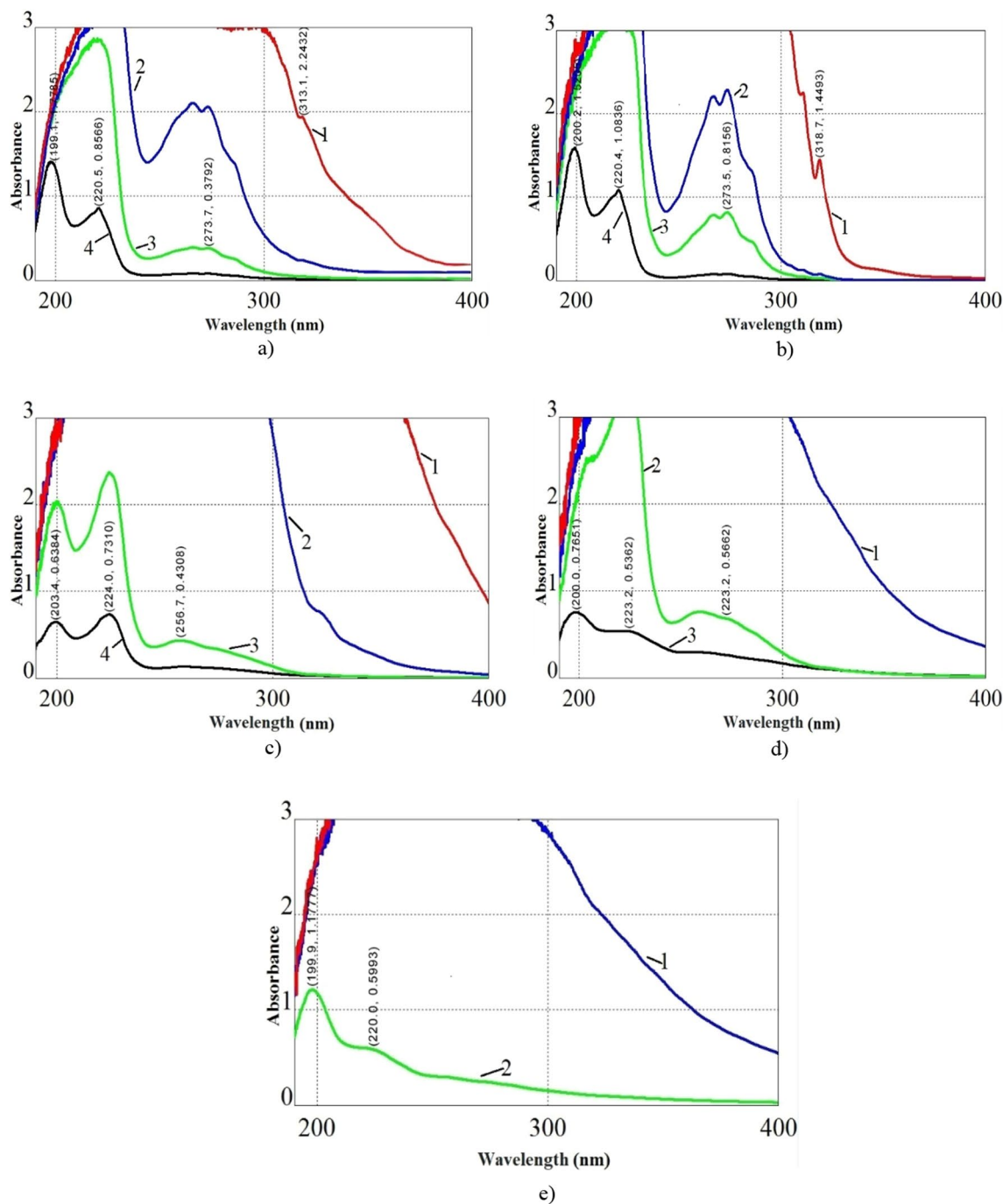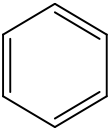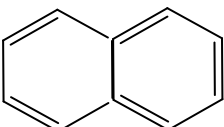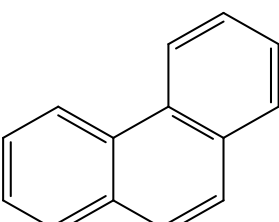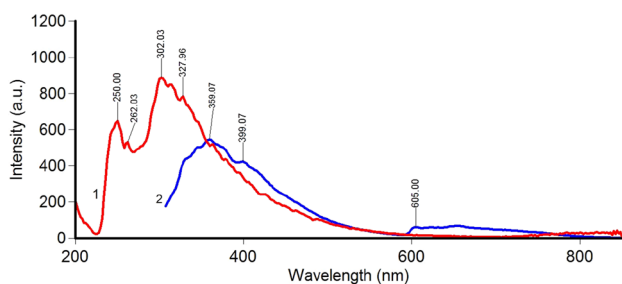
Fig. 5 Electron absorption spectra of SLO and its separated aromatic group components in different concentrations, %: **a** crude oil, 1–c = 0.75; 2–c = 0.21; 3 – c = 0.01; 4 –c = 0.006: **b** 1st group aromatics, 1–c = 0.83; 2–c = 0.29; 3–c = 0.02; 4–c = 0.001: **c** 2nd group aromatics, 1–c = 0.85; 2–c = 0.24; 3 – c = 0.01; 4–c = 0.001: **d** 3rd group aromatics, 1–c = 0.63; 2–c = 0.23; 3 –c = 0.01: **e** tar, 1–c = 0.41; 2–c = 0.02

Table 9 Amount of aromatic hydrocarbons in SLO and its separated components

Compound	SLO	1st group	2nd group	3rd group	Tar
monocyclic aromatic hydrocarbons, %	1.9	31.6	19.6	21.6	13.1
bicyclic aromatic hydrocarbons, %	1.6	19.5	25.7	28.8	8.2
Phenanthrene, %	0	0	0	0.05	0
Total, %	3.5	51.1	45.3	50.45	21.3

Table 10 Characteristic ultraviolet absorptions of di- and trialkyl-substituted aromatic compounds

Compound	The ring number	λ_{max}/nm
	1	199–206
	2	220–226
	3	250–260

Fig. 7 Spectra of luminescence (1) and luminescence excitation (2) of 1st (**a**) and 2nd (**b**) group aromatic components separated from SLO

Fig. 6 Photoluminescence spectrum of SLO (1—luminescence, 2—luminescence excitation)
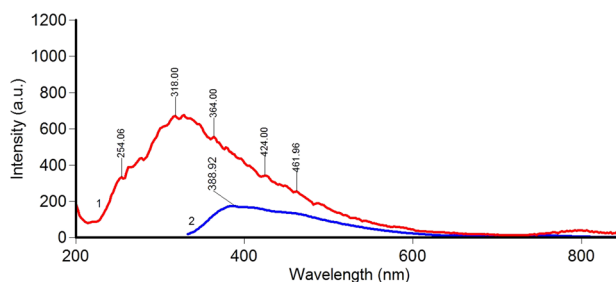
Fig. 8 Photoluminescence spectra of the tar component of SLO

obtained by UV spectroscopy. The absorption maximum of 262 nm gives a luminescence at 357 nm.

The UV spectrum of the tar component separated from SLO is located in the spectral range of 190–700 nm. Studies have shown that a shift in the spectral range of up to 700 nm suggests that the oil contains alkyl-substituted bi- and tricyclic alkylaromatic hydrocarbons. This result is also confirmed by gas chromatography–mass spectrometry (Table 7).

Due to the high viscosity of the tar (185.2 mm^2/s at 40 °C), the interaction of the intermolecular electronsis large. Therefore, the absorption bands of individual substances are not separated from each other, since the luminescence bands overlap. In the first spectral region, as the luminescence bands of the mixed substances present in the tar overlap, excitatory monochromatic light belonging to individual polycyclic aromatic hydrocarbons was used to study its composition as in other substances. It was found that the luminescence bands overlap when

$\lambda_{exc.max.} = 254$, 318, 364 and 424 nm. However, starting from $\lambda_{exc.max.} = 254$ nm, the long-wavelength boundary of the fluorescence spectrum shifts to the low-energy spectral field, and the intensity of luminescence decreases (Fig. 8).

In the UV spectra of tar, the shift of the long wavelength boundary toward the low-energy spectral field is mainly due to mono-, bi- and tricyclic alkylaromatic compounds with relatively weak C–C and C–H bonds. The presence of these compounds in the tar was confirmed by IR spectroscopy.

Summary and conclusions

In this study, unlike conventional fractionation procedures and geochemical methods, the group structure composition of Surakhani light oil was studied with the complex

application of spectroscopic analysis techniques and the following results were obtained:

1. The hydrocarbon composition of SLO consists mainly of paraffin–naphthene hydrocarbons and a small amount of aromatic hydrocarbons.
2. The composition of the paraffin–naphthene fraction separated from SLO includes optically active alkanes with a branched structure, mono- and bicyclic naphthene hydrocarbons substituted by alkyl radicals of various lengths, as well as tetracyclic naphthene hydrocarbons (steroids).
3. SLO aromatic component composition mainly consists of substituted mono- and bicyclic aromatic compounds.
4. According to the structural group parameters of fractionated SLO was determined that the share of H atoms in the aromatic core and alkyl chain is 4.4–20% and 79.9–95.6%, respectively.
5. The isoparaffin indexes of separated aromatic groups are high and make up 50–87%. A high isoparaffin index indicates that aromatic compounds contain a branched alkyl chain.
6. The composition of SLO mainly consists of substituted mono-, bi- and tetracyclic relict structured naphthene and isostructured alkanes

This method allows for a comprehensive investigation of complex systems consisting of various hydrocarbon mixtures and can help researchers find their relevant applications better.

Declarations

Conflict of interest The authors declare that there is no conflict of interest regarding the publication of this paper.

Ethical approval On behalf of all the co-authors, the corresponding author states that there are no ethical statements contained in the manuscripts.

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