

Oil From The Surakhany Field

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Annotation:

The results of a study of unique Surakhany oil, Azerbaijan, using modern instrumental analysis methods, such as GC/MS, ICP/MS, STA, UV spectroscopy, are presented. Hydrocarbon, biomarker (terpanes, steranes, hopanes and adamantanes) and microelement compositions were determined. It has been shown that the type of oil is methane-naphthenic, and steranes predominate among the biomarkers. A study of the microelement composition showed that the highest content of titanium and iron in Surakhany oil; as for noble metals, Au, Pt, Pd, Ru and Ag were found in the oil. Geochemical parameters were also calculated, such as: oddity index -CPI, isoprenoid coefficient-Ki, pristane to phytane ratio-Pr/Ph and Cannon-Cassau coefficients- Pr/n-C17 and Ph/n-C18. It is shown that the oil is mature, catagenetically transformed, with mixed sapropel-humus genesis. Dominance of St 27 and St 28, i.e. zoo- and phytoplankton, confirms mixed sedimentation in this area. An increased value of the ratio of diasteranes to regular steranes indicates the predominance of the clay component in the original source rock.

Keywords: *Surakhany oil, hydrocarbons, ME compositions, biomarkers, geochemical parameters*

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I. INTRODUCTION

Of great interest is the unique white oil of one of the oldest oil and gas fields in Absheron - the Surakhany field. The purpose of this work was geochemical studies of the properties of Surakhany oil using modern instrumental methods of analysis to determine its hydrocarbon, trace element and biomarker compositions, making it possible to reconstruct the conditions of formation and transformation of oil.

II. HISTORY AND GEOLOGY OF THE DEPOSIT

The Arabian scientist and traveler Abul-Hasan al-Masudi, who visited Baku in the 10th century, talks about the Surakhany oil springs in his notes. And as follows from al-Masudi's records, several types of oil were produced in Baku - white, yellow, black. The extracted oil was transported in leather bags on camels to Persia, India, Syria and other countries. At the end of the 17th century, the Ottoman traveler Evliya Celebi, who visited Baku, describes oil production in the following words: "The Baku fortress is surrounded by 500 wells in which white and black oil was extracted."

Development of the Surakhany field began in 1904, in 1911. in Surakhany, rotary drilling was used for the first time (I.S. Guliyev, M. Efendieva. All about oil). The field includes 2,503 wells and is located 16 km northeast of Baku. The bottom depth at the field varies within 70-75 m above the level of the Caspian Sea.

Today, in the village of Surakhany, unique wells have been preserved from which white oil was extracted. One of them in January 1904, from a depth of 209 meters, yielded 35 tons of this most valuable natural wealth. This year, production is expected to reach 1.18 million barrels.

The most complete description of the extraction of white oil was given by the outstanding Russian naturalist E.I. Eichwald in his work "Reise auf dem Caspischen Meere und Caucasus", who in 1825-1827 traveled through the Caucasus and studied the geology of these places.

A Russian scientist, mining engineer, geologist, one of the founders of Russian oil production on the Absheron Peninsula, N.I. Voskoboynikov began an in-depth study of white oil. He compiled a classification of local oil, and also gave a detailed description of each of the wells. In addition, he made a comparative analysis of the oil that was produced in Balakhany with the oil pumped out in the vicinity of Surakhany. Voskoboynikov, using knowledge in the field of chemistry, for the first time gave a scientific basis for the phenomenon called "white oil".

Surakhany white oil was low-resin, low-sulfur and low-paraffin. The oil here was absolutely white, the color of water.

An interesting fact is that different colors of oil can be observed even in the same field. In the Surakhany field, white oil, located at a depth of 200 m, is a transparent, almost colorless liquid; at a depth of 420 m, it is red oil, and even deeper its color changes from brown to black. The oil here was absolutely white, the color of water.

Today, white oil has received the status of a very valuable hydrocarbon raw material, which is widely used in the petrochemical and fuel industries. But there are very few such types of oil and the volume of its production is negligible. Deposits of such oil can be literally listed on one hand.

English geologist K. Craig found similar oil on Lake Trinidad in Venezuela and in the Kala Deribad tract in Southern Iran. Another well-known white oil field being developed in Russia is the Urengoy gas field, located in the Yamalo-Nenets Autonomous Okrug, slightly south of the Arctic Circle.

Surakhany white oil is truly unique; it is widely used in various fields, including medicine. Thus, it was used to treat diseases of the musculoskeletal system, neurological, skin and venereal diseases, cancer, etc. It was used as a healing agent when traditional medicine was powerless.

On the Absheron Peninsula, with the exception of some local uplifts, the entire PT section is oil and gas bearing, on almost 20 anticlinal structures. Further prospects for identifying new hydrocarbon deposits are associated with non-anticlinal type traps [1-2]. The most promising here may be only the lower PT formations (Nad-Kirmakinskaya sandy (NKP), Pod-Kirmakinskaya (PK), Kalinskaya (KaS)) associated with zones of pinching out of sandy horizons in submerged parts of synsedimentally growing anticlinal zones and individual local structures (Zyrinskaya, Galinskaya, Surakhaninskaya, Garachukhurskaya, etc.). This applies, first of all, to the bottom horizons of the PC and KaS of the lower part of the PT, which are characterized by inconstancy of development both in area and in section. Pinchout of the bottom KaS horizons in the eastern and central parts (areas: Gala, Tyurkan, Zyrya, Surakhany, Garachukhur, etc.). One of the main geological tasks at the Surakhany field in the KaS3 horizon is to trace the identified deposits in a southern direction, towards the Karachukhur area and its continuation in the north-western direction from the arch of the Kalinsky uplift.

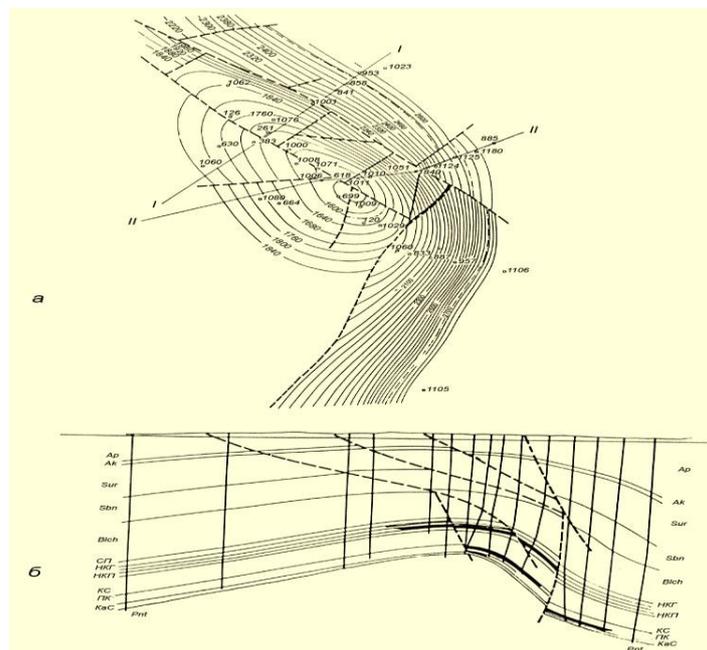


Figure 1 Surakhany field:

a) location of oil deposits in the lower section of the PT (structural diagram); b) placement of oil deposits in the lower section of the PT (profile)[6]

III.OBJECTS AND METHODS OF RESEARCH

As an object of study, oil samples were taken from the Surakhany field from wells No. 1248 and No. 72/19.

The fractional composition was determined, the studies were carried out using the STA (combined thermal analysis) method on a STA 6000 Perkin Elmer thermal analyzer in the temperature range of 20-1000 0C with a heating rate of 10 0/min. in an inert atmosphere.

The study of hydrocarbon (HC) and biomarker (BM) compositions of oil was carried out on Perkin-Elmer chromatography-mass spectrometers (GC/MS) on a system including a Clarus 680 chromatography-mass spectrometer, which has an interface with a highly efficient mass selective detector Clarus SQ8T. Hydrocarbon chromatograms were obtained from total ion current (TIC). The chromatograph is equipped with a quartz

capillary column 60 m long, 0.25 mm in diameter, impregnated with Rtx-1MS phase. Carrier gas - helium, flow rate 1 ml/min. Evaporator temperature 300 °C; programming the temperature rise from 80 to 290 °C at a rate of 2 °C/min, followed by an isotherm for 70 minutes. The ionizing voltage of the source is 70 eV, the source temperature is 250°C. Carbon sulfide CS₂ was used as a solvent.

The trace element composition of oil samples was carried out using a NexION 300 inductively coupled plasma (ICP) mass spectrometer. The detection limit for almost all elements of the periodic table was at the level of 9.1-10 ppm.

Ultraviolet spectra were obtained on a LAMBDA 35 Perkin Elmer UV spectrometer using quartz cuvettes with a 10 mm optical path length; all measurements were carried out at 220C at atmospheric pressure. Oil samples for optical studies were prepared by dissolving in hexane, chemically pure.

IV. RESULTS AND DISCUSSION

Heating of such a complex multicomponent system as oil leads to the evaporation of light gasoline-naphtha fractions first: naphtha - 180 (200) °C, then kerosene-gas oil 200-300 (320) °C and, finally, oil >300 °C. The methods of atmospheric or vacuum distillation of petroleum systems, used for qualitative and quantitative assessment of the properties of a given component, are based on the different volatility of components. The same principle underlies the STA method. The potential fractional composition of oil from the Surakhany field was studied using the STA method. The analysis data are presented in Table 1.

As you can see, the samples contain a small amount of resins and asphaltenes; it contains predominantly a highly volatile fraction - gasoline, naphtha, kerosene, gas oil (BLKG), as well as paraffins and oils (P+O).

Table 1
Fractional composition of oil from the Surakhany field according to STA

Oil Surakhany	start of boiling - 265°C (BLKG) %	265°C-438°C (P+O) %	438°C-528°C (resins) %	528°C-650°C (asphaltenes) %
Well 1248	50.32	43.89	1.76	3.26
Well 72/19	62.44	31.48	2.08	3.42

The hydrocarbon (HC) and biomarker (BM) compositions of Surakhany oil were studied using the GC/MS method; biomarkers were determined: tricyclic terpanes, steranes, hopanes and adamantoids.

Figure 2 shows a chromatogram of an oil sample, and calculations of hydrocarbon composition and geochemical parameters are summarized in Tables 2 and 3.

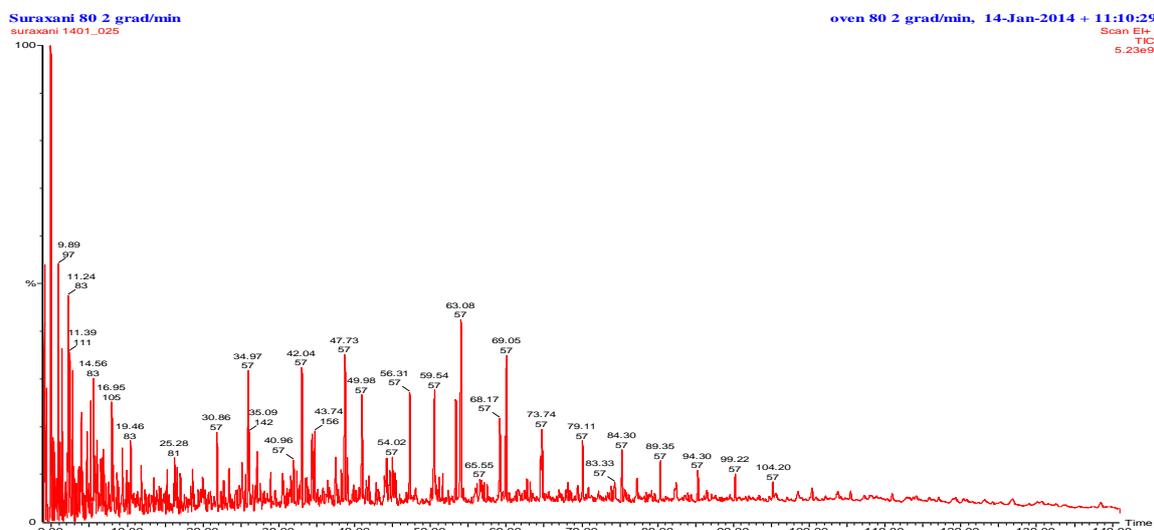


Figure 2. Chromatogram of Surakhany oil

Table 2
Hydrocarbon composition of Surakhany oil

Oil / compound	n-alk. %	iso-alk. %	Iso prenoid %		Σ alkanes	naphthenic					Σ naphthenes	arenas			Σ arenas
						mono	bi	three	tetra	penta		mono	bi	three	
Surakhany well 71/19	7.92	22.82	Pr	Ph	30.74	59.2	1.96	0.14	0.71	0.16	62.2	4.22	2.47	0.38	7.07
			1.82	1.28											

The content of normal alkanes is 7.92% rel., iso-alkanes – 22.82% rel. The number of iso-alkanes exceeds n-alkanes by almost 3 times.

The geochemical parameters of Surakhany oil were calculated and summarized in Table 3. The oddity coefficient (CPI) is – 0.88 and close to 1, which indicates significant catagenetic transformation. The isoprenoid coefficient (Ki) for Surakhany oil is 2.73. According to literature data, $Ki = 0.9 \div 1.3$ refers to mature oil. Pristane slightly predominates over phytane – 1.82 and 1.28% rel. respectively. The ratio $Pr/Ph = 1.42$ indicates the mixed sapropel-humus genesis of the oil. Using the Cannon-Kassau plot, you can evaluate the catagenetic transformation of OM and learn about the transformation of oil. Thus, $Pr/n-C_{17} = 2.84$, $Ph/n-C_{18} = 2.45$; Thus, OM can be divided into humus $Pr/n-C_{17} > Ph/n-C_{18}$ and sapropelic $Pr/n-C_{17} < Ph/n-C_{18}$. A decrease in the ratio of pristane $Pr/n-C_{17}$ and phytane $Ph/n-C_{18}$ according to this graph indicates an increase in OM catagenesis [3].

Table 3
Geochemical parameters of Surakhany oil

Geochemical parameters	Pr/Ph	Pr/n-C ₁₇	Ph/n-C ₁₈	Ki	CPI
	1.42	2.84	2.45	2,73	0,88

Next, biomarkers such as tricyclic terpanes, steranes, hopanes and adamantanes were determined.

Figures 3-8 show mass fragmentograms of tricyclic terpanes, steranes, hopanes and adamantoids with calculations of their content.

Tricyclic terpanes

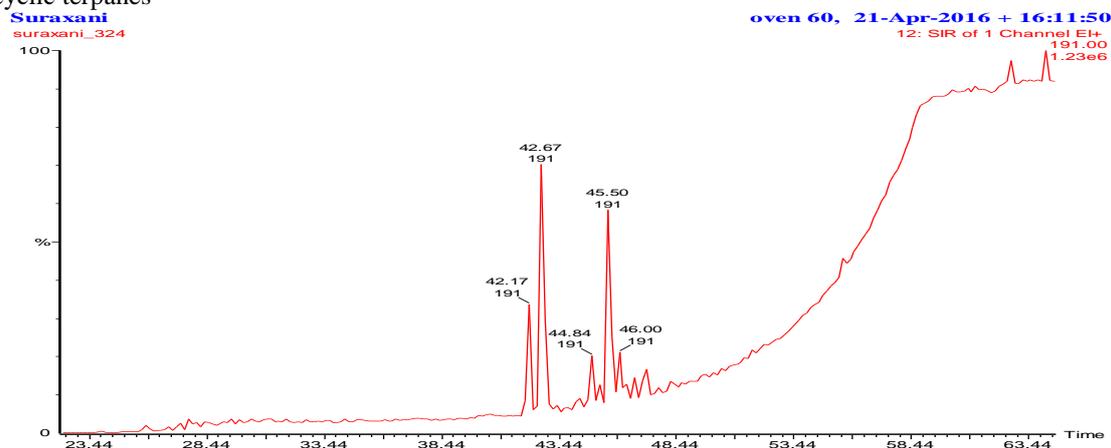


Figure 3. Mass fragmentogram of tricyclic terpanes in Surakhany oil

Table 4
Content of terpanes (m/z 191) in Surakhany oil

terpanes	T ₂₀	T ₂₁	T ₂₂	T ₂₃	T ₂₈	T ₂₉	T ₃₀	tri/penta
% relatively	43,07	0,49	7,7	41,56	1,83	2,64	2,71	1,27

The presence of tricyclic terpanes T₁₉₋₂₀ indicates terrigenous OM in the sedimentation basin, and the high content (43.07% rel.) characterizes the contribution of lower algae. The presence of T₂₃ (41.56% rel.) indicates marine or lacustrine sedimentation conditions (Table 4).

Figure 4 shows the mass fragmentogram of pentacyclic terpanes (hopanes) and the calculation of the content of hopanes (Table 5) in Surakhany oil.

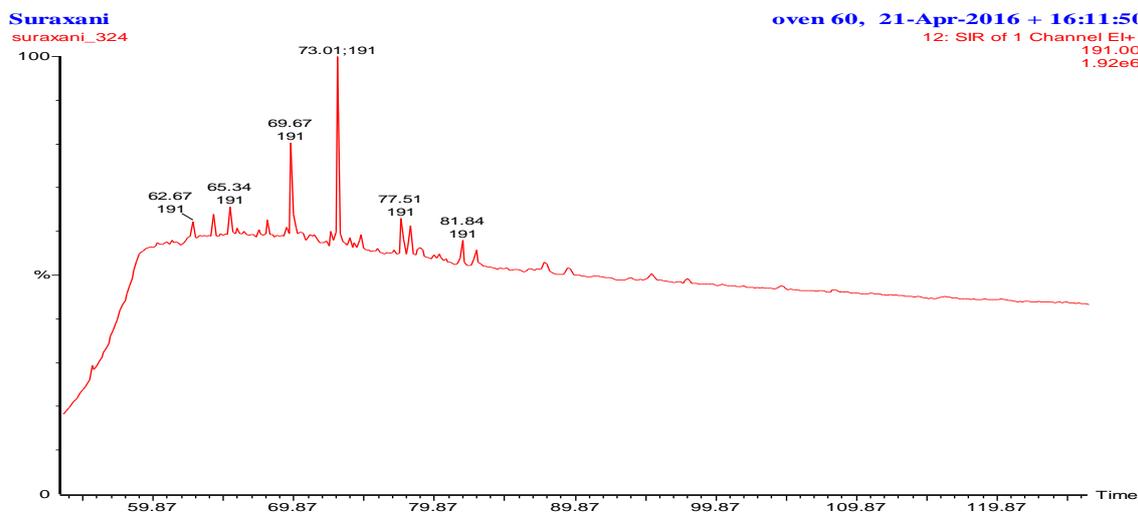


Figure 4. Mass fragmentogram of pentacyclic terpanes (hopanes)

Table 5

Content of hopanes (m/z 191) in Surakhany oil

hopanes	%, relatively
Ts	4,11
Tm	0,88
C29 nor-25- gopane	1,21
adiantan	17,48
moretan C ₂₉ S	3,45
oleanane	1,74
gopane H ₃₀	29,99
moretane C ₃₀	3,3
homohopan C ₃₁	12,85
gammacerane	3,03
moretane C ₃₁	2,03
bishomohopan C ₃₂ S	9,21
trishomohopan C ₃₃ S	4,5
tetrakishomohopan C ₃₄ S	3,7
pentakishomohopan C ₃₅ S	2,52
Ts/Tm	4,67
adiantan/H30	0,58
oleanan/H30	0,06
moretan C30/H30	0,11
C27 : C29 : C30 : C31 : C35	5 : 17 : 30 : 13 : 3

Figure 5 shows the mass fragmentogram of regular steranes, and Table 6 shows their calculations

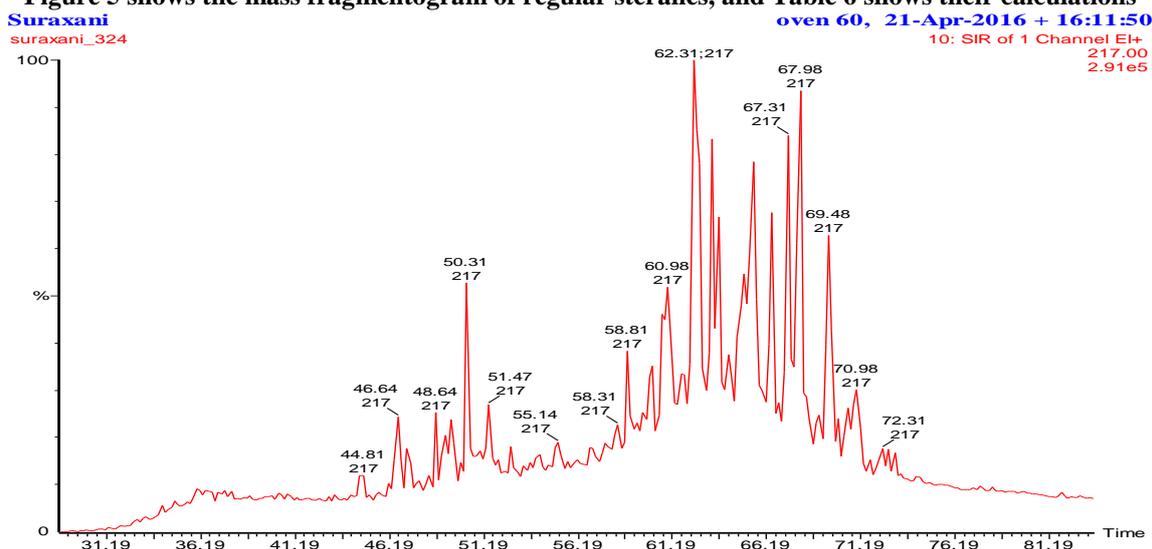


Figure 5. Mass fragmentogram of regular steranes in Surakhany oil

Table 6

Content of regular steranes (m/z 217) in Surakhany oil

Steranes	%, relatively
St ₂₁	0,85
St ₂₂	2,61
Cholane	3,99
dia St	13,72
St ₂₇	36,35
St ₂₈	34,54
St ₂₉	7,94
St ₂₁₋₂₂ /St ₂₇₋₂₉	0,04
dia St/St ₂₉	1,73
St 21 : St 22 : St27 : St 28 : St 29	1 : 3 : 36 : 35 : 8

For steranes, the dominance of St₂₇ and St₂₈ is observed, i.e. zoo- and phytoplankton, which confirms mixed sedimentation in this area. The increased value of steranes dia/reg up to 1.75 ÷ 1.73 indicates the predominance of the clay component in the initial NMP. The degree of transformation of most oils corresponds to the oil window (K = 0.5 Pr/n -C₁₇ - 2.84, Ph /n-C₁₈ - 2.45). For oil from the Surakhany field K = 0.73 ÷ 0.84.

Adamantoids

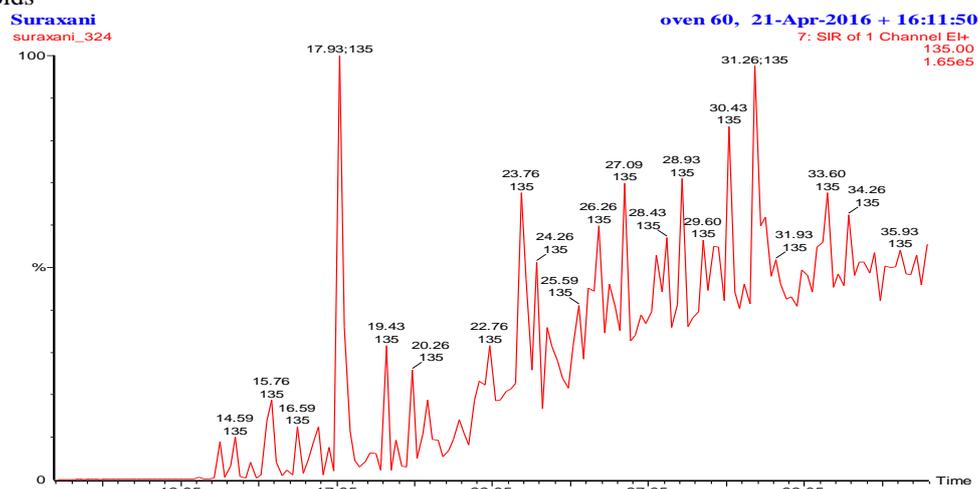


Figure 6. Mass - fragmentogram of alkyladamantanes (m/z 135)

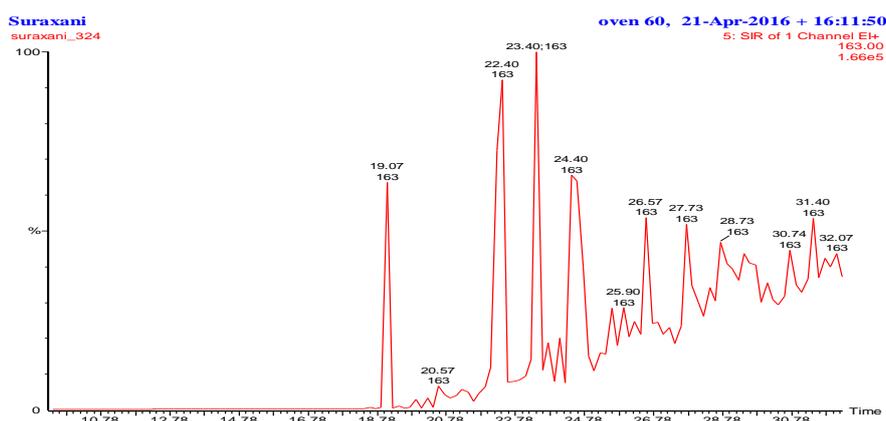
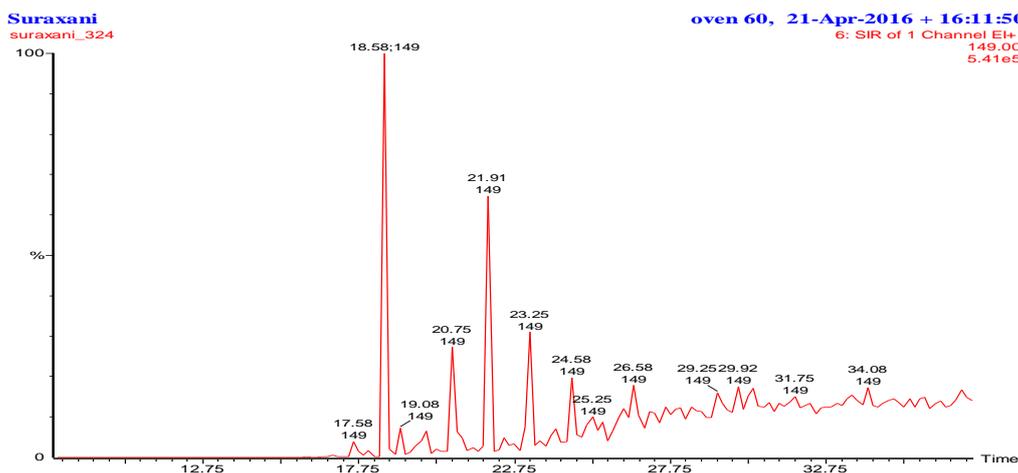


Table 7
Content of adamantanes (m/z 135, 149, 163) in Surakhany oil

Number of carbons in a component	Adamantanes	%, relatively
C ₁₁	1 MA	9.66
C ₁₁	2 MA	4.53
C ₁₂	1 EA	2.45
C ₁₂	2 EA	3.08
C ₁₂	1,3 di MA	22.57
C ₁₂	1,4 di MA	14.41
C ₁₂	1,2 di MA	7.55
C ₁₃	1,3,5 tri MA	4.32
C ₁₃	1,3,6 tri	9.96
C ₁₃	1,3,4 tri MA, cis	6.49

High values of the Adiantan/H₃₀ ratio indicate the presence of carbonate material in the NMP. Close to 1 – for rich carbonate-evaporite rocks. In our case, this value is 0.58 (the predominance of the clay component in the initial NMP). In the total adamantoids, C₁₂ predominates - dimethyladamantane (Fig. 6-8, Table 7). Table 8 shows the content of biomarkers of Surakhani oil. As can be seen, steranes predominate in the sample.

Table 8
Content of biomarkers in Surakhany oil

Oil/ Biomarkers	Triterpanes	Hopanes	Steranes	Adamantanes	Σ %, for oil
Surakhany	0,003	0,161	0,26	0,140	0,566

The content of aromatic hydrocarbons (benzene, naphthalene, phenanthrene) was determined from UV spectra (Fig. 9-10), calculated data are presented in Table 9.

Table 9

Sample	C 200 (benzole) %	C 230 (naphthalene) %	C 255 (phenanthrene) %	Σ arom. %	sample weight mg	Volume of solvent ml
Surakhany well 1248	0.354	2.560	0.762	3.677	1.21	25
Surakhany well 71/19	0.472	3.326	0.882	4.681	1.20	25

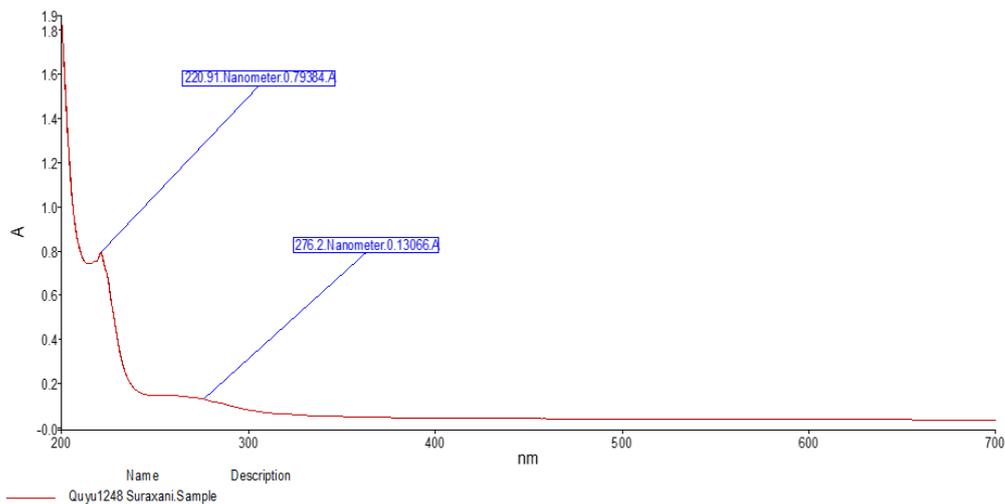


Figure 9. UV spectrum of an oil sample from well 1248

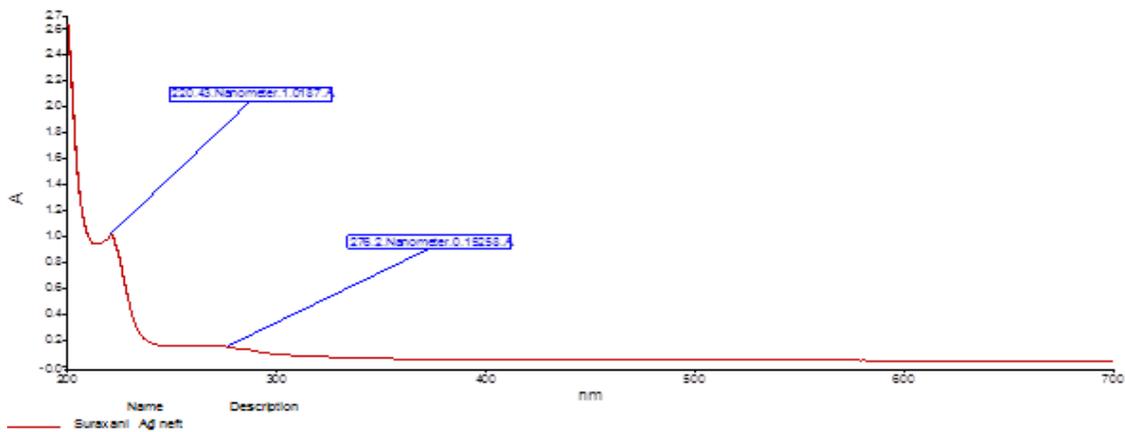


Figure 10. UV spectrum of an oil sample from well 72/19

The microelement composition of oil was determined using the ICP method [5]. A concentration series was compiled in descending order: Ti > Fe > Cr > Ni > As > Co > Sr > Mn > V > Pb, as well as for noble metals: Au > Pd > Pt > Ru > Ag. It has been shown that the highest content in Surakhany oil is titanium (Ti = 7.782-9.217 g/t), then iron (Fe = 2.186-2.307 g/t), as for noble metals, Surakhany oil contains Au, Pt, Pd and no Rh, Os, and Ru are present only in oil from well 1248 (Fig. 11-12).

Today, the unique wells of white oil fields are partially mothballed. The Surakhany oil field is a real geological miracle, a wonderful historical monument of the oil industry.

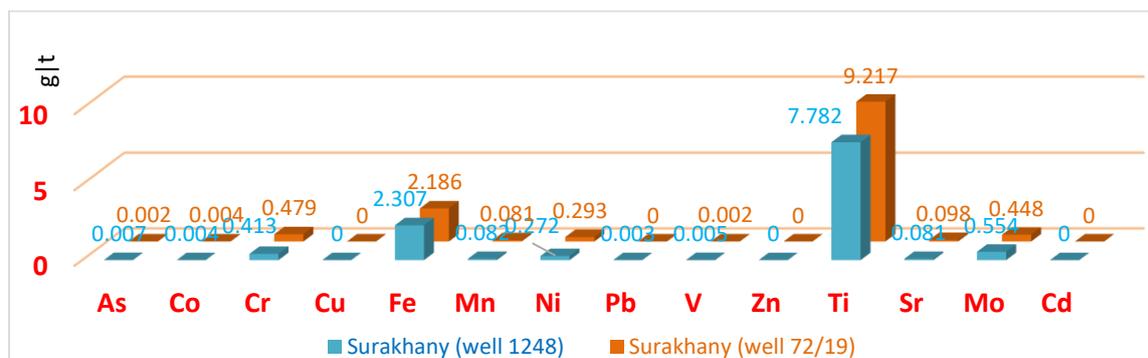


Figure 11. Histogram of ME composition of Surakhany oil

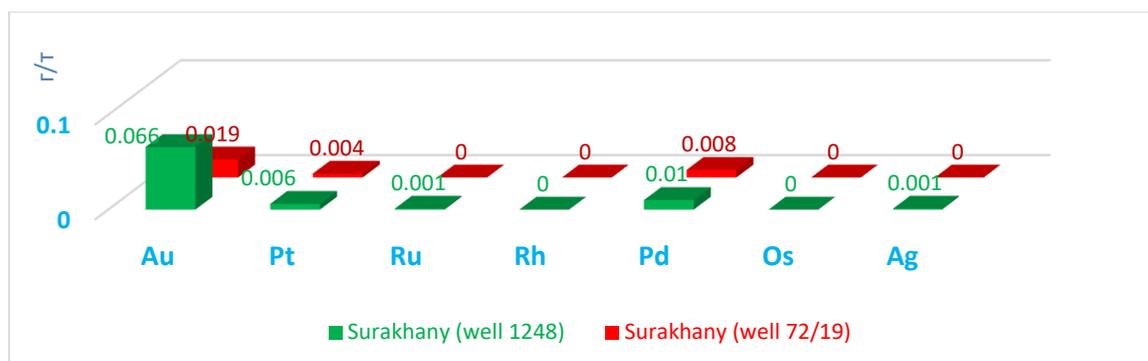


Figure 11. Histogram of ME composition (noble ME) of Surakhany oil

V. CONCLUSION

Studies of Surakhany oil using modern instrumental analysis methods have shown that the oil is low-resin, low-sulfur, low-paraffin; by type - methane-naphthenic. A biomarker passport of oil was obtained, terpanes, steranes, hopanes and adamantanes were identified. Calculations showed that steranes dominate among biomarkers.

Geochemical parameters such as CPI, Ki, Pr/Ph, Pr/n-C₁₇, Pr/n-C₁₈ were calculated. It is shown that the oil is mature, catagenetically transformed, with mixed sapropel-humus genesis. The presence of tricyclic terpanes T₁₉₋₂₀ indicates terrigenous OM in the sedimentation basin, and their high content characterizes the contribution of lower algae. The presence of T₂₃ indicates marine or lacustrine sedimentation conditions. Dominance of St₂₇ and St₂₈, i.e. zoo- and phytoplankton, confirms mixed sedimentation in this area. An increased value of the ratio of diasteranes to regular steranes indicates the predominance of the clay component in the original source rock.

The microelement composition of oil has been studied. It has been shown that the highest content of titanium and iron in Surakhany oil; as for noble metals, Surakhany oil contains Au, Pt, Pd, Ru and Ag.

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