CHEMISTRY

INVESTIGATION OF PETROLEUM FORM NEW WELLS OF EASTERN GEORGIA

[1]*Doctor* ***Natela Khetsuriani***
[2]*PhD* ***Esma Usharauli***
[3]*MS* ***Irina Mchedlishvili***
[4]*MS* ***Madlena Chkhaidze***
[5]*MS* ***Tamar Shatakishvili***

Georgia, Tbilisi, TSU, Petre Melikishvili Institute of Physical and Organic Chemistry, Laboratory of Petroleum Chemistry
[1]*Head of the Petroleum Chemistry laboratory, Chief Research Workers;*
[2]*senior research workers;*
[3]*scientific workers;*
[4]*scientific workers;*
[5]*scientific workers*

DOI: https://doi.org/10.31435/rsglobal_ws/31082019/6624

ARTICLE INFO

Received: 15 June 2019
Accepted: 12 August 2019
Published: 31 August 2019

KEYWORDS

Petroleum,
Tar,
Asphaltens,
nafta,
Diesel,
mikroelements

ABSTRACT

Investigation of new wells of Satskhenisi oil (#7, #11, #12, #13, #14) and Manavi oil (#11, #12) was carried out. By IR spectroscopy it was established that Satskhenisi oil belonged to naphtheno-aromatic type and Manavi oil – to paraffinic type of oils. According to distribution of trace elements V, Fe, Ni, Co, Mo, Cu, Pb, Sn, Zn, Sr, Ba, Ti and the ratio V/Ni <1, these oils refer to tertiary types of oils, which is explained by conditions of accumulation and geochemical transformation of the original organic compounds.
Using simulation chromatographic distillation of Manavi oil from the #12 well were obtained naphtha and diesel fractions. In naphtha by method of gas-liquid chromatography were identified individual paraffinic, naphthenic and aromatic hydrocarbons and in diesel fraction – individual n-paraffinic hydrocarbons.By low content of sulfur, tar-asphaltene compounds and high yield of light fractions, Satskhensi and Manavi crude oils are high-quality raw material for production of commercial oil products for energy purposes.

Citation: Natela Khetsuriani, Esma Usharauli, Irina Mchedlishvili, Madlena Chkhaidze, Tamar Shatakishvili. (2019) Investigation of Petroleum Form New Wells of Eastern Georgia. *World Science.* 8(48), Vol.1. doi: 10.31435/rsglobal_ws/31082019/6624

Introduction. The main energy source in the world's economy is petroleum products of which are used by all other branches of industry and which provides 1/3 of the world's energy demand. According to the data obtained in 2018, the world's reserves of petroleum amount to 7,471.5 billion barrels on land and 160 billion barrels on the seabed.

One of the main problems among the challenges facing humanity in the 21st century is to solve the issue of energy security. Countries that have sufficient oil and gas resources can ensure their energy security, develop their economy and strengthen their independence.

Georgia, in terms of its geological structure, belongs to two oil and gas bearing territories: the Black Sea region and the Caspian province. According to the calculations of foreign and Georgian specialists, the expected oil resources in Georgia make 2 billion 350 million tons, and of gas - 180 billion m^3. Even in case of development of 40-50% of this potential resource, the country's budget will receive a profit of several hundred billion dollars.

It was established that according to the physical and chemical parameters Georgian oils belong to unique, low-sulfur, high-quality oils and from the point of view of processing they are quite an interesting raw material. Studies of these oils have shown that in Georgia there are almost all known types of oils that differ from each other by their chemical nature (paraffinic, naphthenic, naphtheno-aromatic, aromatic, etc.). Through the study of oils and their physical, chemical and geochemical parameters using uniform integrated methods, it is possible to plan the production of commercial oil products for energy purposes of local industry and agriculture, which is of great importance for the determination of the country's energy resources and their rational management [1-5].

The goal of the work was investigation of new wells of petroleum from Satskhenisi and Manavi oilfields for their certification. Satskhenisi oilfield is located at the eastern part of Gare-Kakheti oil region in the north wing of Norio-Khashmi anticlinal at a distance of 30 km to the north-east from Tbilisi. Satskhenisi anticlinal is composed of Maikop and Miocene sedimentary structures [6] and Manavi oilfield is located to the south from the Kakheti Range at a distance of 60 km from Tbilisi, to the north-south of the dome of the Ninotsminda oil-bearing anticline with corresponding sedimentary structures consisting of oil-containing Upper Cretaceous paleogenic sediments.

In connection with the rehabilitation of Satskhenisi oil production and for the purpose of certification of Georgian oils five new wells (№№ 7, 11, 12, 13, 14) of Satskhenisi oil with depth of occurrence 1040-1400m have been studied [7, 8]. Physical and chemical characteristics and the possibility of obtaining commercial oil products were investigated. Physical and chemical characteristics of the investigated oils are shown in Table 1.

Table 1. Physical and Chemical Characteristics of Satskhenisi Petroleum

Parameter	Satskhenisi crude oil				
	Well #7	Well #11	Well #12	Well #13	Well #14
Density at 20^0C, kg/m^3	760,5	808,2	787,1	812,2	804,2
Density at 15^0C, kg/m^3	764,5	812,0	791,0	816,0	808,0
Molecular weight, ^{0}API	53,59	42,76	47,38	41,9	43,62
Kinematic viscosity 20^0C, cSt	0,9232	2,27	1,25	2,41	1,68
Ash content, %	0,0011	0,0021	0,0013	0,0034	0,0020
Asphaltenes, %	0,024	0,08	0,038	0,075	0,007
Resins, %	0,8	1,8	1,2	2,2	1,8
Paraffines, %	0,045	1,05	0,5	1,1	1,03
Sulfur, %	0,1	0,1	0,1	0,1	0,1
Mechanical impurities, %	0,004	0,19	0,071	0,07	0,21
Acidity, mg KOH per 1g of oil	0,65	1,3	0,78	1,5	1,2
Acid number	0,032	0,059	0,035	0,068	0,05
Pour point, ^{0}C	>-30	>-30	>-30	>-30	>-30
V/Ni ratio	<1	<1	<1	<1	<1
Yield of light fractions, %					
Under200^0C	61,0	54,0	63,0	54,0	54,0
Under 320^0C	90,0	84,0	86,0	84,0	85,0

The results showed that all these crude oils are characterized by low density (765.0–816.0 kg/m^3 at 15°C), viscosity (0.92 - 2.48 cSt), small amount of paraffins (0.04–1.1%), sulfur (0.1%), and tar and asphaltenes (0.24-2.27%) [9]. Distillation curves of crude oils of all five wells showed that they are characterized by high content of light fractions boiling below 320 °C with a yield of 80-92%.

Temperature-distillation chart shows that similarly to previously produced crude oils new wells of Satskhenisi oilfields are characterized by high content of light fractions. Temperature-distillation chart of oils from the new wells with initial boiling point below 320 C is shown in Figure 1.

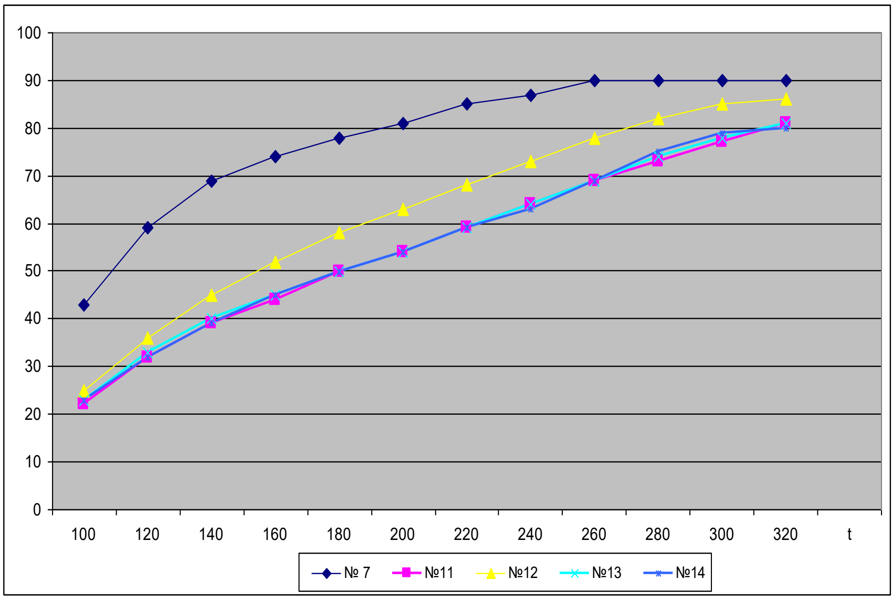

Fig. 1. Temperature-distillation chart of oils from new wells of Satskhenisi Petroleum

At present, general accepted approach for carrying out comprehensive studies of composition of oils is a method of infrared spectrometry. The structural and group composition of crude oils and their components is determined by intensity of characteristic absorption bands in IR spectra using common baseline with fixed points at 1850 and 650 cm^{-1}. Content of methylene groups (CH_2) in average molecule is assessed by absorption band at 720 cm^{-1}, content of methyl groups (CH_3) – by the absorption band at 1380 cm^{-1}, of sulfoxide groups (SO) by the absorption band at 1030 cm^{-1} and of carbonyl group (CO) in the region of 1720-1700 cm^{-1} with respect to C = C aromatic bonds by absorption band at 1600 cm^{-1}.

We have studied the results of infrared spectrometric analysis of crude oils from new wells, which was performed on a Perkin Elmer Spectrum spectrometer (model 10.4.2). The infrared spectra of all studied oils are presented in Figure 2.

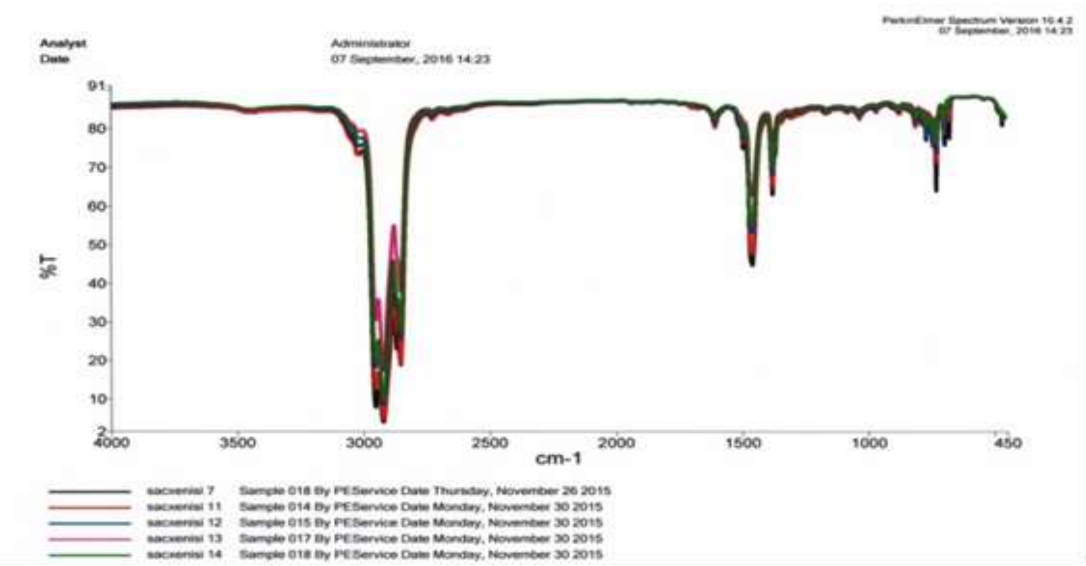

Fig. 2. The IR spectra of all studied crude oils

IR spectra of all wells (№7, №11, №12, № 13, №14) of Satskhenisi oilfield are virtually identical. On spectra of fractions bands corresponding to alkanes (728 cm^{-1}), naphthenes (1030 cm^{-1}) and arenes(1500 cm^{-1}) can be clearly distinguished. This result, along with physical and chemical characteristics of the investigated oils, suggests that oils of new wells of Satskhenisi oilfield have similar chemical composition and belongs to the naphthene-aromatic type of oils.

Due to the high yield of light fractions of the Satskhenisi oil, the light commercial oil products — naphtha, kerosene and diesel fuels — were isolated and investigated. The study of the above mentioned commodity oil products showed that they meet the requirements of the relevant standards.

Oil production in wells #11 and #12 is carried out by the company Canargo Energy Corporation. Reserves of wells make 130 million barrels of oil and 59 billion cubic pounds of 2C gas (NSA). Perforation interval is 4680–4953 m. Physical and chemical characteristics of the crude oil from the Manavi oilfield are shown in Table 2.

Table 2. Physical and Chemical Characteristics of Manavi Petroleum

Parameter	*Manavi Crude Oil*		*Methods*
	Well #11	Wel#12	
Density at 20^{0}C, kg/m^3	826,0	822,5	ASTM D052
Density at 15^{0}C, kg/m^3	829,6	826,5	ASTM D4052
Molecular weight, ^{0}API	39.6	40,0	ASTM D1298
Kinematic viscosity 20^{0}C, cSt	3,4	3,15	ASTM D 445
Ash content, %	0,0141	0,0098	GOST ISO 6245
Asphaltenes, %	1,86	2,7	ASTM D 3279
Tar, %	7,07	8,12	ASTM D 2007
Paraffines, %	6,5	6,2	ASTM UOP46
Sulfur, %	0,18	0,17	ASTM D 4294
Mechanical impurities, %	0,02	0,01	ASTM D 473
Acidity, mg KOH per 1g of oil	0,23	0,20	ASTM D 664
V/Ni ratio	<1	<1	-
Yield of light fractions, %			
Under 200^{0}C	30,0	32,0	ASTM D 2892
Under 360^{0}C	65,0	67,4	ASTM D 2892

The oil under study is characterized by medium density, high yield of light fractions (68%) and low content of sulfur and tar-asphaltenic compounds (8.92%), paraffin content is 6.1%. Simulation of complete distillation of crude oil was performed on a Sim Dis chromatograph, Auto System XL, manufactured by Perkin Elmer, according to ASTM D 2887 standard [10]. The crude oil under study is characterized by a high content of light fraction; the residue above 500°C is 12.5%. The distillation curve for Manavi oil is shown in figure 3.

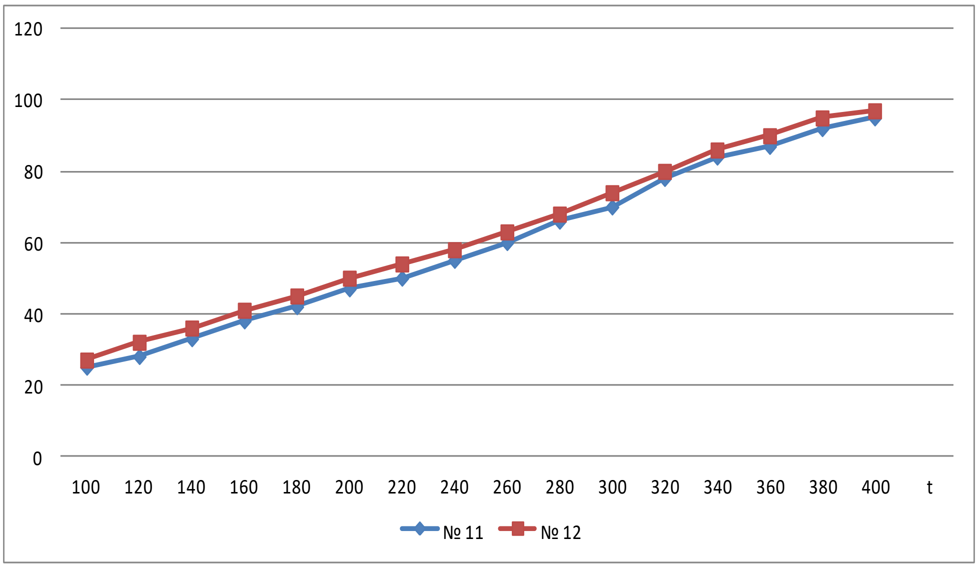

Fig. 3. Distillation curves for Manavi oil, wells #11 and #12

An infrared spectrometric analysis of oils from new wells, carried out on a Perkin Elmer Spectrum spectrometer, model 10.4.2., showed that the IR spectra of the wells are almost identical. The intensity of the absorption bands of 721.4 cm-1 and 1377 cm-1 characterizes the content of methyl and methylene groups in paraffin hydrocarbons. The presence on the spectrum of the band 1600cm-1 characterizes the content of aromatic hydrocarbon. It has been determined that crude oils of the new wells of the Manavi oilfield have the same chemical composition and refer to the paraffin type of Petroleum.

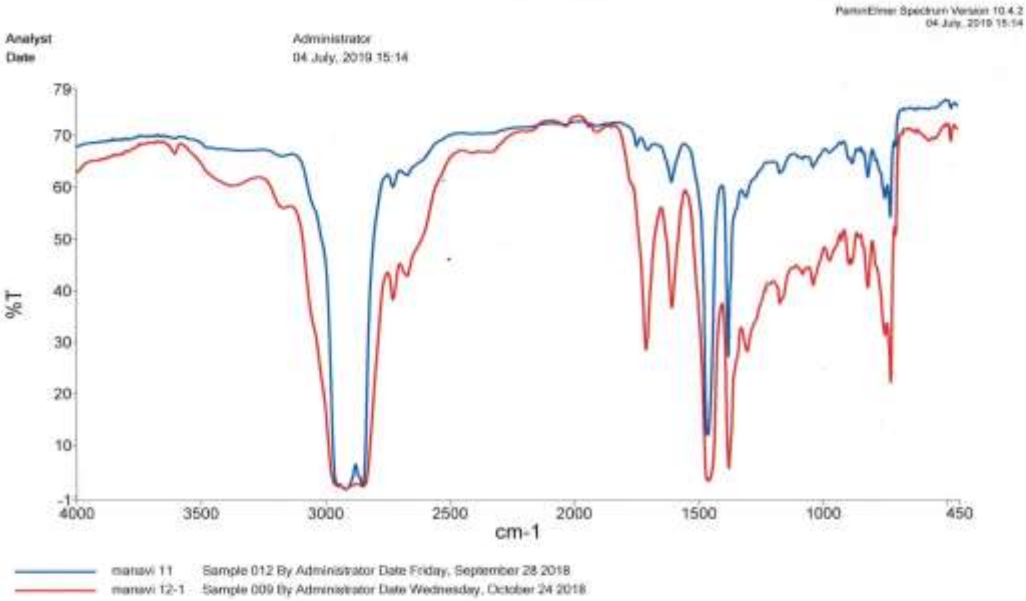

Fig. 4. IR spectra of Manavi Crude Oil

From the results of the study, it turned out that due to the low content of sulfur, tar-asphaltenic compounds and high yield of light fractions, the Manavi oil was high-quality paraffinic oil.

The naphtha fraction isolated from the Manavi crude oil (35–180°C) was studied by the gas chromatography method "PON A" [11]. The elemental and group hydrocarbon composition, molecular weight, relative density, saturated vapor pressure and octane number were determined (Table 3). Individual paraffinic, naphthenic and aromatic hydrocarbons and their derivatives were also identified.

Table 3. Characteristics of the naphtha fraction Manavi Petroleum

The name of indicators		Magnitude			
Density at 20^0C, kg/m^3		736.0			
Molecular weight		101.998			
Vapor pressure, psi		1.7			
Octane number		73.51			
Diatillation, ^0C	s.b.	10%	50%	90%	b.e.
	31	70	110	156	200
Conect - C		86.118			
Conect - N		13.882			
Group composition					
Group		Quput,%mass		Vield,%vol.	
Paraffin		24.027		25.972	
n-paraffin		27.53		29.344	
Olefins		-		-	
Maphthenes		32.531		30.932	
Aromatics		15.751		13.362	
Unknown		0.459		0.399	
Amount		100.0		100.0	
Under 200^0C		30.0		32.0	
Under 320^0C		65.0		67.4	

The physical-chemical indices of diesel fractions with different boiling points are shown in table 5. The study showed that the refractive index, density and kinematic viscosity increase with an increase in the boiling point of the diesel fraction. Fractions are characterized by a high diesel index and cetane number (table 4).

Table 4. Physical and Chemical characteristics of diesel fractions Manavi Petroleum

Fraction, ^{0}C	Output, %	Density at 20^{0}C, kg/m^{3}	n_D^{20}	Kinematic viscosity 20^{0}C, cSt	*Diesel index*	*Cetane number*
			Manavi Petroleum, Well #11			
140-320	42.1	814.2	1.4528	2.61	64.4	57,0
140-350	47.0	820.8	1.4560	3.2	63.3	55,0
180-320	33.0	816.7	1.4542	3.0	63.6	56.0
180-350	37.0	834.3	1.4650	4.5	64.7	50,6
			Manavi Petroleum, Well #12			
140-320	42.0	819.2	1.4580	2.8	64.7	58.0
140-350	49.0	822.3	1.4640	3.3	63.5	55.60
180-320	34.1	817.0	1.4633	3.2	63.8	56.4
180-350	40.0	835.0	1.4682	4.6	61.6	51.8

In the carbamide concentrate of the diesel fraction 180–320ºC, the distribution of n-paraffin hydrocarbons was studied by a gas-liquid chromatography (Table 5). In this table are shown the identified n-paraffin hydrocarbons C_9–C_{26}, with a maximum content of tetradecane ($C_{14}H_{30}$).

Table 5. Paraffin hydrocarbons

Hydrocarbon names	Molecular weight, g/mol	***Relative concentration***	
		Manavi #11	Manavi #12
Nonane	164.40	0.14	1.33
Decane	142.29	2.34	3.80
Undecane	156.31	5.86	7.60
Dodecane	170.34	8.61	8.33
Tridecane	180.40	10,87	9.00
Tetradecane	199,39	12,40	10.77
Pentadecane	221.42	10.37	9.88
Hexadecane	232.41	8.77	7.26
Heptadecane	240.48	7.80	7.05
Octadecane	254..5	6.61	6.73
Nonadecane	268.52	5.70	4.87
Eicosane	282.55	4.78	4.24
Heneicosane	296.58	4.21	4.76
Docosane	310.60	3.98	4.33
Tricosane	324.38	3.88	3.70
Tetracosane	338.65	2.65	2.73
Pentacosane	352.69	1.20	1.70
Hexacosane	366.72	0.79	1.36

The distribution of trace elements V, Fe, Ni, Co, Mo, Cu, Pb, Sn, Zn, Sr, Ba, Ti in Satskhenisi and Manavi oils was also studied. Trace elements were isolated using the developed in the laboratory of petroleum chemistry photochemical method of extracting the concentrate of ash elements from petroleum and petroleum products, which has found wide application in other scientific research organizations. Consequently, on the basis of the study it was concluded that distribution of V, Fe, Ni, Co, Mo, Cu, Pb, Sn, Zn, Sr, Ba, Ti microelements and the ratio V/Ni <1 indicate that these oils are of tertiary type, which can be explained by conditions of accumulation of initial organic substance and by relevant geochemical origin [12].

The results of the study. The oils of the new wells of the Satskhenisi and Manavi oilfields, located quite close to each other in the region of the Kakheti Range were studied. Physical, chemical and geochemical parameters, as well as functional groups by IR spectrometry, were determined. It has been established that Satskhensi oil refers to naphthene-aromatic, and Manavi oil to paraffin types of oils.

According to the distribution of trace elements V, Fe, Ni, Co, Mo, Cu, Pb, Sn, Zn, Sr, Ba, Ti and the ratio V/Ni <1, these oils refer to tertiary types of oils, which is explained by the conditions of accumulation of the original organic matter and corresponding geochemical origin.

By low content of sulfur, tar-asphaltene compounds and high yield of light fractions, Satskhensi and Manavi crude oils are high-quality raw material for production of commercial oil products for energy purposes – gasolines, high-quality organic solvents, aviation and diesel fuels and various petroleum oils for local industry and agriculture.

REFERENCES

1. Chemistry of oil and gas. A.I Bogomolov, A.A. Gaile and others. Publishing house Khimia, 1995, 448p. ISBN: 5-7245-1023-5. (in Russian)
2. Modern methods for investigation of crude oils. Leningrad, "Nedra, 1984, 430p.
3. N.Khetsuriani, E.Usharauli, E.Topuria, I.MchedliShvili. Use of mass-spectrometry for investigation of aromatic structure of high-boiling compounds of oil. IX International massspectrometry conferece in Petrochemistry, ecology and food Chemistry "Petromass2011". Moscow, 2011, pp.128-131. ISBN 978-5-4253-0285-4.
4. James G. Speight. Handbook of Petroleum Analysis. First published: February 2015, 368 pages. ISB 978-1118369265. DOI: 10.1002/9781118986370.
5. V.G.Tsitsishvili, N.T.Khetsuriani. Georgian Crude Oil and Bitumen Deposits. Proceedings of the International Mass Spectrometry Conference on Petrochemistry and Environmental "PETROMASS 2014", 2014, 1-4 September, Tbilisi, Georgia, pp.13-14. ISBN 978-9941-22-378-5.
6. http://www.gogc.ge/ge/oil-production
7. E.P. Gventsadze, P.P. Busel. To the investigation of Georgian oil deposits. Proceedings of the Georgian National Academy of Sciences, Chemical Series, 1978, v. 4, #1, h. 66-75.
8. Ketsuriani N.T., Usharauli E.A., Goderdzishvili Q.G., Topuria E.N., Chkhaidze M.N. Investigation of new Wells of Satskhenisi Grude Oil. Proceedings of the Georgian National Academy of Sciences, Chemical Series. 2016, v.42, #4, p.501-503. ISSN-0132-6074.
9. N. Khetsuriani, E. Usharauli, K. Goderdzishvili, K. Ebralidze, I. Mchedlishvili. Mass Spectrometric Study of Tar-Asphaltenic Compounds of Georgian Oils. World Science (Multidisciplinary Scientific Edition), Warsaw, Poland, 2018, # 5(33), vol. 3, pp. 19–25. p-ISSN - 2518-167X; e-ISSN - 2518-1688.
10. ASTM D2887. Standard Test for Boiling Range Distribution of Petroleum Fraction by Gas-Chromatography.https://www.astm.org/DATABASE.CART/HISTORICAL/D2887-2.htm.
11. ASTM D 3710 Standard Test Method for Boiling Range Distribution of Gasoline and Gasoline Fractions by Gas-Chromatography. https://www.astm.org/Standards/D3710.htm
12. L.D. Melikadze, Q.G. Goderdzishvili, G.I. Zulfigarli. To the investigation of trace elements in Georgian oils. Tbilisi, "Mecniereba", 1976, 98p.