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CRYSTALLINE AND HETEROCYCLYC AROMATIC COMPOUNDS IN GEORGIAN PETROLEUM

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ABSTRACT

The individual composition of polycyclic aromatic hydrocarbons has been studied in high boiling (340–590°) fractions of Norio oil (wells 200, 201) which are characterized by high content of aromatic hydrocarbons and high intensity fluorescence. The eluates obtained by adsorption fractionation of aromatic hydrocarbons separated by aniline and concentrates of their crystalline components have been studied by GC, MS and GC-MS methods. For analysis of the obtained data an automated system of mass deconvolution and identification (AMDIS) was used. In the eluates under investigation the following structures were identified: indenes, tetralines, dinaphtilbenzenes, naphthalenes, fluorenes, phenantrenes, antracenes, mono- and polyalkyl derivatives of naphtofluorene and phenantrene, and terpeniles. In crystal samples of the eluates the banzantracene, chrizene, their methyl-, dimethyl and trymethyl-analoges, phenantrene derivatives, antracenes and pyrenes were identified. The heterocyclic analogues of polycyclic aromatic hydrocarbons like methylbenzoanthracenes, benzonaphthothiophenes, benzocarbazoles and dibenzthiophene were identified in Georgian oils for the first time.

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Introduction. Georgian petroleum deposits are known since the ancient times. There are more than 1500 manifestations of oil and gas fields. According to quantitative estimates of oil and gas resources (2002) it is determined that geological resources of petroleum in Georgia make up to 2 billion 350 million tons, including 400 million tons on the Black Sea shelf. Anticipated resources of gas are estimated up to 180 billion m^3 only on land. As a result 1 gas (5.3 trillion cubic meters) and 16 petroleum fields were discovered.

Systematic research of Georgian petroleum began in the 50's of the last century at the Petre Melikishvili Institute of Physical and Organic Chemistry under the guidance of the academician Leonide Melikadze and continues to this very day. It is established that there are all known types of petroleum in Georgia. Because of low content of sulfur and tar-asphaltenic compounds Georgian petroleum is the best raw material for technological processing.

The territory of Georgia simultaneously includes two regions containing oil and gas: the Black Sea water basin and the Caspian province. In Figure 1 is shown a map of the currently operating wells of the licensed blocks of Georgia.

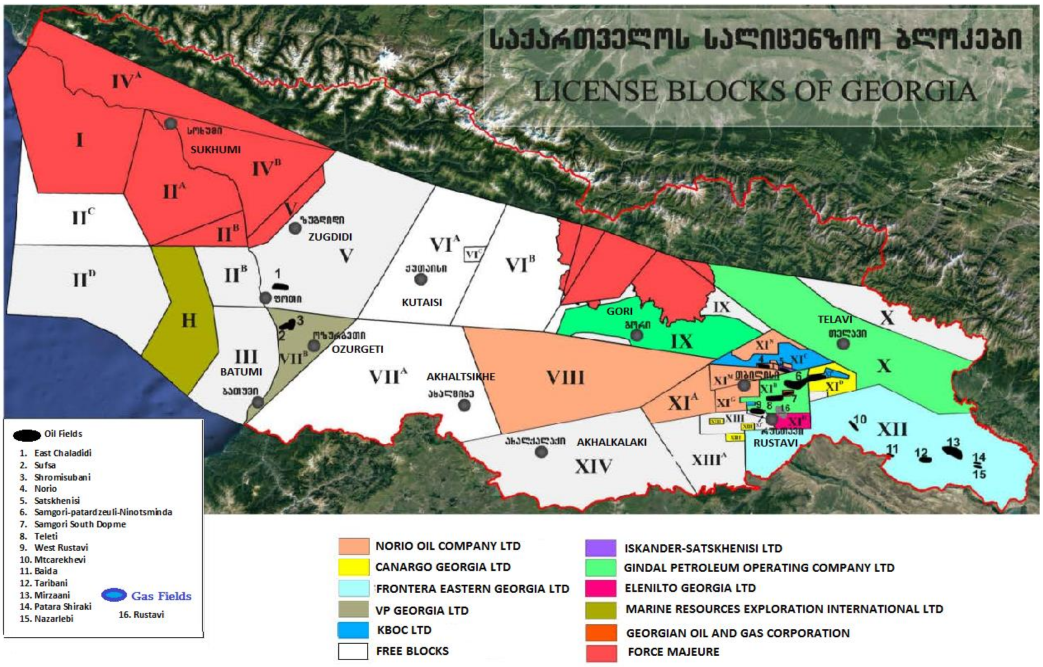

Fig.1.

Purpose of the study. The main goal of the present work was investigation of petroleum from Norio deposit with the high boiling fractions rich in aromatic hydrocarbons and characterized by high intensity luminescence. The sphere of our interest was study and identification of individual composition of aromatic compounds in crude oils by modern research methods.

The Norio deposit located to the North-East of Tbilisi at a distance of 30-35 km from it and is associated with sedimentary rocks of the Middle Miocene, the lower and middle Sarmatian layers. Depth of oil and gas horizons makes 1200 m. Relatively deep-seated horizons have not been studied and are considered to be the prospective object for petroleum and gas exploration [1].

Research methods. The research was carried out using modern instrumental methods of analysis: gas-liquid chromatography (GC) on highly effective capillary columns, mass-spectroscopy (MS) and chromato-mass-spectrometry (GC/MS) using AMDS identification system.

Experimental part. Samples of Norio petroleum from wells #200 and #201 were selected for analysis. The physical and chemical and geochemical characteristics as well as the group hydrocarbon composition of Norio petroleum wells with different depths of occurrence were studied. Their physical and chemical characteristics are presented in Table 1. It has been established that this petroleum is characterized by a low content of sulfur, paraffin hydrocarbons and asphaltenes. Petroleum of the Norio deposit belongs to the naphtheno-aromatic type. The vacuum distillation fraction 340-590^{0}C.was selected as a study object.

For separation of aromatic hydrocarbons was developed a complex method consisting of atmospheric and vacuum distillation of the crude oil, selective extraction of aromatics by aniline and by liquid-adsorption chromatography on aluminum oxide. 1000 concentrates of aromatic hydrocarbon were obtained: petroleum ether eluates and benzene extracts. By their crystallization and recrystallization 90 white and yellow crystalline compounds were obtained from petroleum for the first time. These compounds had intense luminescence from blue to yellow-green in the visible part of the spectrum. As a result of crystallization-recrystallization of some eluates the extraction of non-fluorescent nitrogen-containing red crystals were also obtained. The crystalline and orderly structures were confirmed by X-ray structural analysis. Structural-group composition of these components was studied by IR-, UV- and mass- spectrometric methods [2]. It was established that the crystalline compounds of Norio petroleum were hybrid aromatic hydrocarbons with complex structure composed of naphthenic and alkylated naphthalenes, phenanthrenes, chrizens, 3,4-benzphenantrenes, benzfluorenes and pyrenes [3].

Table 1. Physical and chemical characteristics of Norio petroleum

Characteristics	Well #200	Well #201	Determination method
Perforation depth, m	1200	840	-
Density at 20^{0}C, kg/m^3	843,8	816.3	ASTM D 1298
Density at15^{0}C, kg/m^3	847,4	820.0	ASTM D 1298
Specific gravity, ^{0}API	35,4	41.55	GOST R 51069
Kinematic viscosity, 20^{0}C, cSt	6,09	1,89	ASTM D 445
Dynamic viscosity, MPa.s	5,14	1,5	ASTM D 445
Pour point, ^{0}C	> -65	> -72	ASTM D 97
Ash content, %	0,009	0,0075	ASTM D 5630
V/Ni ratio	< 1	< 1	ASTM D5708
Acidity, mg KOH/100 cm^3 of fuel	3,9	2,34	ASTM D664
Acid number	1,5	0,97	ASTM D664
Content, %			
Asphaltenes	0,33	0,328	GOST 11858
Tars	2,2	0,95	GOST 11858
Mechanical impurities	0,11	-	ASTM D 473
Water	0,03	0,03	ASTM D4377
Paraffins	0,34	0,28	GOST 11851
Sulfur	0,15	0,18	ASTM D1266
Distillation, % < 200°C < 350°C	 34 73	 46 76	ASTM D 86

The individual composition of the petroleum eluate and crystalline compounds of the high-boiling fractions of Norio petroleum (well200) have been studied by chromatographic, mass-spectral, and chromatomass-spectral methods. Gas-chromatographic (GC) separation of the samples of concentrates was carried out of capillary columns (15 m and 30 m) by dimethyl-polysiloxane in programmed temperature conditions. The corresponding chromatogramme is given on Fig. 2 [4]. GC-MS experiment was performed in the magnetic field of the device under standard conditions, data analysis was performed using an automated MS deconvolution and identification system (AMDIS).

Research results. Based on the analysis of electron ionization fragmentation and GC retention indices, the following polycyclic aromatic structures in the study eluates were identified: mono- and polyalkyl derivatives of indenes, tetralines, dinaphthylbenzenes, naphthalenes, acenaphthylenes, fluorenes, phenanthrenes, anthracenes, naphthofluorenes and phenanthrenes, as well as terphenyls.

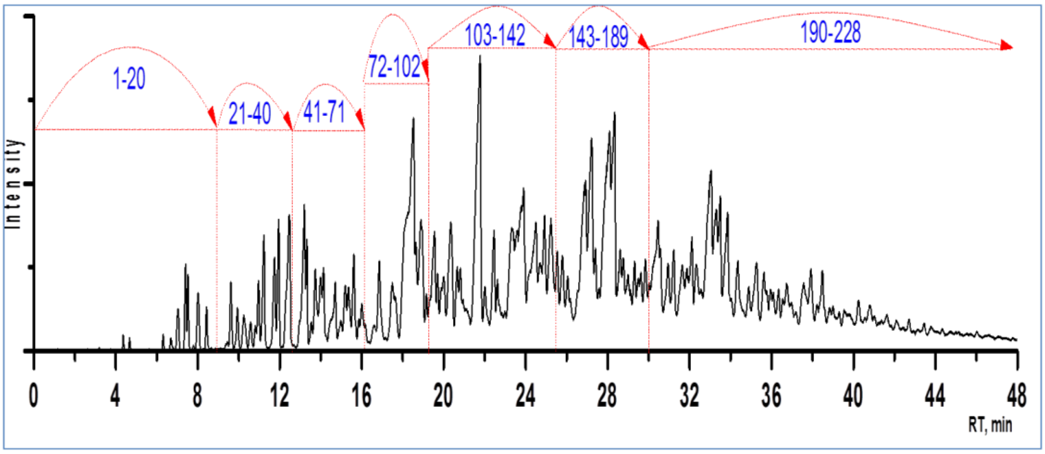

Fig. 2. GC of a petroleum ether eluate concentrate

In crystalline components separated from the eluate the following compounds were identified: benzanthracenes, chrysenes, their methyl-, dimethyl- and trimethyl-analogues, phenanthrene derivatives, anthracenes and pyrenes (fig. 3).

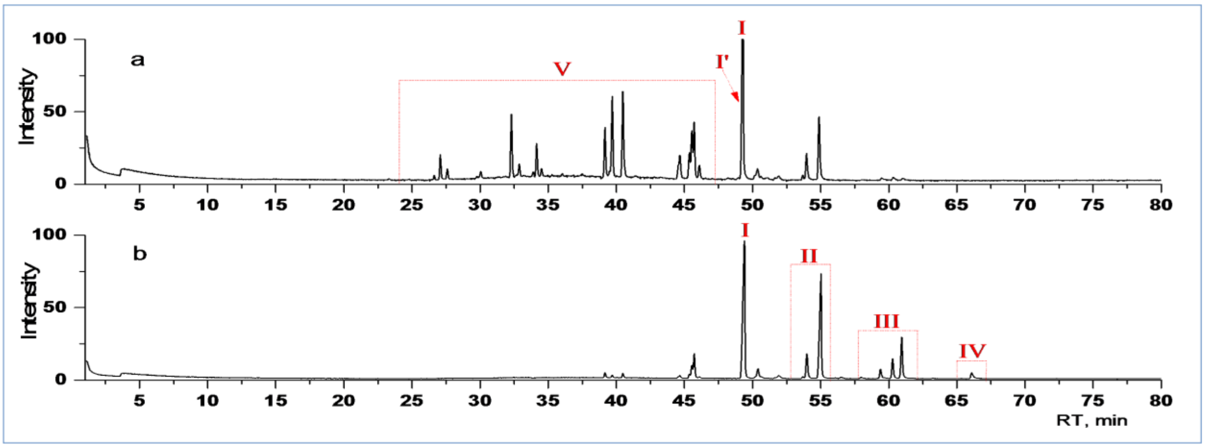

Fig. 3. GC of crystallization (a) and recrystallization (b) products obtained from petroleum ether eluate. Major components: I, I' - benz[a]anthracene and chrysene, their II - methyl-, III - dimethyl- and IV - trimethyl-derivatives, V – substituted phenanthrenes, anthracenes, pyrenes

The components identified in crystal concentrates and their mass-spectra are presented on Fig. 4, (a, b and c).

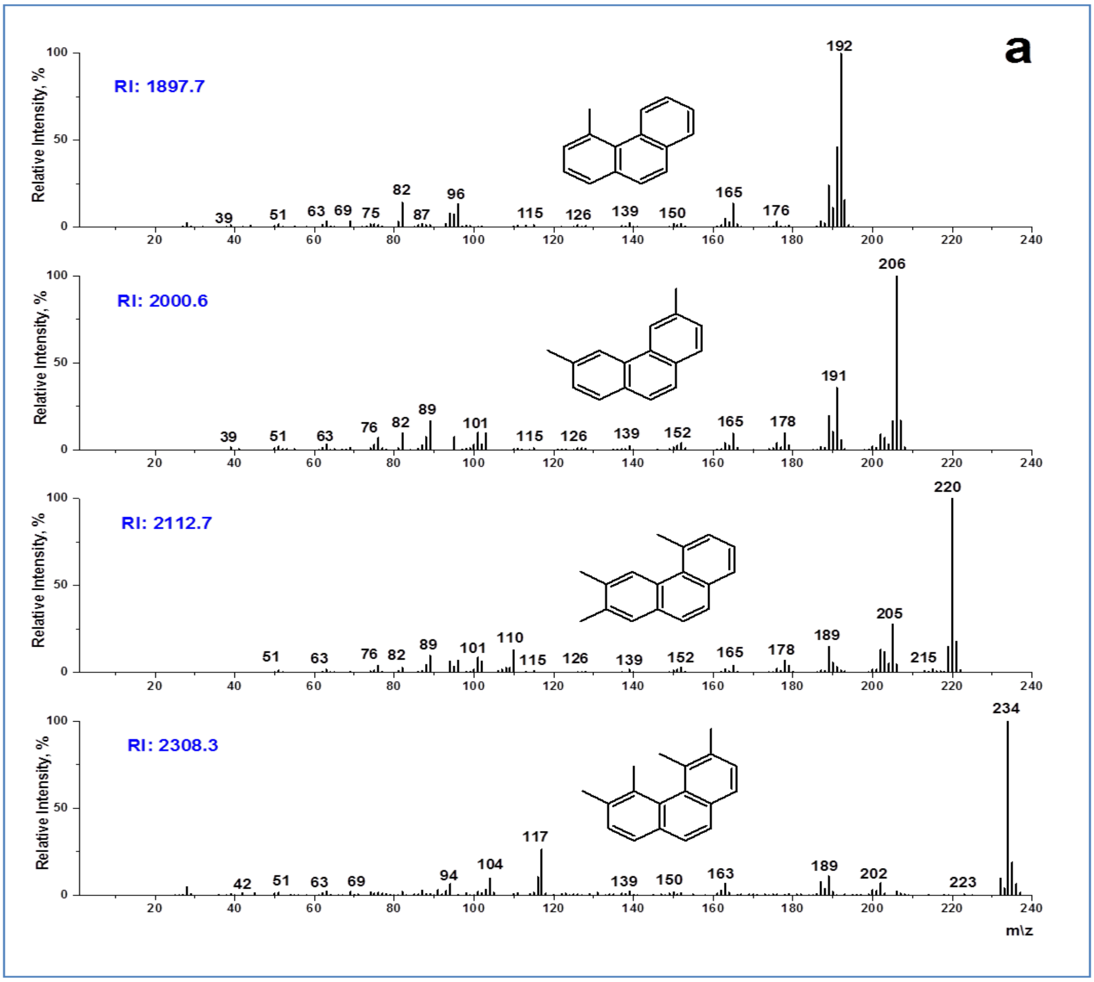

Fig. 4. a. Mass spectra of (a) 4-methyl-, 3,6-dimethyl-, 2,3,5-trimethyl- and 3,4,5,6-tetramethylphenanthrenes

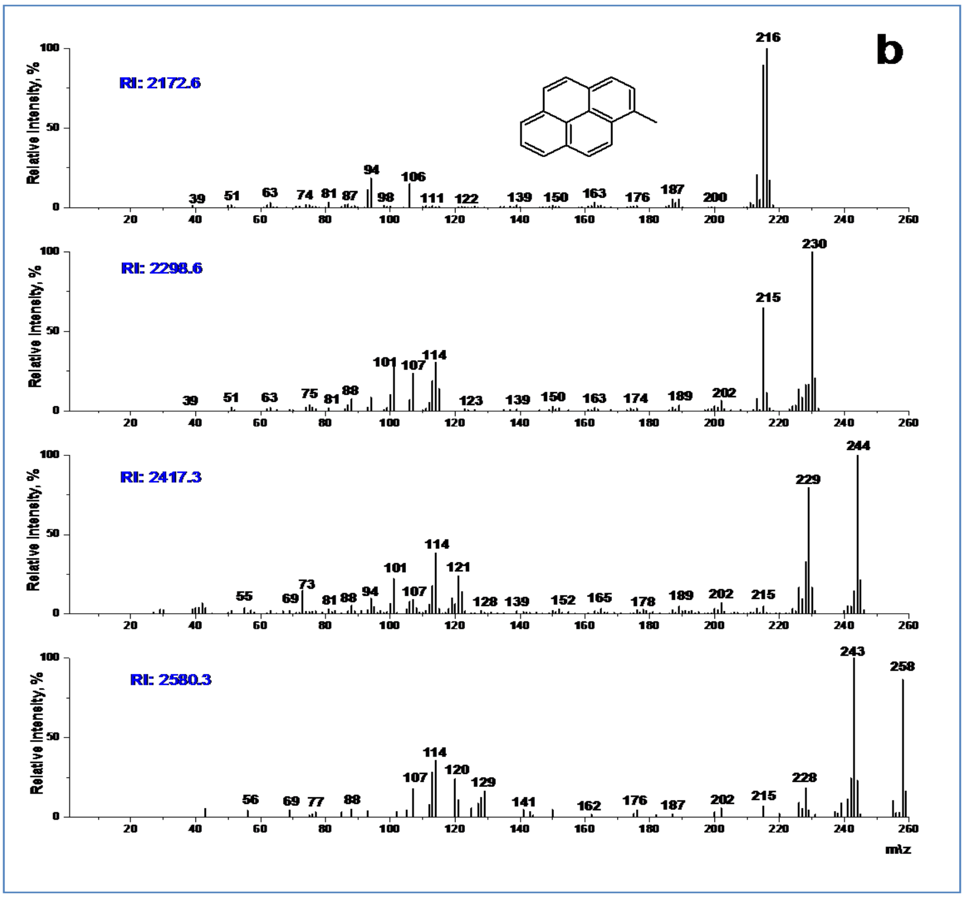

Fig. 4. b. Mass spectra of 1-Methylpyrene and its Dimethyl-, Trimethyl- and Tetramethyl-analogs

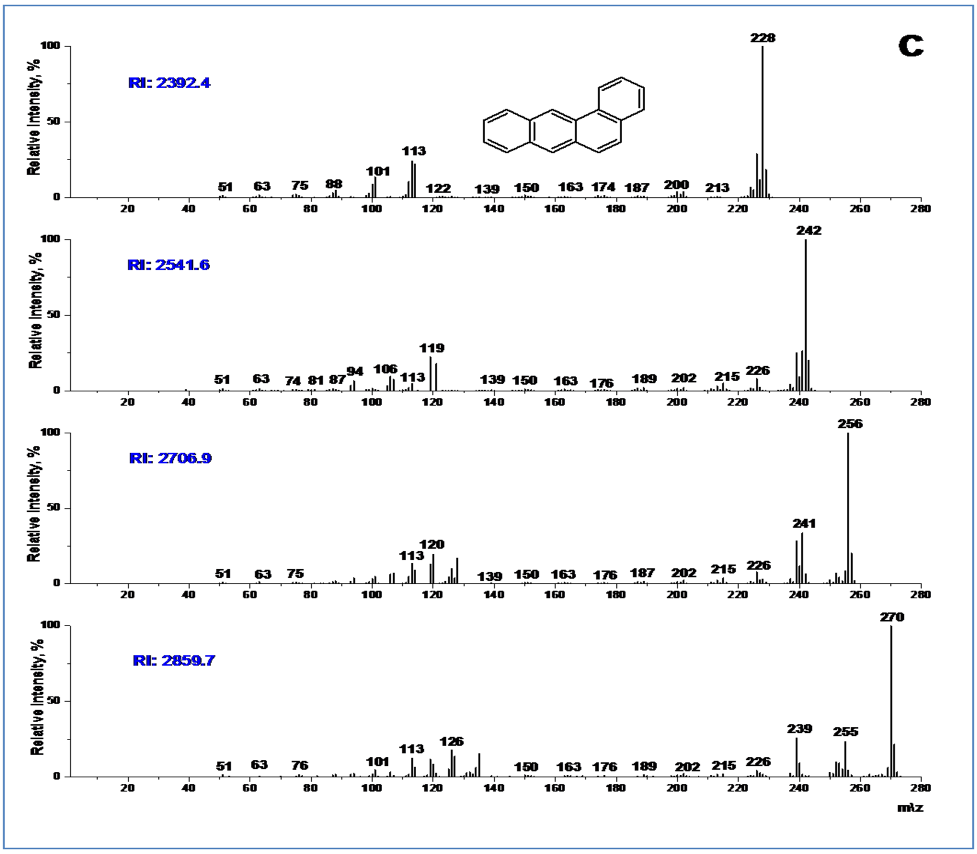

Fig. 4. c. Mass spectra of Benz[a]anthracene and its methyl-, dimethyl- and trimethyl-analogs

On the basis of the TIC (Total Ionic Chromatogram) of the crystalline samples for the first time in Georgian crude oils were identified the sulfur and nitrogen heteroanalogues of high-molecular polycyclic aromatic hydrocarbons: benzonaphthothiophenes in the “benzanthracene” fraction, benzocarbazole and dibenzthiophenes in the “phenanthrene” fraction [5].

It was found that isolated crystalline substances are native components of petroleum and not the products formed during its processing. It was on the basis of the fluorescent components of Norio petroleum that the technological process for production of luminophore “Noriol” was further developed and has found wide practical application for luminescent defectoscopy of critical machine parts and metal constructions.

Conclusions.

- In the eluate under investigation the following structures were identified: indenes, tetralines, dinaphtilbenzenes, naphthalenes, fluorenes, phenantrenes, antracenes, mono- and polyalkyl derivatives of naphtofluorene and phenantrene, and terpeniles.
- The crystalline components are complex hybrid structures containing nuclei of naphthenes and alkylated aromatic hydrocarbons: banzantracene, chrizene, their methyl-, dimethyl and trymethyl-analoges, phenentrene derivatives, antracenes and pyrenes.
- The heterocyclic analogues of polycyclic aromatic hydrocarbons like methylbenzoanthracenes, benzonaphthothiophenes, benzocarbazoles and dibenzthiophene were identified in Georgian oils for the first time.

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