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Organic Chemistry

High Molecular Heterocyclic Aromatic Compounds in Georgian Petroleum

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Polycyclic aromatic compounds that are components of crude oils and make a lot of ecological problems are the subject of the study using various separation and mass spectrometry methods. Crystalline and heterocyclic aromatic compounds present in high-boiling petroleum fractions are of particular interest. Polycyclic aromatic hydrocarbons isolated from vacuum gas oil fractions of Georgian petroleum of various types (paraffinic, aromatic and tarry) had been studied by gas-liquid chromatography (GC), mass-spectrometry (MS) and chromato-mass-spectrometry (GC-MS) methods. Fractional vacuum distillation, selective dissolution in aniline, adsorption chromatography and crystallization/recrystallization of aromatic eluates were used to isolate polycyclic aromatic hydrocarbons. By their crystallization and recrystallization a large number of crystalline substances of two types: fluorescent (white and yellow) in the visible region of the spectrum from Norio and Samgori petroleum and red non-fluorescent nitrogen-containing substances were obtained. Among the crystalline components were identified the following hydrocarbons: benzanthracene, chrysene, their methyl-, dimethyl- and trimethyl-analogues, phenanthrene derivatives, anthracenes and pyrenes. Among the red crystalline samples of Norio petroleum were identified the sulfur and nitrogen heteroanalogues of high-molecular polycyclic aromatic hydrocarbons: benzonaphthothiophenes in the "benzanthracene" fraction, carbazole and its methyl-, dimethyl-, trimethyl-homologues, benzocarbazole and its mono-, dimethyl-homologues and dibenzothiophenes in the "phenanthrene" fraction. It was established that the non-fluorescent red nitrogen-containing crystalline components, as well as the fluorescent ones, are natural genetic components of petroleum. *© 2023 Bull. Georg. Natl. Acad. Sci.*

petroleum, polycyclic and heterocyclic aromatic hydrocarbons, MS, GC/MS

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 petroleum 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 one 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 tarasphaltenic compounds Georgian petroleum is the best raw material for technological processing [1]. The territory of Georgia simultaneously includes two regions containing oil and gas: the Black Sea basin and the Caspian province.

Experimental

Various chemical types of petroleum were chosen as objects of study: Samgori (paraffinic), Norio (aromatic) and Supsa (tarry). The physical, chemical and geochemical characteristics as well as the group hydrocarbon composition of petroleum under investigation were studied. Their physical and chemical characteristics are presented in Table. It has been established that this petroleum is characterized by low content of sulfur, paraffin hydrocarbons and asphaltenes [2].

The vacuum distillation fraction (160-270°C of 0,5-1,0 mm Hg) was separated from the petroleum under investigation. 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 hydrocarbons were obtained: petroleum ether eluates and benzene extracts. By their crystallization and recrystallization 17 of white and yellow crystalline compounds were obtained from Norio and Samgori petroleum for the first time. These compounds had intense luminescence from blue to yellow-green in the visible part of the spectrum [3]. As a result of crystallization-recrystallization of some eluates the extraction of non-fluorescent nitrogen-containing red crystals were also obtained. They were isolated from all studied oil samples in the amount of approximately 7% from aromatic hydrocarbons. Among Georgian petroleum, the largest amount of red crystals was isolated from the high-boiling 300-500°C and 500-525°C fractions

Table. Physical and chemical characteristics of Georgian Petroleum

Characteristics	Petroleum field		
	Norio	Samgori	Supsa
Depth of bedding, m	1050-1400	1516-2830	2362 - 3350
Density at 20°C, kg/m^3	900.0	837.3	943.0
Viscosity at 20°C, sSt	19.0	4.69	22.0
Cloud Point, °C	-45.0	3.0	15.0
Flash Point, °C	15.0	-10.0	40.0
Content in mass %			
Sulfur	0.23	0.17	0.42
Silica gel tars	8.58	7.0	14.4
Asphaltenes	1.22	0.95	4.19
Paraffin	0.82	6.8	3.1
Cocking ability, %	3.93	1.0	10.7
Ash content, %	0.011	0.018	0.043
Structural-group composition of hydrocarbons, %			
Aromatic	33.56	23.34	30.52
Naphthenic	42.02	23.93	53.36
Paraffinic	24.42	52.73	16.12

of the Supsa (tarry) petroleum. It is not possible to isolate fluorescent crystalline substances from Supsa petroleum [4-7].

The individual composition of the petroleum eluate and crystalline compounds of the high-boiling fractions of petroleum have been studied by chromatographic, mass-spectral, and chromate-mass-spectral methods. Gas-chromatographic (GC) separation of the samples of concentrates was carried out on highly effective capillary columns (15 m and 30 m) by dimethyl-polysiloxane in programmed temperature conditions. 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) [8].

Results and Discussion

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. These structures are presented in Fig. 1.

Crystallization of chromatographic eluates was carried out by cooling their petroleum ethers at 0°C. 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. It was established that the crystalline compounds of Norio petroleum were hybrid aromatic hydrocarbons with complex structure composed of naphthenic and alkylated naphthalenes, phenanthrenes, chrysenes, 3,4-benzophenanthrenes, benzofluorenes and pyrenes.

From crystalline components were identified the following hydrocarbons: benz[a]anthracene, chrysene, phenanthrene, anthracene, pyrene and their methyl-, dimethyl-, and trimethyl-derivatives. These hydrocarbons are presented in Fig. 2.

It has been established that the nitrogen content in non-luminescent red crystalline components is 10%. The crystals are insoluble in water, but in organic solvents they give strongly colored red solutions. Nitrogen content was confirmed by X-ray diffraction and elemental analysis.

Red crystals are not thermally stable. Their number was significantly higher in the 300–500°C fractions. It was found that aniline and Al_2O_3 do not affect the formation of crystals. It was also found

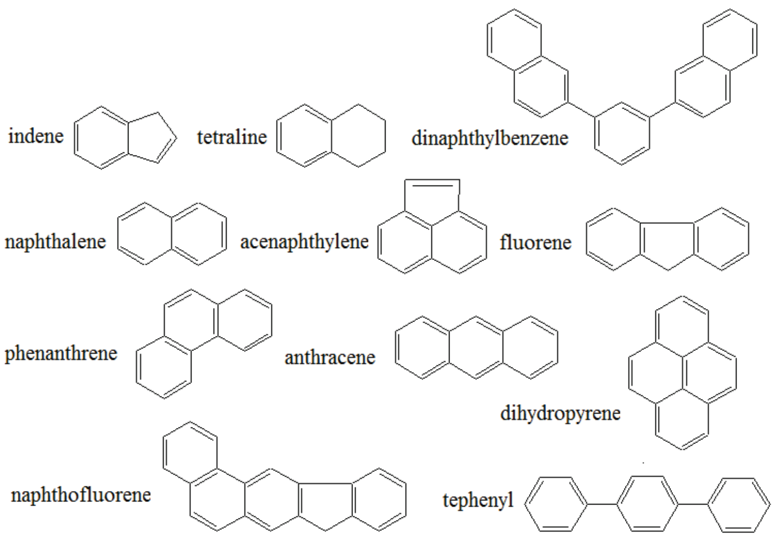

Fig. 1. Structures identified in eluates.

that the molecules of red crystals, along with aromatic rings, contain other thermally less stable structures and this confirms once more that petroleum formation proceeds at low temperatures. It has been revealed that nonfluorescent nitrogencontaining (red) crystals and fluorescent (white and yellow) components are natural genetic compounds of petroleum and depend on its type. In particular: luminescent crystals of hydrocarbon nature (white and yellow) were separated from paraffinic petroleum (Samgori); non-luminescent red crystals – from highly tarry petroleum (Supsa); and both types of crystals – from aromatic petroleum (Norio).

Based on the results of this study it can be concluded that the non-fluorescent red nitrogen-containing crystalline components, as well as the fluorescent ones, are natural genetic components of petroleum [9].

On the basis of the TIC (Total Ionic Chromatogram) of the crystalline samples obtained from the Norio petroleum were identified the sulfur and nitrogen heteroanalogues of high-molecular polycyclic aromatic hydrocarbons: benzonaphthothiophenes in the "benzanthracene" fraction, carbazol and its methyl-, dimethyl-, trimethyl- homologues, benzocarbazol and its mono-, dimethyl- homologues and dibenzothiophenes in the "phenanthrene" fraction [10].

The nitrogen content in the red crystals indicates the presence of nitrogen-containing heterocyclic hydrocarbons in these components, the structures of which are shown in Fig. 3.

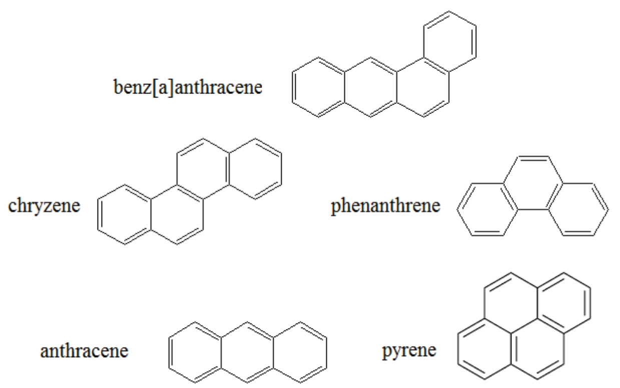

Fig. 2. Structures identified in crystalline components.

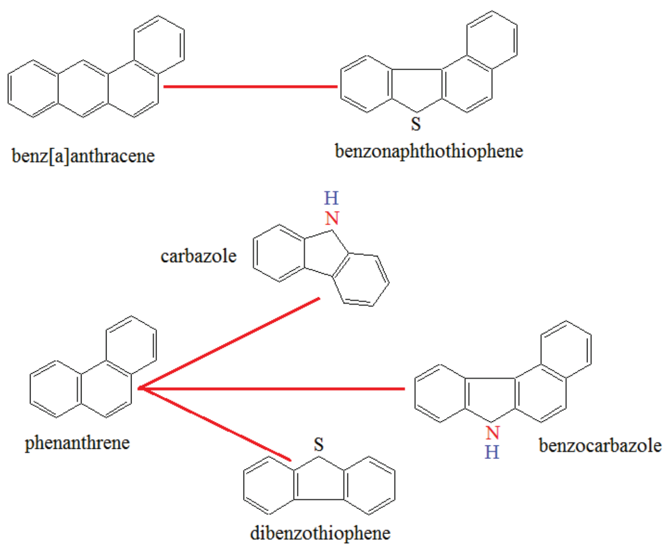

Fig. 3. Structures of sulfur- and nitrogen-containing heterocyclic components.

Conclusions

• In the eluates under investigation the following structures were identified: indenes, tetralines, dinaphtylbenzenes, naphthalenes, fluorenes, phenanthrenes, anthracenes, mono- and polyalkylderivatives of naphthofluorene and phenanthrene, and terphenyles.

• The crystalline components are complex hybrid structures containing nuclei of naphthenes and alkylated aromatic hydrocarbons: banzanthracene, chrysene, their methyl-, dimethyl and trimethyl-analogues, phenenthrene derivatives, anthracenes and pyrenes.

• The heterocyclic analogues of polycyclic aromatic hydrocarbons like benzonaphthothiophenes in the “benzanthracene” fraction, carbazol and its methyl-, dimethyl- and trimethyl- homologues, benzocarbazol and its mono- and dimethyl- homologues (in nitrogen-containing polycyclic aromatics), dibenzthiophenes in the “phenanthrene” fraction were identified.

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ორგანული ქიმია

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**ივანე ჯავახიშვილის სახ. თბილისის სახელმწიფო უნივერსიტეტი, პეტრე მელიქიშვილის ფიზიკური და ორგანული ქიმიის ინსტიტუტი, თბილისი, საქართველო*
***აკადემიის წევრი, საქართველოს მეცნიერებათა ეროვნული აკადემია; პეტრე მელიქიშვილის ფიზიკური და ორგანული ქიმიის ინსტიტუტი, თბილისი, საქართველო*

ნავთობის შემადგენლობაში შემავალი პოლიციკლური არომატული ნაერთები ქმნის მრავალ ეკოლოგიურ პრობლემას, რაც წარმოადგენს შესწავლის მნიშვნელოვან ობიექტს. განსაკუთრებით მნიშვნელოვანია ჰეტეროციკლური და კრისტალური ნაერთები, რომლებიც ძირითადად თავმოყრილია ნავთობის მაღალმდუღარე ფრაქციებში. შესწავლილია საქართველოს სხვადასხვა ტიპის ნავთობებიდან – სამგორი (პარაფინული), ნორიო (არომატული) და სუფსა (ფისოვანი) – გამოყოფილი მაღალმდუღარე პოლიციკლური არომატული ნახშირწყალბადები. გამოყენებულია კვლევის შემდეგი კომპლექსური მეთოდები: ვაკუუმური დისტილაცია, ანილინით ექსტრაჰირება, ადსორბციული ქრომატოგრაფია, ელუატების კრისტალიზაცია/რეკრისტალიზაცია დაბალ ტემპერატურაზე. არომატული ელუატების კრისტალიზაციით და რეკრისტალიზაციით მიღებულ იქნა ორი ტიპის მაღალი ინტენსივობის ლუმინესცენციის მქონე კრისტალური ნაერთები (თეთრი და ყვითელი ფერის) და არალუმინესცირებადი წითელი ფერის კრისტალური ნაერთები, რომლებიც წყალში უხსნადია და პიკრატებთან არ შედის რეაქციაში. ორივე ტიპის კრისტალური კომპონენტები შესწავლილია თანამედროვე ინსტრუმენტული მეთოდებით: აირთხევადი ქრომატოგრაფიით პროგრამირებული ტემპერატურის პირობებში. MS მასსპექტრომეტრია გამოყენებულია კრისტალების სტრუქტურულ–ჯგუფური შემადგენლობის დასადგენად, ხოლო GS-MS მეთოდი ინდივიდუალური ნახშირწყალბადების იდენტიფიცირებისთვის. მონაცემთა ფაილების ანალიზი შესრულდა ავტომატური MS დეკონვოლუციისა და იდენტიფიცირების სისტემის (AMDIS) გამოყენებით. ელექტრონული იონიზაციით ფრაგმენტაციისა და GC შეკავების ინდექსების ანალიზის საფუძველზე საკვლევ ელუატებში იდენტიფიცირებულია პოლიციკლური არომატული სტრუქტურების: ინდენების, ტეტრალინების, დინაფტილბენზოლების, ნაფტალინების, აცენაფტილენების, ფლუორენების, ფენანტრენების, ანტრაცენების, ნაფტოფლუორენებისა და ფენანტრენების მონო- და პოლიალკილწარმოებულები, აგრეთვე ტერფენილები; ხოლო ელუატის კრისტალურ ნიმუშებში იდენტიფიცირებულია: ბენზანტრაცენი, ქრიზენი, მათი მეთილ-, დიმეთილ- და ტრიმეთილ-ანალოგები, ფენანტრენის წარმოებულები, ანტრაცენები და პირენები. ნორიოს ნავთობიდან გამოყოფილ წითელ კრისტალებში იდენტიფიცირებულია გოგირდ– და აზოტშემცველი ნაერთები: ბენზონაფტოთიოფენები „ბენზანტრაცენის“ ფრაქციაში; კარბაზოლი და მისი მეთილ–, დიმეთილჰომოლოგები, ბენზოკარბაზოლი და მისი მონო– და დიმეთილჰომოლოგები (აზოტის შემცველ პოლიციკლურ არომატულ ნახშირწყალბადებში),

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