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COMPREHENSIVE METHODOLOGY FOR INVESTIGATION OF MIDDLE FRACTIONS OF PETROLEUM

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ABSTRACT

A methodology has been developed for separation and identification of hydrocarbons of middle 250-350°C fractions of Taribani and Mirzaani petroleum (Georgia) in order to determine their individual hydrocarbon composition. The middle fractions of petroleum are difficult to study objects due to the huge variety of hydrocarbon isomers present in them. The methodology includes the following complex of physical and chemical methods for processing of petroleum: distillation, dearomatization by adsorption chromatography, thorough separation of isoalkanes from cycloalkanes using three stages thermal diffusion, processing of the obtained concentrates with thiocarbamide. To determine the individual composition of the fractions, instrumental methods of gas-liquid chromatography analysis on capillary columns, MS and GC/MS were used. The developed methodology has been successfully applied to the separation of paraffinic, isoparaffinic and cycloparaffinic hydrocarbons and to determine molecular composition of the middle fractions. Separation of isomers from the concentrates obtained by way of thermal diffusion fractions of Taribani and Mirzaani petroleum was achieved and a number of isoprenoids of C11-C23 composition were identified, in thiocarbamide concentrates there were polycyclic alkanes of C11-C16 composition, and in filtrates - relict, polymethyl-substituted decalins of C14-C16 composition.

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Introduction. The in-depth study of the hydrocarbon composition of petroleum provides an opportunity to improve rational schemes for processing black gold into valuable oil products. Intensive development of physical and chemical methods of analysis since the 60th years of the last century, especially of instrumental technology (gas-liquid chromatography, mass spectrometry, NMR spectrometry on ^{13}C nuclei, chromatography-mass spectrometry, etc.) and their use in scientific petrochemical experiments significantly increased the reliability of the data obtained and greatly

increased the level of our knowledge about the composition and structure of petroleum. The widespread introduction of research technology into practice has made it possible to conduct research at the molecular level. Thanks to highly effective instrumental technology, many structural groups and individual compounds of petroleum have been studied quite fully by now. Most of researchers working in the field of petrochemistry use methods of conventional traditional mass-spectrometry.

However, until recent times without preliminary separation of petroleum into fractions it was practically impossible to carry out studies of both group structure and molecular composition of these fractions. The main task of mass spectrometry in petroleum chemistry today is qualitative and quantitative component analysis of complex mixtures of organic compounds of various origin [1].

Systematic studies of Georgian petroleum began in the 30th years of the last century and as a result of many years of work the presence of all known types of petroleum was established in the country. Their characteristic feature is low sulfur content (<0.3%); they mainly relate to paraffinic, low-tar type of petroleum with a high yield of light fractions and, in this respect, they are valuable raw material for chemical processing and petrochemical synthesis [2].

Purpose of the study. The purpose of this work was to develop a comprehensive methodology for separation and study of concentrates of structurally homogeneous groups of saturated hydrocarbons from middle 250-350°C fractions of petroleum – Taribani and Mirzaani deposits from the main petroleum and gas region of Eastern Georgia – and to obtain maximum information about the individual hydrocarbon composition of these fractions. The 8th and the 10th fractions (naphthenic concentrates) of the three stage TDF separation and the thiocarbamide extract of the 10th TDF fractions were studied. The research data on chemical composition and type of the investigated crude oils are of scientific and practical interest from the point of view of rational development of Georgian petroleum as valuable chemical raw material and for solving various problems of petroleum geochemistry.

Experimental part. Petroleum under investigation belongs to petroleum deposits located in Eastern Georgia, in the Shiraki valley, close to each other. They belong to the Tertiary period, have different depths of occurrence and ages of the host rocks. The Taribani petroleum was taken from the sediments of the upper Sarmatian of the Eldar suite (well #18) at a depth of 2723–2748 m; and Mirzaani petroleum – from the sediments of the Lower Pliocene (well #73) from a depth of 1460 m. The first of them is highly paraffinic (6%) petroleum, and the second one belongs to the naphthenic aromatic type. The characteristics of the Taribani and Mirzaani petroleum are shown in Table 1.

Table 1. Characteristics of petroleum from Taribani and Mirzaani deposits

Characteristics	Name of petroleum deposit	
	Taribani, well #18	Mirzaani, well #73
Depth of bedding, m	2723	1460
Density at 20°C, kg/m^3	858.0	918.4
Tars and asphaltenes, mass %	6.8; 5.9	16.07; 6.8
Sulfur, %	0.25	0.45
Composition of fraction, mass %		
Boiling point, °C	85.0	90.0
B.p. - 100	7.3	5.0
100 – 150	8.7	7.0
150 – 200	6.0	9.0
200 – 250	11.5	10.7
250 – 350	13.0	14.0
Carbon content in structural fragments (%) according to IR spectroscopy		
Aromatic - C_A	20.0	34.0
Paraffinic - C_P	58.9	15.5
Naphthenic - C_N	22.0	50.5
Content of hydrocarbon classes, mass %		
Aromatic hydrocarbons	22.0	58.0
Paraffin–cycloparaffin hydrocarbons	78.0	42.0

To study the individual hydrocarbon composition of the middle fractions 250-350°C of the studied petroleum a complex of modern methods of separation and research was used in order to achieve greater differentiation by type of molecular structure of complex hydrocarbon mixtures, and

thereby to ensure high and reliable efficiency of methods for their analysis. The developed technique included the following stages: distillation, dearomatization by adsorption chromatography on silica gel, thermal diffusion (TDF) separation of paraffinic (PIPCP) and iso-paraffin-cycloparaffin (IPCP) fractions, reactions of formation of thiocarbamide complexes with polycycloalkanes. The main research and identification methods were GLC (gas-liquid chromatography), MS (mass spectrometry) and GC/MS (gas chromatography/mass spectrometry) which, due to combination of analytical capabilities of MS and GLC and being the most highly sensitive and not requiring preliminary isolation of individual substance, is widely used in the practice of crude oil researches [3, 4].

Main attention was paid to the thermal diffusion (TDT) separation, because it is almost the only method that allows successful solving of the problem of separation isoparaffins from cycloparaffins and the latter ones by the degree of their cyclicity. In this study large 1500 cm/50 ml and micro 120 cm/3-4 ml TDF columns were used. The columns of the original construction were designed and prepared in the laboratory of Petroleum Chemistry of the Petre Melikishvili Institute of Physical and Organic Chemistry. Microcolumns of Melpolder's column type were made of stainless steel, had a spiral in the annular space and a minimum gap width between the tubes (0.01-0.03 mm). They are characterized with high separating ability. Their efficiency in separating of cis-trans decalines is maximal S = 99% during 8-10 hours of operation at 90°C [5, 6].

For the purpose of TDF separation of these fractions, aromatic hydrocarbons were removed from them by adsorption chromatography of the original and dearomatized paraffin-cycloparaffin fractions. Characteristics of these fractions are given in Tables 2 and 3.

Concentration of certain groups of saturated hydrocarbons (PCP) from 250-350°C fractions (n_D^{20} 1.4495 and 1.4536 for Taribani and Mirzaani petroleum, respectively) was carried out by three-stage TDF separation. It was taken into account that at the additional stage simultaneously with separation of n-paraffins from the initial fraction the process of separation of isoparaffins from cycloparaffins should have proceeded in part. Conditions of the first stage separation - 70 hours, temperature of the hot wall – 100°C and of the cold wall (5°C), the mixture of the 10th fractions from parallel experiments was subjected to the second stage of separation.

Table 2. Characteristics of 250-350 °C fractions of Taribani and Mirzaani petroleum

Name	Petroleum fractions, °C	
	Taribani	Mirzaani
Fraction yield, mass %	13.0	14.0
Refractive indices, n_D^{20}	1.4500	1.4602
Density at 20°C, kg/m^3	805.2	878.4
Carbon content in structural fragments, %		
Aromatics - C_A	14.3	45.4
Paraffins - C_P	71.2	8.0
Naphthenic - C_N	14.5	46,6
Content of aromatic hydrocarbons, mass %	14.0	44.0
Content of n-paraffins, mass %	65.0	10.0

Table 3. Characteristics of saturated hydrocarbons (PCP and IPCP) from 250-350°C fractions of Taribani and Mirzaani petroleum

Tetracycloalcanes	250-350°C fraction of petroleum	
	Taribani	Mirzaani
Structural-group composition of paraffin-cycloparaffin (PCP) hydrocarbons, in % (according to mass-spectra)		
Paraffines	65.0	50.0
Monocycloalcanes	6.0	23.0
Bicycloalcanes	12.0	15.0
Tricycloalcanes	9.0	8.0
Tetracycloalcanes	8.0	4.0
Isocycloparaffin-cycloparaffines (ICPCP)		
Yield of fraction, (mass %)	15.0	10.0
Refractive indices, n_D^{20}	1.4500	1.4705
Density at 20°C, kg/m^3	799.0	875.0

Second stage of separation lasted for 95 hours, temperature of the hot wall was 160°C and of the cold wall – 5°C, the 10th fraction was subjected to the third stage of separation. Third stage of separation lasted for 95 hours, the temperature of the hot wall was 170°C, the temperature of the cold one – 5°C. The separation effect was quite high. The refractive index changed significantly during the process: if the initial fraction in case of Taribani oil had n_D^{20} – 1.4500, then at the end of the process it was 1.5160. In case of Mirzaani petroleum the initial n_D^{20} was 1.4705 and at the end of process n_D^{20} was 1.5205.

Separation efficiency could be well traced at the chromatograms of fractions according to stages. Chromatographic analyses were carried out on a capillary column (40m x 0.25mm, Apiezon L, linear programming of temperature from 130°C with a speed of 3°/min). The obtained results show that in the course of separation at the 1st stage n-paraffins were gradually removed from the initial fraction, occupying the upper positions in the column; then, at 2nd and 3rd stages the same positions were occupied by isoparaffins, surrendering the bottom of the column to cycloparaffins, which were located in lower fractions according to the degree of their cyclicity. On Figures 1 and 2 two chromatograms are shown, which demonstrate a significant change in the composition of the PCP fraction in the process of TDF separation: (Fig.1. n-paraffins separated from PCP fraction 250-350°C of Taribani crude oil – the 10th fraction from 1st stage of separation, showing a pattern of normal petroleum paraffins from C_{11}, with only minor traces of isoparaffinic and isoprenoid hydrocarbons; there is almost no naphthenic background here; Fig.2. – the 10th fraction from 3rd stage of separation denoted by the presence of a very high naphthenic background, indicating a high concentration of polycycloalkanes in it.

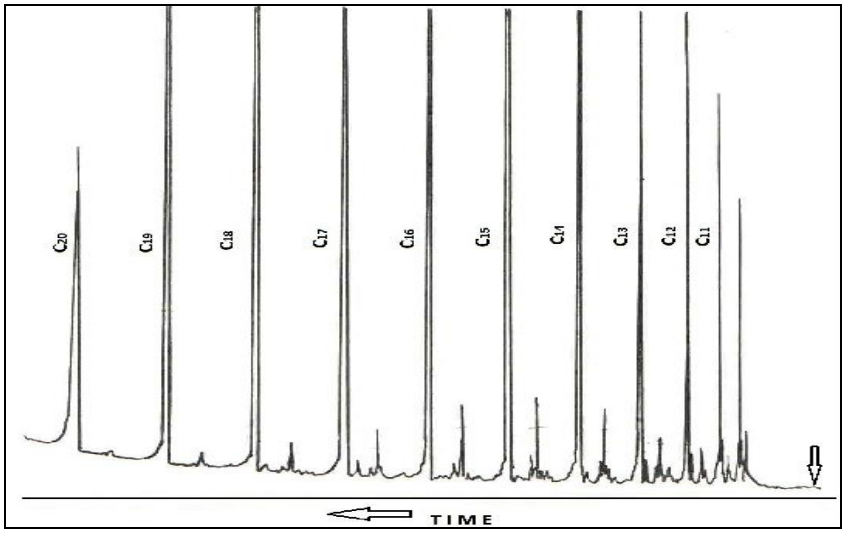

Fig. 1. Chromatogram of the 10th fraction from the 1st stage of separation of PCP obtained from the 250-350°C fraction of Taribani petroleum

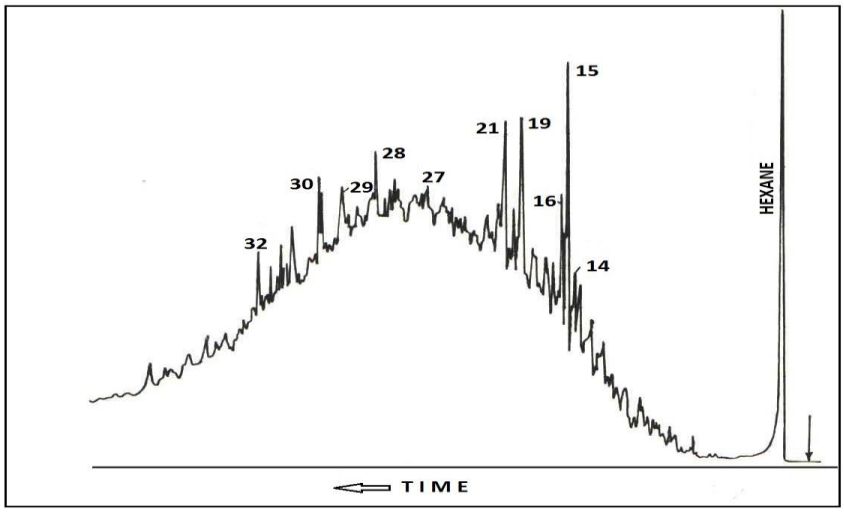

Fig. 2. Chromatogram of the 10th fraction of the TDF separation of PCP obtained from the 250-350°C fraction of Taribani petroleum. Capillary column – 60 m x 25 mm, Apiezon L, linear programming of the temperature from 100°C with a speed of 2°C/min

To assess the group composition of samples obtained during stage-by-stage separation, as well as the TDF fractions at all stages of the process, the MS method was widely used, which made it possible to track the degree of concentration of polycycloalkanes. The analysis was carried out on LKB-2091 device at ion source temperature of 250°C and ionizing electron energy of 70 eV.

As it was already mentioned, the characteristics of the saturated fractions are given in Table 3, and the results of the analysis of the group hydrocarbon composition of naphthenic concentrates (of the 10th fractions), obtained also by the MS method, are shown in Table 4.

Table 4. Group structure composition of naphthenic concentrates (determined by mass-spectrometry method)

Polycyclic naphthenes	Content of naphthenic concentrates, mass %	
	Taribani	Mirzaani
	250-350℃	250-350℃
Monocyclic	-	-
Bicyclic	3	8
Tricyclic	18	42
Tetracyclic	50	31
Pentacyclic	24	18
Hexacyclic	5	1

The data in Table 4, as well as the data of refractive indices, chromatograms and mass-spectra of TDF fractions confirm that narrow > 90% concentrates of polycyclic naphthenes were obtained from saturated hydrocarbons of the middle fractions of the studied crude oils, containing mainly tri-, tetra- and pentacycloalkanes of fractions 250–350℃.

The TDF concentrates (the 8th and the 10th) were subjected to the extraction crystallization by reaction with thiocarbamide 1: 1 (as a solvent was used benzene); treatment was carried out for 25-35 hours at 6℃. The reaction with thiocarbamide led to concentration in the extract mainly of polycycloalkane hydrocarbons, the cross sections of the molecules of which corresponded to the size of the inclusion channel formed by thiourea [6]. In favor of the homogeneity of the composition of the extracts is the fact that out of 70 compounds almost all are isomers of only a few groups of polycycloalkanes with molecular weights of 150, 164, 176, 178, 190, 202 and 204 [7].

Chromatograms of TDF concentrates were remarkable by a very complex composition, representing, in essence, a continuous "hump" (Fig. 2, Taribani petroleum). The presence of a high background complicates the qualitative interpretation of chromatograms using the GC/MS method. Chromatograms of thiocarbamide extracts were much simpler in composition, individualized and the naphthenic background in them was significantly reduced (Fig. 3, Taribani petroleum), although the presence of high peaks above the chromatographic background in the case of TDF concentrates made it possible to subject the samples to study by GLC and GC/MS analysis.

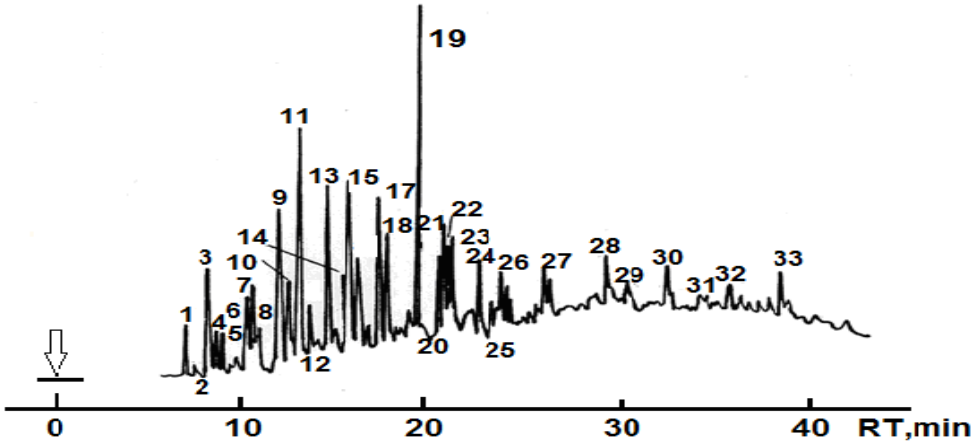

Fig. 3. Chromatogram of the thiocatbamide extract, separated from the naphthenic concentrate (the last 10th fraction from the 3rd stage) of the 250-350°C fraction from Taribani petroleum. (Capillary column 40 m x 0.25 mm, Apiezon L, linear programming of temperature from 130°C with the speed of 3°C /min)

Conclusions. In all studied samples, based on the analysis of the obtained mass spectra certain series of saturated hydrocarbons of the C_{11}-C_{16} composition were found. Interpretation of these spectra, comparing them with the mass spectra of the model analogues, as well as with known petroleum hydrocarbons, in combination with chromatographic retention indices, made it possible to identify most of them:

- In the 8th concentrate obtained after thermal diffusion the presence of C_{11}-C_{22} isoprenoides is determined: 1 – undecane 2,6-dimethyl-(C_{13}); 2 – dodecane 2,6-dimethyl-(C_{14}); 3 – dodecane 2,6,10-trimethyl-(C_{15}); 4 – tridecane 2,6,9 trimethyl-(C_{16}); 5 – tetredecane 2,6,10-trimethyl-(C_{17}); 6 – pentadecane 2,6,10-trimethyl-(C_{18}); 7 – pristan-(C_{19}); 8 – pristan-(C_{20}); 9 – heptadecane 2,6,10,15-tetramethyl-(C_{21}); 10 – octadecane 2,6,10,15-tetramethyl-(C_{22}); 11 – nonadecane 2,6,10,15-tetramethyl-(C_{23}).
- In filtrates of thyocarbamide extracts of the 10th concentrates obtained by TDF the relict type bicyclic hydrocarbons of C_{14}-C_{16} composition are identified, the polymethylsubstituted decalins: 1,1,2-trimethyldecaline; 1,2,3,7,7-pentamethyldecaline; 1-(2-methylhexyl)perhydroindane; cis-1,3,7,7-tetramethyltrans-bicyclo-/4,4,0/decane; trans-2,3,3,7,7-pentamethyltrans-bicyclo-/4,4,0/ decane; 1,3,3,7,7-pentamethyltrans-bicyclo/4,4,0/-decane; cis-2,2,3,7,7-pentamethyl-trans-bicyclo-/4,4,0/decane; trans-cis-1,2,3,7,7-pentamethyltrans-bicyclo/4,4,0/decane; 1,3,7,7-tetramethyl-2-ethyl-transbicyclo /4,4,0/decane.
- In thiocarbamide thyocarbamide extracts 42 polycycloalcane hydrocarbons are identified: tricycloundecanes, C_{11}; tricyclododecanes C_{12}, tricycle-tridecanes C_{13}, tricyclodecanes –C_{11}-C_{14}-adamantanes tetracyclododecanes C_{12}, tetracyclotridecanes C_{13}, tetracyclotetradecane C_{14}-C_{16}, pentacyclotetradecanes C_{14}-C_{15}-diamantanes.

Application of the method for isolation of polycycloalkanes of certain groups from crude oil, including distillation, liquid adsorption chromatography, thermal diffusion separation, thiocarbamide extraction, proved to be sufficient for successful determination of petroleum polycyclic naphthenes at a molecular level in the middle fractions of Georgian oils by means of traditional GC/MS.

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