

## Distribution and Composition of Nitrogen-Containing Compounds in Petroleum from the Lower and Middle Jurassic Deposits in West Siberia

N. N. GERASIMOVA, E.YU. KOVALENKO and T. A. SAGACHENKO

*Institute of Petroleum Chemistry, Siberian Branch of the Russian Academy of Sciences,  
Prospekt Akademicheskiiy 3, Tomsk 634021 (Russia)*

*E-mail: lgosn@ipc.tsc.ru*

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### Abstract

The distribution and composition of low-molecular nitrogen-containing components in petroleum from the Lower and Middle Jurassic complex of West Siberia were investigated. The dependence of the quantitative content and qualitative composition of hetero-organic compounds of nitrogen on the geological-geochemical bedding conditions was revealed. It was established that the group and individual composition of nitrogen-containing compounds of the Lower and Middle Jurassic petroleum is typical also for petroleum from the Cretaceous and Upper Jurassic deposits of the West Siberian oil-and-gas province. No evident differences in the distribution of predominant types of low-molecular nitrogen-containing compounds were revealed in the investigated kinds of petroleum.

### INTRODUCTION

West Siberia is one of the largest oil-producing regions of the world. The main part of liquid hydrocarbons produced at the territory of West Siberia is extracted from the Cretaceous and Upper Jurassic deposits [1]. Intensive exploitation of these complexes resulted in exhaustion of explored resources in these deposits which do not get compensated. Stabilization of the level of oil production in the region is believed to be linked with the development of Lower and Middle Jurassic petroliferous strata. Their promising character determines the necessity to carry out investigations aimed at an increase in the efficiency of prospecting and technological processes of mining and processing oil from the new deposits. The basis of these investigations is composed of the data on the features of chemical composition of petroleum. At present, rather well investigated aspects include the hydrocarbon composition of Lower and Middle Jurassic petroleum of West Siberia, several

regularities of the changes in hydrocarbon composition depending on various natural factors [2, 3–5]. The data available on the composition of heteroatomic compounds in these kinds of petroleum does not allow us to get a full notion of the chemical composition of petroleum in general.

The present work deals with the investigation of the quantitative composition of low-molecular nitrogen-containing compounds (NC) in petroleum from the Lower and Middle Jurassic complex of West Siberia. Attention to the investigation of low-molecular nitrogen-containing components is due to the substantial negative effect of the organic nitrogen-containing compounds on oil mining [6] and catalytic processing of oil fractions [7], the quality of combustive-lubricating materials [8], environment [6].

### EXPERIMENTAL

Petroleum samples investigated in the present work were collected from the territories

situated in the Tomsk region and in the south-east of the Tyumen Region within the Nyurol'ka depression (Nizhnetabaganskaya, Gerasimovskaya, Zapadno-Ostaninskaya, Kulginskaya, Shirotnaya), Nizhnevartovsk (Prikkoltogorskaya) and Demyansk (Pikhtovaya, Novo-Yutymyskaya) crests. The studied samples were extracted from the depth of 3292–2681 m and differ from each other by the ratio of pristane to phytane concentrations ( $Pr/Ph = 1.0\text{--}4.4$ ), which characterizes to a definite extent the oxidative-reductive conditions of the accumulation of the initial organic matter [9] (Table 1).

Total content of NC ( $N_{tot}$ ) was determined with the help of Pokrovskiy's reactor [10], nitrogen-containing organic bases ( $N_{bas}$ ) – by means of anhydrous potentiometric titration with a solution of perchloric acid in dioxane [11].

Separation of low-molecular NC and their subsequent fractionating into strongly and weakly basic components were carried out by means of acidic extraction [12] and liquid adsorption chromatography [13]. The products obtained after this procedure were: a mixture of strong and weak bases ( $K, K_0, K_{01}, K_{011}$ ), only strong bases ( $K_1, K_2, K_{02}$ ) and only weak ones ( $K_{012}$ ). According to [14], strong bases  $K_0$

and the products of their consecutive chromatographic separation with silica gel modified with HCl ( $K_{01}$ ) and NaOH ( $K_{011}$ ) differ from strongly basic compounds  $K_1$  and  $K_2$  by a better developed alkyl and/or naphthene substitution of azaarene cycles. Strong bases  $K_1$  differ from strong bases  $K_2$  by smaller molecular mass and higher degree of aromaticity [12, 14].

In order to isolate azaarene fraction,  $K_1$  compounds were separated by means of the two-step linear eluting adsorption chromatography with aluminium oxide modified with 3.75 %  $H_2O$ , using binary mixtures of solvents [15]. Thus we obtained the product ( $K_1^A$ ) eluted with the system with  $\epsilon_{AB}^0 = 0.30$ , which contains the major part of strong bases of the initial concentrate. These bases are represented by the compounds with the screened nitrogen atom [15].

Mass spectrometry analysis (MSA) of the products of extraction and chromatographic separation was carried out with MKh/1320 instrument with the direct introduction of the sample into the ion source (electron energy was equal to 70 eV). Optimal temperature of sample evaporation (with the heating rate of 7 °C/min) was determined on the basis of the full ion

TABLE 1

Characteristics of petroleum from the Lower and Middle Jurassic deposits of West Siberia

Sample No.	Territory, well	Sampling depth, m	Pr/Ph [9]	Content, %		Tectonic element
				$N_{tot}$	$N_{bas}^*$	
<i>Lower Jurassic</i>						
1	Prikkoltogorskaya, 2	3280–3292	4.2	0.06	0.011/18	Nizhnevartovsk crest
2	Shirotnaya, 53	3033–3052	1.8	0.12	0.020/17	Nyurol'ka depression
3	Zapadno-Ostaninskaya, 444	2834–2860	4.4	0.10	0.019/19	
4	Gerasimovskaya, 10	2828–2857	1.3	0.09	0.016/18	
<i>Middle Jurassic</i>						
5	Shirotnaya, 53	2908–2920	2.7	0.10	0.016/16	Nyurol'ka depression
6	Zapadno-Ostaninskaya, 444	2800–2814	1.2	0.10	0.018/18	
7	Gerasimovskaya, 12	2770–2780	1.3	0.10	0.023/23	
8	Zapadno-Ostaninskaya, 444	2764–2774	1.2	0.09	0.018/20	
9	Gerasimovskaya, 10	2742–2750	1.2	0.10	0.023/23	
10	Gerasimovskaya, 1	2737–2748	1.0	0.10	0.024/24	
11	Kulginskaya, 141	2744–2746	2.1	0.07	0.018/26	
12	Nizhnetabaganskaya, 18	2712–2727	1.2	0.14	0.030/21	
13	Pikhtovaya, 200	2906–2927	1.2	0.15	0.034/23	Demyansk crest
14	Novo-Yutymyskaya, 41	2681–2695	1.0	0.14	0.032/23	

\*The first value is absolute content (in mass %), the second value is relative content.

current at the maximal value of which the mass spectra were recorded [16]. In order to calculate the structural and group composition of samples, we used the ratios of intensities of the peaks of molecular and pseudo-molecular ions in monoisotopic mass spectra [17].

Chromato-mass spectrometry of nitrogen bases  $K_1^A$  was carried out with R10-10C instrument of NERMAG company (France) with the system of data collection and processing Spectral-500. Separation of basic compounds was carried out on a quartz capillary column with dimensions  $30 \times 0.32$  mm with the immobile phase DB-5 (SE-54); helium was carrier gas. Mass spectra were recorded at ionization energy of 70 eV; temperature of the ionizing chamber and the interface was 230 °C, spectrum sweep time was 0.4 s, the recorded mass range was 33–450. Identification was carried out by comparing the results with the spectra obtained with the phases of the same type by the authors of [18, 19].

## RESULTS AND DISCUSSION

As it follows from the data shown in Table 1, total nitrogen content of petroleum samples under investigation varies within a broad range

(0.06–0.15 mass %). In Lower Jurassic petroleum, the mass concentration of NC is lower (0.09 % as a mean) than that in Middle Jurassic petroleum (0.11 % as a mean). Among nitrogen-containing components, there are basic (concentration 0.011–0.034 mass %) and neutral compounds. Up along the section of the Lower and Middle Jurassic complex, concentration of bases changes from 17 to 26 rel. % comprising the mean value of 18 rel. % for Lower Jurassic petroleum and 22 rel. % for Middle Jurassic petroleum.

The concentration of low-molecular NC in the samples under investigation varies within the range from 0.078 to 0.262 mass % (Table 2). Among them, 7.0–21.5 rel. % of strong bases of petroleum are distinguished. Due to the errors of determination of absolute concentrations of weak bases in petroleum by means of anhydrous potentiometric titration [2], the degree of extraction of this type of nitrogen-containing compounds was not calculated.

Among strong bases, the portion of the most low-molecular aromatic compounds  $K_1$  is 1.2–5.7 rel. %; strong bases  $K_2$  account for 2.1 to 5.8 rel. %. The amount of bases with a screened nitrogen atom in a molecule ( $K_0$ ) varies within the range 2.4–11.7 rel. %.

TABLE 2

Distribution of strong nitrogen-containing bases over the products of extraction and separation in petroleum from the Lower and Middle Jurassic deposits of West Siberia

Product, parameter	Content, %, in sample														
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	
$K$	0.078	0.241	0.152	0.102	0.184	0.262	0.087	0.141	0.086	0.183	0.200	0.184	0.182	0.193	
$N_{bas}$	abs.	1.60	1.30	1.69	1.50	1.70	1.48	1.93	2.80	1.90	1.00	1.00	1.20	1.30	1.20
	rel.	12.5	15.6	18.3	7.7	17.3	21.5	7.3	21.5	7.1	8.0	11.0	7.4	7.0	7.2
$N_{weak/bas}$	abs.	1.59	2.03	2.05	1.04	1.04	0.64	0.80	1.21	0.77	1.19	1.28	1.38	1.31	1.33
$K_1$	0.005	0.008	0.015	0.008	0.006	0.022	0.006	0.026	0.008	0.006	0.007	0.016	0.016	0.014	
$N_{bas}$	abs.	4.60	4.80	4.60	4.60	4.60	4.00	4.60	4.00	4.60	4.60	4.70	4.60	4.70	4.80
	rel.	2.1	2.0	3.6	1.8	1.4	4.9	1.2	5.7	1.6	1.2	1.8	2.5	2.2	2.1
$K_2$	0.018	0.033	0.030	0.021	0.038	0.033	0.022	0.039	0.023	0.027	0.042	0.025	0.026	0.026	
$N_{bas}$	abs.	2.00	2.40	2.70	2.20	2.20	2.70	2.70	2.70	2.60	2.80	1.50	3.00	2.80	3.00
	rel.	3.3	4.0	4.3	2.5	4.2	5.0	2.6	5.8	2.6	3.1	3.5	2.5	2.1	2.4
$K_0$	0.055	0.200	0.107	0.073	0.140	0.207	0.059	0.076	0.055	0.150	0.151	0.143	0.140	0.153	
$N_{bas}$	abs.	1.42	0.96	1.85	0.93	1.33	1.00	1.40	2.40	1.20	0.59	0.68	0.50	0.66	0.56
	rel.	7.1	9.6	10.4	3.4	11.7	11.6	3.5	10.0	2.9	3.7	5.7	2.4	2.7	2.7
$N_{weak/bas}$	abs.	2.26	2.50	2.35	1.44	1.37	0.81	1.18	2.24	1.20	1.45	1.70	1.66	1.70	1.68
	rel.	100.0	99.7	100.0	99.0	100.0	100.0	100.0	100.0	100.0	99.9	100.0	100.0	99.7	100.0

Note. Here and in Tables 4, 5: samples Nos. 1–4 belong to Lower Jurassic deposits, Nos. 5–14 to Middle Jurassic ones.

TABLE 3

Distribution of weakly basic nitrogen-containing compounds over the products of fractionating in petroleum from Lower and Middle Jurassic deposits of West Siberia

Sample No.	Content in petroleum, with respect to $K_0^*$ , %				
	$K_0$	$K_{01}$	$K_{02}$	$K_{011}$	$K_{012}$
<i>Lower Jurassic</i>					
2	0.200/100.0	0.051/26.0	0.149/74.0	0.031/16.0	0.020/10.0
3	0.133/100.0	0.029/22.0	0.104/78.0	0.017/13.0	0.012/9.0
4	0.073/100.0	0.018/25.0	0.055/75.0	0.011/15.0	0.007/10.0
<i>Middle Jurassic</i>					
5	0.140/100.0	0.050/36.0	0.090/64.0	0.026/19.0	0.024/17.0
6	0.076/100.0	0.018/24.0	0.058/76.0	0.014/18.0	0.004/6.0
7	0.059/100.0	0.012/20.0	0.047/80.0	0.008/14.0	0.004/6.0
9	0.055/100.0	0.012/22.0	0.043/78.0	0.007/13.0	0.005/9.0
10	0.150/100.0	0.030/20.0	0.120/80.0	0.012/8.0	0.016/12.0
11	0.151/100.0	0.039/26.0	0.112/74.0	0.018/12.0	0.021/14.0
12	0.153/100.0	0.031/20.0	0.123/80.0	0.015/10.0	0.016/10.0
13	0.140/100.0	0.028/20.0	0.110/80.0	0.012/9.0	0.016/11.0
14	0.153/100.0	0.030/20.0	0.123/80.0	0.012/8.0	0.018/12.0

\*The first value is absolute content, the second value is relative content.

TABLE 4

Structural and group composition of low-molecular strong nitrogen-containing organic bases of Lower and Middle Jurassic petroleum of West Siberia

Compounds	$z^*$	$m^{**}$	Content, with respect to the sum of strong bases, rel. %, in sample							
			2	3	5	8	9	11	12	14
$C_nH_{2n-z}N$			63.9	65.4	65.1	65.4	65.7	64.4	65.6	65.7
Pyridines	9-13		1.0	2.4	6.7	6.9	6.1	7.1	7.0	8.8
	11	129	0.9	1.0	4.1	3.5	3.5	4.8	4.3	4.3
	13	169	2.4	2.2	3.6	5.0	3.7	3.6	4.7	5.1
	15	209	4.2	4.8	3.1	5.4	5.0	4.4	4.3	3.6
	17	249	6.3	6.0	3.6	3.0	2.1	2.9	3.3	3.5
	19	289	0.3	0.2	2.1	1.5	2.5	3.0	2.3	1.8
Quinolines			14.1	14.2	16.5	18.4	16.8	18.7	18.9	18.3
	17	179	5.7	5.3	4.1	5.3	3.8	5.4	4.0	4.8
	19	219	7.6	4.6	4.3	4.1	4.7	3.8	3.2	4.1
	21	259	5.6	4.7	3.1	2.6	4.5	3.3	4.5	3.0
	23	299	0.2	2.9	1.6	1.8	2.1	1.1	2.8	0.6
Benzoquinolines			19.1	17.5	13.1	13.8	15.1	13.6	14.5	12.5
Dibenzoquinolines	23-29		9.4	11.0	7.1	6.2	5.8	6.4	6.5	7.5
Azapyrenes	21-25		8.9	11.6	9.3	9.1	9.2	6.9	8.4	8.6
MCC	27-37		11.4	8.7	12.4	11.0	12.7	11.7	10.3	10.0
$C_nH_{2n-z}NS$			36.1	32.8	34.9	34.6	34.3	35.6	34.4	34.3
Thiazoles	9-13		7.3	6.5	9.7	11.1	8.7	9.6	9.2	11.1
Thiophenoquinolines	15-19		8.1	7.1	9.1	9.7	9.4	10.3	10.3	10.5
Benzothiophenoquinolines	21-27		13.9	13.4	9.5	9.6	10.2	9.0	9.2	9.1
Dibenzothiophenoquinolines	27-31		6.8	5.8	5.2	3.4	4.6	4.7	4.4	3.3
MCC	33, 35		-	-	1.4	0.8	1.4	2.0	1.3	0.3

\*Here and in Tables 5, 6:  $z$  is the degree of hydrogen non-saturation.

\*\* $m$  is molecular mass.

In Lower Jurassic petroleum, total concentration of low-molecular strong bases is higher than that in Middle Jurassic petroleum: 13.5 and 11.5 rel. % as a mean, respectively. This is mainly due to an increase in relative content of strongly basic compounds of concentrates  $K_0$ . While the concentration of strong bases  $K_1$  and  $K_2$  in petroleum of Lower and Middle Jurassic complex remains almost unchanged (as a mean, 2.4–2.5 and 3.4–3.5 rel. %, respectively), amount of strong bases of concentrate  $K_0$  decreases upward along the section from 7.6 to 5.7 rel. %.

The highest concentration of all the types of low-molecular compounds was detected in petroleum from the Zapadno-Ostaninskaya territory situated at the boundary between the Nyurol'ka depression and the Pudino megaswell (see Table 2).

The major part of compounds  $K_0$  of all the petroleum samples investigated (64.0–80.0 rel. %) is comprised by strong bases of fractions  $K_{02}$  (Table 3). The fraction of strong and weak bases  $K_{011}$  which are similar in their properties to the former ones varies from 8.0 to 19.0 rel. %, the

fraction of weakly basic components  $K_{012}$  varies from 6.0 to 17.0 rel. %. Lower and Middle Jurassic Petroleum samples only slightly differ from each other in the distribution of the above-indicated types of compounds. For instance, content of compounds  $K_{02}$ ,  $K_{011}$  and  $K_{012}$  in Lower and Middle Jurassic petroleum is 76, 15, 10 and 77, 12, 11 rel. % as a mean, respectively.

Small number of samples of petroleum deposited within the crests does not allow us to make conclusions concerning the effect of geological structure on the distribution of low-molecular NC in petroleum, though a definite trend may be observed. In general, petroleum of the Nyurol'ka depression contains more these compounds than petroleum of the Demyansk and Nizhnevartovsk crests does.

Among polyfacial petroleum samples from the Nyurol'ka depression, the samples with  $Pr/Ph > 2$  are distinguished on average by higher content of low-molecular strong bases (15.5 against 12.0 rel. %), strongly and weakly basic compounds with similar properties (15.0 against 12.0 rel.%) and weakly basic components (13.0 against 9.0 rel. %).

TABLE 5

Structural and group composition of low-molecular weakly basic nitrogen-containing compounds of Lower and Middle Jurassic petroleum of West Siberia

Compounds	$z$	$m$	Content, with respect to the sum of weak bases, rel. %, in sample						
			2	3	5	9	11	13	14
$C_nH_{2n-z}NO$			55.9	55.2	56.8	62.0	59.7	60.1	60.1
	3	153	2.2	2.1	4.4	4.7	3.1	4.8	4.2
	5	165	3.7	7.4	4.4	4.9	6.8	5.7	6.3
	9	147	3.2	2.8	3.1	3.7	3.1	2.7	2.9
	15	197	7.5	6.7	3.2	4.7	4.5	4.8	4.8
	17	237	1.5	1.2	2.9	2.8	3.1	2.6	2.7
Lactams			18.1	20.2	18.0	20.8	20.6	20.6	20.9
Pyridones	7–9		8.7	7.9	8.7	10.0	9.9	8.7	9.9
	11	145	1.9	1.2	4.7	5.4	4.9	4.9	5.4
	13	185	2.2	4.9	2.1	2.4	2.4	2.8	2.3
	15	225	4.4	2.5	5.6	5.1	4.9	5.9	5.4
Quinolones			8.5	8.6	12.4	12.9	12.2	13.6	13.1
	17	209	4.4	3.3	6.0	5.8	4.8	5.0	4.5
	19	235	7.0	6.0	2.0	2.8	2.9	3.0	2.3
	21	275	3.6	3.4	3.1	3.4	3.5	3.0	3.4
Benzoquinolones			15.0	12.7	11.1	12.0	11.2	11.0	10.2
Dibenzoquinolones	23–27		5.6	5.8	6.6	6.3	5.8	6.2	6.0
$C_nH_{2n-z}NO_2$			44.1	44.8	43.2	38.0	40.3	39.9	39.9
Quinoline carboxylic acids	9.13–21.25		27.2	27.3	27.8	25.8	27.7	25.0	25.1
Esters of quinoline carboxylic acids	13–21.25		16.9	17.5	15.4	12.2	12.6	14.9	14.8

According to the data of MSA, which is widely used to study the group composition of petroleum components, the qualitative composition of NC of petroleum of Lower and Middle Jurassic complex of West Siberia is characterized by a set of sequences typical for petroleum of the Mesozoic complex of West Siberia [21].

Low-molecular NC are represented by alkyl and naphthene derivatives of pyridine, quinoline, benzo- and dibenzoquinoline, azapyrene, thiazole, thiopheno- and benzothiophenoquinoline, cyclic amides like pyridones, their hydrogenated analogues lactams, quinoline carboxylic acids and their esters, more condensed polycycloaromatic compounds (MCC) (Tables 4, 5). The distribution of the established types of NC is almost independent of bedding conditions for the investigated petroleum samples. Among strongly basic compounds of Lower and Middle Jurassic petroleum, predominant nitrogenous compounds are azaarenes (63.9–65.7 rel. %), quinolines being most abundant in this group (14.1–18.9 rel. %) along with benzoquinolines (12.5–19.1 rel. %). Thiazole content of petroleum kinds under investigation varies within 6.5–11.1 rel. %, thiophene- and benzothiophene-naphthalenes account for 7.1–10.5 and 9.0–13.9 rel. %, respectively.

The prevailing type of weak bases is heterocyclic amides (pyridones, quinolones, benzo- and dibenzoquinolones); their total content varies from 35.0 to 41.2 rel. %. Their main part is comprised by quinolones (8.5–13.6 rel. %) and benzoquinolones (10.2–15.0 rel. %). Lactam content varies from 18.0 to 20.9 rel. %. Weak bases containing both nitrogen and oxygen atoms in the molecule are represented mainly by acids (60.9–68.7 rel. %).

In the absence of distinct differences in the distribution of prevailing types of low-molecular NC, Lower Jurassic petroleum is characterized by higher relative content of the structures with large-sized aromatic nuclei and increased total cyclic character. Passing from Lower Jurassic petroleum to Middle one, mean content of benzoquinolines decreases from 18.3 to 13.8 rel. %, benzothiophenoquinolines and benzoquinolones from 13.0 to 9.4 rel. % and from 13.9 to 11.1 rel. %, respectively. The maximum

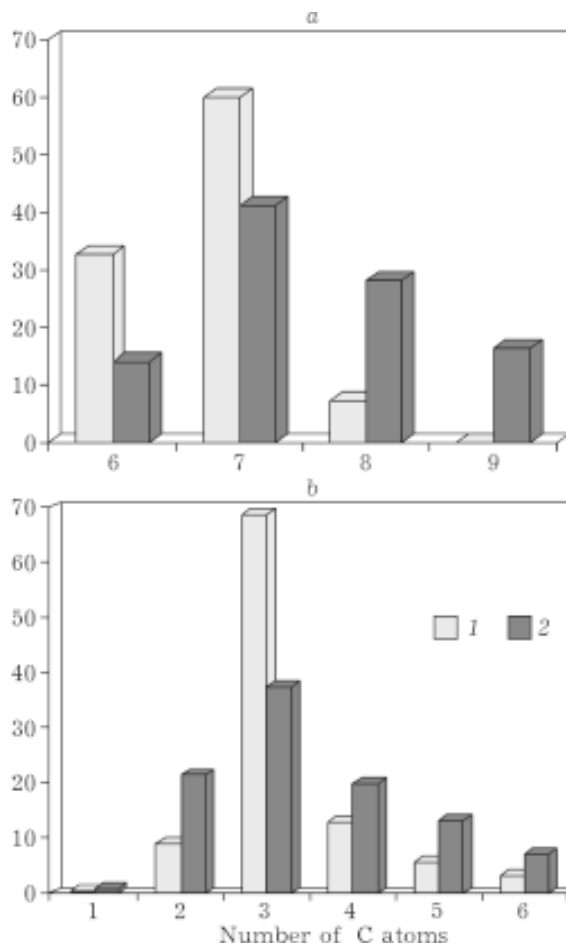


Fig. 1. Distribution of alkyl quinolines (a) and alkyl benzoquinolines (b) in petroleum samples of different age from the Gerasimovskaya territory: 1 – Lower Jurassic, sample 4; 2 – Middle Jurassic, sample 9.

of distribution of these compounds shifts, too. Thus, for benzoquinoline bases and benzoquinolones in Middle Jurassic petroleum, the maximum falls at alkyl derivatives ( $z = 17$ , 33.3 and 33.6 rel. % on average, respectively), while in Lower Jurassic petroleum it is at mononaphthene derivatives ( $z = 19$ ) and is equal to 33.3 and 46.8 rel. % for strongly and weakly basic compounds, respectively.

Investigations carried out with the help of chromato-mass spectrometry did not allow us to reveal differences in the individual composition of low-molecular NC in Lower and Middle Jurassic petroleum.

The products isolated from samples 4, 9, 11, 12, 14 were analyzed. Within all the azaarene fractions, the sets of series corresponding to alkyl derivatives of quinolines ( $m/z = 213, 227, 241$ ) and benzoquinolines ( $m/z = 193, 207, 221, 235, 249$ ) were identified.

TABLE 6

The measured composition of C<sub>7</sub>-alkyl quinolines and C<sub>3</sub>-alkyl benzoquinolines of petroleum samples of different age from the Gerasimovskaya territory (according to the data of MSA, general formula: C<sub>16</sub>H<sub>21</sub>N)

<i>m/z</i> *	Structure**	Content, rel. %, in sample	
		4	9
<b>C<sub>7</sub>-alkyl quinolines</b>			
227	8-Isopropyl,C <sub>4</sub> alkyl quinoline	2.7	6.8
227	8-(Methyl,propyl),C <sub>3</sub> -alkyl quinoline	2.7	5.6
227	8-Isopropyl,C <sub>4</sub> -alkyl quinoline	3.2	6.3
227	8-Isopropyl,tetramethyl quinoline	45.7	21.4
227	«	18.4	20.4
227	«		
	8-(Methyl,propyl),C <sub>4</sub> -alkyl quinoline	15.7	13.5
227	Ethyl(1),C <sub>3</sub> -alkyl quinoline	2.1	6.8
227	Ethyl(1),C <sub>3</sub> -alkyl quinoline	1.0	6.8
227	Heptamethylazaarene	5.8	7.5
227	C <sub>7</sub> -alkylazaarene	2.7	4.9
<b>C<sub>3</sub>-alkyl benzoquinolines</b>			
221	Trimethylbenzoquinoline	4.9	4.0
221	«	5.2	4.5
221	«	2.9	2.9
221	«	7.3	9.8
221	«	12.2	11.4
221	«	9.2	9.1
221	«	14.6	14.1
221	2,4,6-Trimethylbenzo(h)quinoline	21.8	14.7
221	Trimethylbenzoquinoline	7.8	12.0
221	«	11.2	12.0
221	«	2.9	4.5

\* MSA data.

\*\* Literature data.

No non-substituted structures were detected. Among quinoline compounds of Lower and Middle Jurassic petroleum, C<sub>7</sub>-alkyl derivatives are prevailing; among benzoquinoline ones C<sub>3</sub>-alkyl derivatives dominate. The distribution of alkylated homologues of quinoline and benzoquinoline in petroleum samples of different age from the Gerasimovskaya territory (samples 4, 9) is shown in Fig. 1. One can see that the content of prevailing homologues in the azaarene portion decreases when passing from Lower to Middle Jurassic petroleum: C<sub>7</sub>-alkyl quinolines from 59.0 to 41.1 rel. %, C<sub>3</sub>-alkyl benzoquinolines from 68.7 to 37.2 rel. %.

Comparative analysis of the obtained data with the literature data allowed us to establish

the presence of structures with methyl, ethyl and isopropyl substituents among C<sub>7</sub>-alkyl quinolines (*m/z* = 227) of all the petroleum kinds [18]. The prevailing compound is 8-isopropyl,tetramethylquinoline (Table 6). C<sub>3</sub>-Alkyl benzoquinolines (*m/z* = 221) are represented only by methyl-substituted structures [19] among which the prevailing compound is 2,4,6-trimethylbenzo(h)quinoline (see Table 6). The fraction of prevailing isomers is higher in Lower Jurassic petroleum than in petroleum from Middle Jurassic deposits (79.8 against 55.3 and 21.8 against 14.7 rel. % for 8-isopropyl,tetramethylquinoline and 2,4,6-trimethylbenzo(h)quinoline, respectively (see Table 6).

## CONCLUSIONS

It was established in the investigation that low-molecular nitrogen-containing compounds of petroleum of the Lower and Middle Jurassic complex of West Siberia are represented by a mixture of strongly and weakly basic components. The group and individual composition of these compounds is independent of petroleum bedding conditions and is characteristic of the petroleum of Mesozoic complex of the West Siberian oil-and-gas province. Low-molecular NC of Lower and Middle Jurassic petroleum are represented by alkyl and naphthene derivatives of pyridine, quinoline, benzo- and dibenzoquinoline, azapyrene, thiazole, thiopheno- and benzothiophenoquinoline, cyclic amides like pyridones, their hydrogenated analogues lactams, quinoline carboxylic acids and their esters, more condensed polycycloaromatic compounds. In all kinds of petroleum, prevailing compounds are azaarenes and heterocyclic amides. The major part of these compounds is comprised by quinolines, benzoquinolines and benzoquinolones. Among strong bases, prevailing compounds are C<sub>7</sub>-alkyl quinolines and C<sub>3</sub>-alkyl benzoquinolines. In all kinds of petroleum, C<sub>7</sub>-alkyl quinolines ( $m/z = 227$ ) are represented by the structures with methyl, ethyl and isopropyl substituents, C<sub>3</sub>-alkyl benzoquinolines ( $m/z = 221$ ) only by methyl-substituted structures. Predominance of 8-isopropyl, tetramethyl quinoline and 2,4,6-trimethylbenzo(h)quinoline is characteristic of all the samples investigated.

No clear differences in the distribution of prevailing types of low-molecular NC were revealed in petroleum samples under investigation. However, it should be noted that relative content of strong bases with developed alkyl and/or naphthene substitution in low-molecular NC increases with an increase in the age of bearing deposits. Stronger transformed petroleum gets enriched with the structures with larger size of aromatic nuclei and increased general cyclic character.

The data obtained may be used to solve the problems connected with the formation of

petroleum in the Earth's interior and with the choice of technologies of mining and processing petroleum raw material.

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