

NITROGEN COMPOUNDS OF PETROLEUM OILS (REVIEW)

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The literature data on the quantitative percentages, group and individual compositions, and structures of nitrogen compounds of all types that have been identified in petroleum oils and directly distilled petroleum fractions are systematized. The general regularities in the structures of the molecules of petroleum nitrogen compounds and their structural relationship with other aromatic components of petroleum oils are noted. The modern concepts regarding the genesis of the most important classes of nitrogen-containing components of petroleum are discussed.

Nitrogen in the form of diverse organic compounds is included in the composition of virtually all petroleum oils. The nitrogen components of petroleum oils and petroleum products have a negative effect on petroleum refining processes [1, 2] and reduce the performance qualities of fuels and oils. A knowledge of the nature of the nitrogen compounds is necessary for the solution of fundamental problems that are associated both with the formation and transformations of petroleum oils under the conditions in the depths of the earth and with the search for ways to utilize these compounds. The unflagging interest of researchers in nitrogen-containing petroleum substances is reflected in the previously published reviews (e.g., see [3-8]).

The overall fraction of nitrogen in the elementary composition of most petroleum oils ranges from 0.1 to 0.3%, although in some cases it may reach 0.8-1.5% [9, 10]. It has been shown that the nitrogen concentration in petroleum oils from various regions (Uralo-Povolzhe and Western Siberia [11, 12], the Fergansk Basin [13], Daghestan [14], etc.) is related in a regular way to the tar content and density of petroleum oils and to the percentage of sulfur and metals in them. The bulk of the nitrogen is concentrated in the tar-asphalt components of petroleum oils. Thus, according to the data in [11], 52-63% of the total nitrogen content is associated with the neutral tars extracted from petroleum oils from Povolzhe and Siberia, and another 37-42% is associated with the asphaltenes. It is proposed that during the isolation of the tar-asphalt substances the nitrogen compounds may coprecipitate with them in the form of associates that are formed by means of donor-acceptor interactions [15]. A correlation of the percentage of nitrogen with the above-noted properties of petroleum oils is natural, since most of the heteroelements are concentrated in the tar-asphalt compounds, and the density of an oil is also determined to a great extent by its tar content.

Statistical analysis of the voluminous literature data (more than 1200 samples of petroleum oils of all of the petroliferous provinces of the USSR [4, 9, 16-25]) shows that the average nitrogen concentration in the oils of almost all of the regions and the stratigraphic complexes decreases as the degree of stratification and catagenic transformational character of the system increases, in conformity with the concepts of Dobryanskii [26]. The youngest (Pliocene) petroleum oils, for which a reverse dependence is observed, constitute an exception to this. Thus the overall percentage of nitrogen compounds in petroleum oils is intimately associated with the conditions under which the petroleum components were formed, accumulated, and found throughout the entire history of the existence of the deposit.

A great deal of data on the distribution of nitrogen compounds in petroleum oils, directly distilled fractions, and the products of thermal and thermal-catalytic refinement of crude petroleum oil has been accumulated thus far. Unfortunately, in many cases it is difficult or even impossible to establish whether the detected components are present in the crude oil or were formed in one or another step of refining and concentration. Measures designed to preserve the original nature of the compounds have been established only in a few studies, as,

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for example, in the proceedings of the American Petroleum Institute [27-35]. In these studies all of the procedures were carried out in a pure nitrogen atmosphere (containing no more than 0.0002% O₂). The temperature during the operations involving heating did not exceed 225°C, and the duration of the action of temperatures above 100°C was no longer than 1 min; the action of light was excluded.

A promising possibility for the preservation of the original structures of the nitrogen compounds is their isolation from the deasphalted oil by means of chromatographic methods [36-41] or complexing methods [42] that make it possible to exclude thermal action on the substances to be analyzed.

Group Composition of Petroleum Nitrogen Compounds

The nitrogen compounds of petroleum oils are traditionally divided into two large groups in conformity with their chemical behavior: basic groups, which are extracted by mineral acids, and neutral groups [43]. The fraction of basic nitrogen in petroleum oils may vary over wide ranges: 25-34% in oils from the United States and the Near East [44], 30-48% in oils from Sakhalin [9], 10-40% in the oils from Belorussia [25, 45, 46], and 21-58% in the oils from Tadzhikistan [13].

Bezinger and Gal'pern [47] have suggested that the group analysis of nitrogen component of oil be detailed by using potentiometric titration before and after reduction of the neutral and weakly basic substances with lithium aluminum hydride. This formed the basis of the development of a classification scheme, according to which the petroleum nitrogen bases are divided into A (strong bases), B (weak bases), and C (untitrable or neutral compounds) groups. The weak bases were divided, according to their behavior during reduction [48], into B₁ (reduced to strongly basic substances), B₂ (reduced to neutral substances), and B₃ (unreducible substances) types [48].

Researchers who made analyses by means of these schemes [25, 27, 47, 48] assumed that group A includes pyridines and their benzologs, group B₁ includes amides, group B₃ includes pyrrole and indole derivatives, and group C includes carbazole derivatives. Okuno and co-workers [49] isolated components of the B₂ group and found that they are absent in crude oil, develop during its storage in air, and correspond in composition to saturated cyclic sulfoxides — products of the oxidation of petroleum thiacyclanes. It was therefore proposed that the B₂ type be excluded and that petroleum nitrogen compounds be divided into four groups instead of five. It was shown that group C includes not only carbazoles but also large polycyclic molecules of many types [5, 50]. Kiričenkova and co-workers [51] demonstrated experimentally that group analysis by titration before and after reduction with lithium aluminum hydride does not give accurate results for amides and compounds of the pyrrole type. Thus the possibility of a clear assignment of each of groups A-C to a definite structural type of compound is not realized in practice.

Nitrogen Bases

Because of the relative ease of isolation, bases have been the subject of the greatest amount of study of the entire group of nitrogen compounds of oil. It has been reliably established that the overwhelming mass of the nitrogen compounds with basic character in crude oils and directly distilled fractions is represented by derivatives of pyridine and its benzologs. The presence of small amounts of primary and secondary amines (primarily aromatic) has also been noted in individual studies. Thus amines have been detected in the oils of the Tadzhik depression [25] in 4-9% amounts of the total base content. Much higher concentrations of amines are found in the products of thermal refining: in shale gasoline [52], in clear hydrocracking products [53-58], and in commercial reactive fuels [59]. There is some basis for the assumption that primary and secondary amines are not characteristic for crude oils and may be regarded as products of degradation of high-molecular-weight compounds in the oil. In any case, there are no reliable indications of their presence in oils that have not been subjected to heat treatment.

Ion-exchange chromatography on various cation-exchange resins [25, 41, 60, 61] and adsorption chromatography on silica gel and aluminum oxide [25, 40, 41, 62] or in activated charcoal, which makes it possible to effect separation with respect to the number of aromatic rings in the molecule, are frequently used for fractionation of the bases. Molecular distillation and thermal diffusion are used less frequently [63]. Potentiometric titration in conjunction with acylation or hydroformylation [25, 60, 61], spectral methods, and, particularly

TABLE 1. Fraction of Derivatives of Pyridine and Its Benzologs among the Heterocyclic Bases from Various Petroleum Oils and Petroleum Fractions (normalized in 100%)

Deposit (region)	Product or boiling range, °C	Fraction, %		
		pyridines	quinolines	benzoquinolines and more condensed quinolines
Khaudag (Tadzhikistan) [25, 61]	Petroleum	21	32	47
Isbaskent (Tadzhikistan) [25]	Petroleum	18	38	44
Dzharkurgan (Tadzhikistan) [64]	110—300	19	42	39
Ekhabi (Sakhalin) [65]	Petroleum	30	50	20
Tungor (Sakhalin) [65]	Petroleum	19	66	15
Kolendo (Sakhalin) [65]	Petroleum	25	57	18
Okha (Sakhalin) [65]	Petroleum	27	52	21
Wilmington (California) [29-31]	200—370	60	35	5
	370—455	25	65	10
	455—538	26	41	33
Kuwait [35, 66]	290—310	72	21	7
	370—535	17	35	48

often, mass spectrometry have been used for quantitative determination or identification. Typical results of such investigations are presented in Table 1.

Pyridines most often predominate in the clear fractions; as the boiling point increases the preponderant types of bases become initially quinolines, followed by benzoquinolines and higher benzologs. Since the total percentage of nitrogen compounds increases as the fractions become heavier, it may be assumed that bases with three or more condensed rings in the molecule predominate in the overall mass of crude oils, as in the case of Tadzhik oils. However, quinolines are found in the largest amounts in Sakhalin oils [65]; it is not clear whether this is a specific peculiarity of the oils of this region or the result of insufficiently complete extraction of the polycyclic bases by means of ion-exchange chromatography on KU-23 ion-exchange resin.

Derivatives of the isoquinoline series were not detected in oils and directly distilled fractions with a relatively high percentage of quinolines. Isoquinoline derivatives were identified only in the products of thermal destruction of petroleum residues and in coal-tar resins [3, 67-69].

It has been proposed that tricycloaromatic petroleum bases also contain acridine derivatives. However, detailed studies of the directly distilled fractions of California oil [29, 30, 70] led to the identification of only 3,4- and 7,8-benzoquinolines (I and II) as major structural types. Precisely these types were found to be the definitive types among tricycloaromatic bases of the 316-538°C fraction according to the data in [71]. Similar results were obtained during a study of the bases of the same oil by UV, IR, and fluorescence spectroscopy [35]. However, the tetracyclic bases were found to be represented primarily by 1,2- and 3,4-benzacridines (III, IV); the presence of a small amount of azapyrenes (V) with an unestablished position of the nitrogen atom is not excluded, but acene structures are rejected. It is possible that this distribution of the heterocyclic nitrogen bases, which is characterized by significant preponderance of angularly- and (to a lesser extent) peri-condensed aromatic systems over the acene systems and is similar to general features to the known distribution of petroleum polycycloaromatic hydrocarbons [72-75], is also characteristic for other oils.

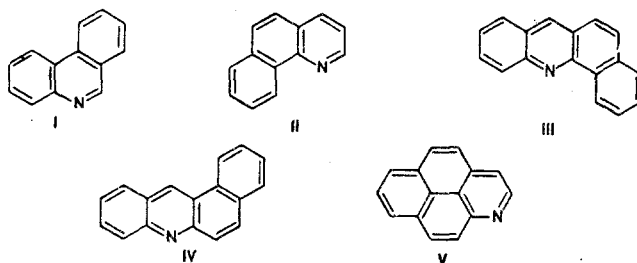


TABLE 2. Composition of the Nitrogen Bases from Some Oils and Petroleum Fractions according to Mass-Spectrometric Data (normalized to 100%)

Boiling range of the fraction, °C	z value in the general formula $C_nH_{2n-z}N$									
	5	7	9	11	13	15	17	19	21	23
	Dzharkurgan oil (Tadzhikistan) [64]									
—	6,2	—	12,9	25,8	13,9	2,1	18,3	14,6	6,2	—
	Wilmington oil (California) [28]									
130—250	36,9	55,3	—	7,8	—	—	—	—	—	—
250—300	4,8	44,8	19,1	31,7	—	—	—	—	—	—
300—350	—	17,6	4,7	60,6	10,1	—	6,8	—	—	—
	Kuwait oil [66]									
290—310	54,4	17,0	—	15,9	5,4	—	7,3	—	—	—
	Libyan oil [78]*									
350—430	4,0	11,7	—	32,5	18,2	—	24,8	5,8	—	1,3

*Probably without allowance for the dinaphtheno derivative present.

Each of the types of nitrogen bases found in the oil includes several groups that differ with respect to the degree of hydrogen unsaturation and belong to one or another isobaric $C_nH_{2n-z}N$ series. The presence in the oil of series with $z = 5-27$ was established by means of low-voltage mass spectrometry. In addition to alkylpyridines ($z = 5$), alkylquinolines ($z = 11$), and higher alkylbenzologs, compounds that contain at least one naphthene ring are distributed among the bases [29-31, 76, 77]. Examples of such analyses are presented in Table 2.

It is clear that this method cannot distinguish the individual homologous series that may be included in the composition of almost each isobaric $C_nH_{2n-z}N$ series. This is responsible for the ambiguous character and, as a result, the partially unsubstantiated and even erroneous character of the interpretation of the results. Thus in [63] the terms of the series with $z = 7$ and 9 were arbitrarily called mono- and dinaphthenopyridines, respectively; Nishishita and co-workers [66] regard the series with $z = 7$ as tetrahydroquinoline compounds without any basis; Brandenburg and Latham [28] assigned the compounds with $z = 7$ to cycloalkylpyridines and those with $z = 9$ to cyclopentapyridanes on the basis of the fact that single individual components of these series were identified in the investigated fractions.

It was found [29-31] that it was possible to expose the individual homologous series in each of the $C_nH_{2n-z}N$ series by a combination of chromatographic, spectral, and mass-spectrometric methods of analysis. Brodskii and co-workers [65] developed a method for joint analysis of the mass spectra obtained at low (molecular ions) and high (fragment ions) ionization energies; this method makes it possible to distinguish cycloalkyl- and cycloalkanopyridines ($z = 7$), trinaphthenopyridines and alkylquinolines ($z = 11$), etc. Data on the composition of nitrogen bases from Sakhalin oils (Table 3) were obtained by this method.

The components that contain two naphthene rings in addition to heteroaromatic rings ($z = 9$ and 15 , respectively) are the predominant components in the distribution of the pyridine and quinoline bases in these oils. The increased overall cyclic character of these bases is in agreement with the naphthene character of the hydrocarbon portion of the Sakhalin oils [9]. In the fractions of the less cyclic oils [28, 64, 66] the percentage of alkylbenzologs of pyridine among the bases is considerably higher, but the accumulated data are as yet insufficient for a derivation of the principle that links the overall cyclic character of the nitrogen bases with the chemical nature of the oil as a whole.

It was found by a combination of IR, PMR, and mass spectroscopy that the naphthene rings in the bases from the Sakhalin oils are primarily five-membered rings and are angularly or, less frequently, peri-condensed with the heteroaromatic rings [65]. The average naphthenopyridine and naphthenoquinoline molecule contains one long chain (4 to 10 carbon atoms) and up to three shorter (mainly methyl) substituents. The methyl groups are the predominant type of substituent in the heteroaromatic bases from other oils and petroleum products.

TABLE 3. Composition of Nitrogen Bases from Sakhalin Oils (weight, %)*

Deposit	Type of compound												
	pyridines					quinolines			benzoquinolines				
	z												
	5	7	9	11	13	11	13	15	17	17	19	21	23
Okha	2	5	8	7	1	10	13	27	4	8	7	4	3
Ekhabi	1	6	12	9	2	7	15	21	5	4	8	6	3
Tungor	1	3	10	5	1	8	18	35	3	6	4	3	2
Kolendo	4	5	9	5	2	10	17	23	6	5	4	4	2

*Rounded off from the data in [65].

TABLE 4. Individual Nitrogen Compounds of Basic Character Identified in Oils and Directly-Distilled Petroleum Fractions

Compound	Compound
Pyridine [80]	2,4,7a,8,8-Pentamethylcyclopentapyridine [28]
2-Methylpyridine [81]	5,6,7,8-Tetrahydroquinoline [43]
3-Methylpyridine [43]	Quinoline [43]
4-Methylpyridine [26]	2-Methylquinoline [43]
2,3-Dimethylpyridine [43]	7-Methylquinoline [81]
2,4-Dimethylpyridine [81]	2,3-Dimethylquinoline [93]
2,5-Dimethylpyridine [80]	2,4-Dimethylquinoline [93]
2,6-Dimethylpyridine [26]	2,8-Dimethylquinoline [94]
3,4-Dimethylpyridine [80]	2,3,8-Trimethylquinoline [95]
3,5-Dimethylpyridine [43]	2,4,8-Trimethylquinoline [96]
2,3,4-Trimethylpyridine [43]	2-Methyl-8-ethylquinoline [97]
2,3,5-Trimethylpyridine [43]	2,3-Dimethyl-8-ethylquinoline [98]
2,4,6-Trimethylpyridine [26]	2,4-Dimethyl-8-ethylquinoline [99]
3-Methyl-5-ethylpyridine [82]	2,3-Dimethyl-8-n-propylquinoline [100]
2,3-Dimethyl-6-isopropylpyridine [83]	2,4-Dimethyl-8-n-propylquinoline [101]
di-2-sec-Butyl-4,5-dimethylpyridine [84]	2,4-Dimethyl-8-sec-butylquinoline [102]
3-Cyclopentylpyridine [85]	2,3,4,8-Tetramethylquinoline [100, 103]
4-Cyclopentylpyridine [85]	2,3,4-Trimethyl-8-ethylquinoline [103, 104]
2-(2,2,6-Trimethylcyclohexyl)-4,6-dimethylpyridine [28, 86, 87]	2,3,8-Trimethyl-4-ethylquinoline [105]
6,7-Dihydro-1,5-pyridine [88, 89]	2,3,4-Trimethyl-8-isopropylquinoline [106]
2-Methyl-6,7-dihydro-1,5-pyridine [90]	2,3,4-Trimethyl-8-n-propylquinoline [104]
3-Methyl-6,7-dihydro-1,5-pyridine [91]	2,3-Dimethyl-4,8-diethylquinoline [107]
5-Methyl-6,7-dihydro-1,5-pyridine [92]	2,3-Dimethyl-4-ethyl-8-n-propylquinoline [107]
trans-5,7-Dimethyl-6,7-dihydro-1,5-pyridine [91]	2,3-Dimethylbenzo[7, 8]quinoline [108]
5,7,7-Trimethyl-6,7-dihydro-1,5-pyridine [91]	2,4-Dimethylbenzo[7, 8]quinoline [108]

A comparison of the intensities of the resonance signals of the aromatic protons in weak and strong fields in the PMR spectra showed [65] that most of the substituents in the quinolines from Sakhalin oils are concentrated in the heteroaromatic ring rather than in the homoaromatic ring and are located in the so-called active positions (2, 4, and 6 in the pyridine derivatives and 2, 4, and 8 in the quinoline derivatives). The same tendency was noted during an analysis of the vacuum-gas oil (343-455°C) from petroleum from the Ventura Basin (California) [79]. Unfortunately, these studies were made primarily on California and Sakhalin oils that are naphthene oils that are weakly metamorphized and genetically similar to one another; it is therefore difficult to judge the extent to which the described results are characteristic for oils of a different nature.

Thus far ~ 50 individual basic nitrogen compounds have been identified in oils and directly-distilled fractions (Table 4). The substituents in all of the detected di-, tri-, and tetraalkylquinolines are located exclusively in the 2, 3, 4, and 8 positions; only methyl groups are found in the 2 and 3 positions. The 2, 3, 5, and 7 positions were found to be preferred for dihydropyridines. It is possible that these specific structural peculiarities convey definite but as yet unclear genetic information.

Nitrogen Compounds with Weakly Basic and Neutral Character

The problem of the nature of the "nonbasic" nitrogen compounds of oils began to be solved

TABLE 5. Group Composition of Nitrogen Compounds (weight, % per fraction) from Wilmington Oil (California) [70]

Nitrogen compounds	Boiling range of the fractions, °C			
	204—370	370—455	455—538	538—700
Benzologs of pyridine	0,6	2,7	5,0	8,2
Amides	0,2	1,2	2,1	9,3
Benzologs of pyrrole	0,3	4,5	6,1	15,2

TABLE 6. Percentage of Benzologs of Pyrrole (weight, %) in the 204-538°C Fraction of Wilmington Oil Calculated from the Data in [29-31, 70]

z	Indoles	Carbazoles	Benzocarbazoles	Total
9	0,025	—	—	0,025
11	0,073	—	—	0,073
13	0,077	—	—	0,077
15	0,065	0,711	—	0,776
17	0,052	0,547	—	0,599
19	0,044	0,340	—	0,384
21	0,027	0,174	0,319	0,520
23	0,010	0,100	0,088	0,198
25	0,010	0,044	0,032	0,086
27	0,002	0,012	0,015	0,029
Total	0,385	1,928	0,454	2,767

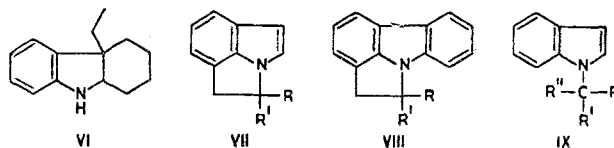
only in the last decades. Gal'pern and co-workers [47, 109-111] used titration before and after reduction with lithium aluminum hydride to arrive at the conclusion that more than 85% of the natural nitrogen compounds in various oils of the USSR were aromatic amines. Amides were proposed as the main type of neutral nitrogen compounds in oils from Tadzhikistan [25], Western Siberia [112], and the United Arab Republic (UAR) [113]. At the same time, it was shown by colorimetric analysis and UV and mass spectrometry [29, 71, 114, 115] that the most important components in the analogous fractions of California and Kuwait oils are benzologs of pyrrole: indoles, carbazoles, and benzocarbazoles (Table 5). This discrepancy was initially explained by the difference in the nature of the oils [50], but it was subsequently established that it may be associated with the insufficient accuracy in the results of titrimetric analysis before and after reduction.

Benzologs of pyrrole were first found in cracking products and in shale oil [69]; carbazole was subsequently isolated from oil, and the presence of its homologs was established [116]. Alkylindoles, benzocarbazoles, etc. were later detected [71]. Convincing evidence for the presence of pyrrole or its homologs in crude oils has not yet been obtained.

The composition of the benzologs of pyrrole in Wilmington oil, in which carbazoles were found to be the most representative compounds, has been subjected to the most detailed study [29-31, 70]. Compounds with $z \leq 27$ were found among indole, carbazole, and benzocarbazole derivatives. The compounds with $z = 11-15$ (mono-, di-, and trinaphthendoindoles or phenylindoles) are the most important components in the distribution of the members of the indole series, whereas the alkylbenzologs predominate in the carbazole and benzocarbazole series (Table 6). The aliphatic groups in the naphthendoindoles, naphthenocarbazoles, and carbazolenines are linked primarily with the naphthene rings [117]. The chief compounds among the benzocarbazoles were found to be 1,2-benzocarbazoles (up to 85%); the remainder consists of the 3,4 isomers, and 2,3-benzocarbazoles are virtually absent [70, 118]; in this, one sees a complete analogy with the character of the fusion of the aromatic rings in benzoquinolines.

In addition to carbazole, only a few individual compounds of the type under examination were isolated from the crude oils and their directly distilled fractions. Carruthers [115] isolated 1,2,6,8- and 1,2,7,8-tetramethylcarbazoles, as well as a pentamethyl derivative that is not identical to 1,2,3,5,7-pentamethylcarbazole, from Kuwait oil. 11-Ethyl-1,2,3,4-tetrahydrocarbazolenine (VI) was identified in Wilmington oil from spectral data [71].

In addition to the enumerated neutral nitrogen compounds, which are not substituted at the nitrogen atom, components that, from their chromatographic behavior and mass spectra, are similar to N-alkylindoles and N-alkylcarbazoles were isolated from the heavy petroleum distillate [29]. The PMR spectra of these substances did not contain signals of protons of N-CH- groups. Snyder and co-workers [29] feel that such compounds should have N-cycloalkanoindole (VII) and N-cycloalkanocarbazole (VIII) structures rather than tert-alkylindole structures of the IX type, since the quaternary carbon atoms in the alkyl chains are in general only slightly distributed among the petroleum components.



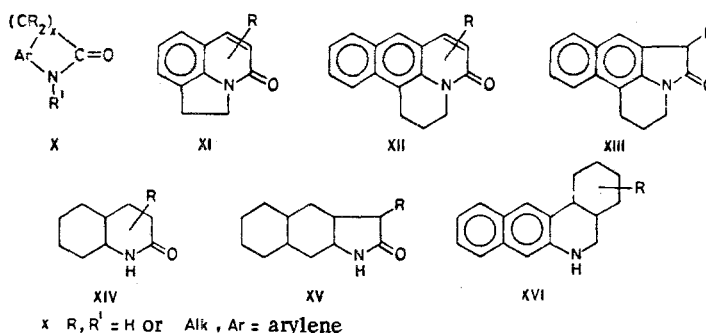
Nitrogen Compounds That Contain More Than One Heteroatom

Amides. We have already noted these are the secondmost significant class of neutral nitrogen compounds in oils. Gal'pern and co-workers [111] on the basis of IR spectra concluded that these compounds have the X structure, i.e., they contain an aromatic ring and a lactam group. The same conclusions were reached in a study of oils from Tadzhikistan [25] and the United Arab Republic (UAR) [113, 119]. It was later ascertained [120] that benzologs of pyridine, which, according to the mass spectral distribution, are very similar to the petroleum bases, are formed in the reduction of the amide fraction of Tadzhik oil with lithium aluminum hydride. These amides should have the nature of pyridones, quinolones, etc. [35].

Prior to this, 2-quinolones were identified as the major amide components of gas oil from California petroleum [79], which constitute 0.4% of the gas oil (0.05% based on the oil). This product did not contain 4-quinolones. The substances isolated were in the NH form (75%) and in the N-alkyl-substituted form (25%). The aliphatic substituents in their molecules contained an average of five carbon atoms and were bonded primarily to the heteroaromatic ring.

Pyridones and their benzologs were also found in Wilmington oil [29-31, 70]. With respect to their spectral properties, these compounds are closest to the benzologs of 2-pyridone, but the authors did not exclude the possibility of the presence also of 4-pyridones or 3-acetylindoles, which have similar spectra. In this study also the bulk of the isolated substances consisted of derivatives with an N-H group, and the smaller portion consisted of derivatives with an N-R group. As in the case of N-alkylindoles, the cycloalkanoquinolone structure (XI) was assigned to the later, since most of them have the composition $C_nH_{2n-13}NO$ according to the mass-spectrometric data. McCay and co-workers [35] isolated two fractions from petroleum amides. The components of one of them did not contain NH groups, and the N-cycloalkanobenzo[6, 7]quinolone structure (XII) or the XIII structure, which is similar to X, was assigned to them. Structures XIV-XVI were proposed for the components of the second fraction.

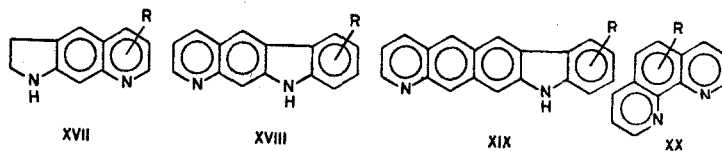
No individual amides have yet been isolated from crude oils, and all of the above-noted structures are only hypothetical structures that are in best agreement with the known IR, UV, and mass-spectrometric data.



Nitrogen-containing Carboxylic Acids. Seifert and Teeter [121, 122] isolated acids from Midway Sunset oil (California) by alkaline extraction and reduced them to alcohols, which were converted to hydrocarbons by tosylation and subsequent hydrogenation. Nitrogen-containing substances with the composition $C_nH_{2n-z}N$ ($z = 15, 17, 19,$ and 21), which were tentatively classified as alkylcarbazoles, alkylacridines, and their benzologs and various azapyrenes and azahydropyrenes, were detected in the resulting mixture. The detected nitrogen-containing carboxylic acids were distinguished by the presence of long alkyl chains containing an average of 10 to 18 carbon atoms.

Hydroxyl-containing Nitrogen Compounds. Hydroxypyridines and their benzologs, as well as dihydroxyquinolines, were found in the 370-455 and 455-538°C distillates from Wilmington oil [29, 31]. According to the IR spectroscopic data, the OH group is generally found in the 2 or 4 position. Kotova and co-workers [123] feel that when oil is fractionated, these compounds react with metal ions to give volatile quinoxides, which are carried over into the distillate fractions.

Compounds with Two Nitrogen Atoms. Since the percentage of basic nitrogen in the acid extracts from 316-538°C gas oil was found to be appreciably lower than the total nitrogen concentration, it has been assumed [71] that among the nitrogen bases there are compounds with two nitrogen atoms in the molecule: one in a basic function, and the second in a neutral function. The spectral data indicated the possible presence of pyrrolo-, indolo-, and carbazoloquinolines (XVII-XIX), but the mutual orientation of the rings and alkyl substituents was not established. The presence of compounds with a 1,10-phenanthroline structure (XX) was also ascertained.

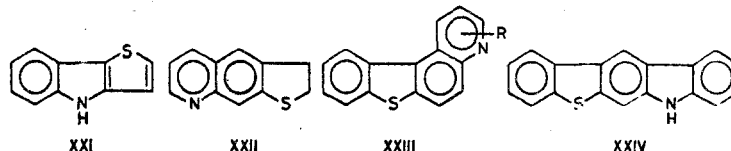


Compounds with two nitrogen atoms, which were eluted along with the benzologs of pyridine during chromatography, constituted 4% of the high-boiling fractions of Wilmington oil [29, 31]. The $C_nH_{2n-14}N_2$ series gave the most intense peaks in the mass spectrum. Snyder and co-workers [29, 31] felt that it was most likely that these compounds were 2-azacarbazoles and 6-azaindoles; azapyridine, 1-azacarbazole, and imidazole benzolog structures were considered to be unlikely, since they should have been eluted along with carbazoles because of their reduced basicity. However, different results were later obtained during an analysis of the same oil [35]: The chromatographic fraction of the benzologs of pyridine did not contain components with two nitrogen atoms, but compounds of the $C_nH_{2n-z}N_2$ series ($z = 12, 14,$ and $16,$ and $n = 15-31$) were eluted along with benzologs of pyrrole and amides. The problem of the structures of the petroleum components under examination is still open to discussion.

Compounds Containing Nitrogen and Sulfur. The concentrates of the nitrogen compounds isolated from oil by acid extraction usually contain a certain amount of sulfur. A mercurate with the composition $C_8H_9NSHg_2O_4$, which was assumed to be the double mercury salt of methylthiazole, was isolated from oil (Uzbekistan) in 1945 [124]. Gusinskaya and co-workers [4, 125-128] identified 4,5-diethyl-, 4,5-ethylpropyl-, 2-phenyl-4-methyl-, and 2-phenyl-4,5-dimethylthiazoles in oils from Southern Uzbekistan. On the basis of mass-spectrometric data, [62, 64, 78] benzothiazole structures were assigned to compounds isolated from oils from Tadzhikistan without evidence that the nitrogen and sulfur atoms are located in the same ring.

Thiazoles are not the most important components of oil that contain nitrogen and sulfur simultaneously, since only a small amount of sulfur can be removed in the form of mercurates from concentrates of the nitrogen compounds [125]. It has been shown by means of selective hydrogenation [129] that most of the heteroatoms in such substances are located in different rings. According to the data in [31], compounds that contain nitrogen and sulfur atoms are present only in the higher fractions (~2% of all of the nitrogen compounds in the 455-538°C distillate) and have $z \geq 15$. Most of these substances have basic character, and the rest have neutral character. A thiophenoindole (XXI) or thiophenoquinoline (XXII) structure is assumed to be most likely for them [70]. McCay and co-workers [35] isolated compounds containing nitrogen and sulfur atoms from the fractions of strong and weak bases and assigned XXIII and XXIV structures, respectively, to them. Substances containing two nitrogen atoms per sulfur atom have also been detected [35] among the weak bases by mass spectrometry.

Sulfur-containing compounds with spectral properties similar to those of quinolones were found [79] in the fraction of neutral nitrogen compounds of California oil; the presence of 2-thioquinolones in the oil was proposed on the basis of this finding.



Porphyrins

There are a number of reasons for the special interest of researchers in porphyrins. Porphyrins constitute the only reliably identified class of metal-containing components of petroleum cells. Because of their appreciable volatility porphyrins may be responsible for the passage of metal ions into the distillates during the fractionation of oil. The surface activity of porphyrins may promote stabilization of water-oil emulsions. The diphilic character of their molecules gives rise to specific interactions with rocks and plastic fluids and, consequently, to differentiation during the migration of oil; data on the percentage of porphyrins therefore sometimes make it possible to form a judgment regarding the processes involved in the formation of petroleum deposits [130-132]. It is assumed that porphyrins are inherited by oils from ancient organisms but underwent certain changes under the conditions in the depths of the earth. The exceptionally important role of porphyrins in biological oxide-reductase processes and the abundance of these pigments in all caustobioliths, carbonaceous meteorites, etc. make them a valuable subject for the study of the organization of an organic substance at different levels of its development, the genesis of petroleum, and other problems in the chemical evolution of organic compounds in nature [133, 134].

The concentration of porphyrins in oils varies from a vanishingly small value to hundreds of milligrams per liter (and, rarely, to several grams per liter) and increases on the average as the density, tarriness, and sulfurous character increase [135, 136].

The isolation of pure porphyrins from oil, which is described in detail in a review [134], is a difficult task. According to the experiments of Titov and co-workers [137, 138], the most acceptable method is one based on the extraction of the polar components of oil with dimethylformamide and subsequent concentration of the porphyrins by means of liquid adsorption chromatography.

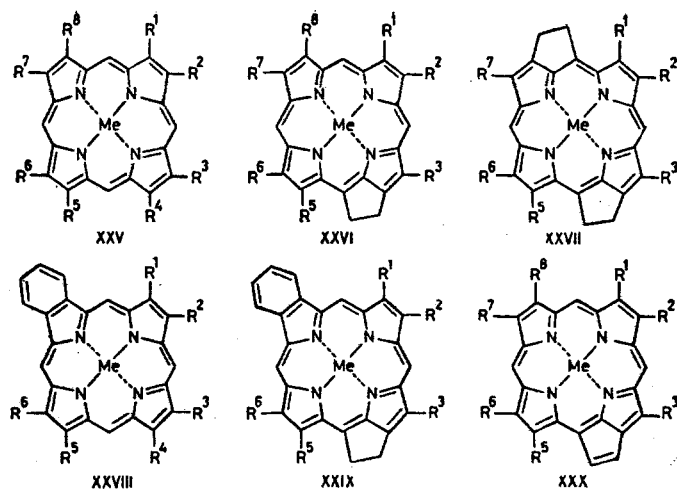
It has been established that oils contain porphyrins only in the form of metal complexes. Free porphyrin bases have been noted in the composition of a dispersed organic substance of rocks [139, 140]; it is possible that these results need to be verified. The number of metals included in the composition of petroleum porphyrins is extremely small: It usually includes vanadium in the vandyl (VO) form [141] and nickel. The presence of Fe porphyrins in oils is assumed in [142-145] on the basis of spectral data. Heavy sulfurous oils are usually rich in VO porphyrins, whereas Ni porphyrin complexes may be the dominant type in other (most often the youngest) oils [146-147].

Porphyrins that are not chemically bonded with other petroleum components have been investigated in the overwhelming majority of studies. However, gel chromatography demonstrated the presence among the porphyrin pigments of the oil of small amounts of compounds with molecular masses of 2000-20,000 and higher [148, 149], which are evidently products of condensation of the metalloporphyrins with components of the petroleum resins and asphaltenes. There are indications [150] of the presence in petroleum-saturated shales of dimeric VO porphyrins with a molecular mass of ~ 1100 . The chromatographic mobility and the intensity of the absorption bands in the IR spectra of these dimers are close to the corresponding characteristics of monomeric substances, but the coefficient of extinction in the electronic spectra is somewhat higher. It is assumed that the porphyrin rings undergo dimerization to give an aliphatic bridge between them; in this case the aromatic layers of asphaltenes serve as matrixes that give rise to the necessary orientation of the molecules [151].

A rather extensive chromatographic distribution of porphyrins was revealed in earlier studies [143, 152-155]. The authors of these papers, who did not have information on the character and orientation of the substituents in the porphyrin ring, attempted to explain the fractionation by the presence in the molecules of one or another number of carboxyl groups [143, 154]. However, the first mass-spectrometric studies [140, 156] refuted these

opinions and demonstrated that petroleum porphyrins are a complex mixture of alkyl-substituted compounds that form several homologous series. Demetallated porphyrins constitute two major series [157] with masses of $310 + 14n$ (series M, alkylporphyrins XXV) and $308 + 14n$ (series M - 2, cycloalkanoporphyrins XXVI), where n is the number of methylene groups in the alkyl chains, which ranges from 6 to 16. The molecular weight distribution of the members of each series is unimodal. Systematic studies later revealed the presence of another three homologous series (M - 4, M - 6, and M - 8) and the presence in each series of higher members containing up to 40-45 carbon atoms in side chains [158-162]. Bicycloalkano-, monobenzo-, and monobenzomonocycloalkanoporphyrin structures (XXVII-XXIX) were proposed for the components of the M - 4, M - 6, and M - 8 minor series [158, 159].

It was found that the relative fraction of the porphyrins of the M series decreases as the cyclic character of the hydrocarbon chain of the oil increases, the range of the change in the molecular masses becomes narrower, and the maxima in the distribution of the members of the individual homologous series are shifted [163].



The affiliation of the porphyrins of the M series with the etio type, which contain only alkyl substituents, is confirmed by all of the experimental data; their chromatographic mobility coincides with the mobility of synthetic alkylporphyrins with the same molecular mass. The mobility of compounds with close masses that belong to different series decreases [155, 157, 158, 161] in the order $M - 6 > M - 8 > M > M - 2 > M - 4$. The spectral and chromatographic properties of members of the M - 2 and M - 4 series are in agreement with the XXVI and XXVII structures proposed for them but do not exclude the possibility of the presence also of mono- (XXV, $R^2 = \text{cycloalkyl}$) or bicycloalkyl- and even cycloalkeno porphyrins (XXX). The XXVIII and XXIX structures assigned to the components of the M - 6 and M - 8 series are also questionable; it is unlikely that the chromatographic mobility of the compounds with this structure would be higher than that of alkylporphyrins. The mass-spectrometric data make it possible to assume the existence in these series also of phenyl-substituted (XXV, $R^2 = \text{C}_6\text{H}_5$) compounds, including also those containing additionally a naphthene ring. Demetallated porphyrins enriched in compounds of the M - 6 and M - 8 series have electronic spectra close to the rhodo type [140, 157, 158] (the spectra of the corresponding VO complexes are presented in [164-166]). There is no unified opinion regarding the true character of the electronic spectra of benzoporphyrins. Gurinovich and co-workers [167] feel that it should be of the khlorin type. In [155, 164, 168] porphyrins with spectra of the rhodo type were classified as compounds that contain COOH groups conjugated with the macroring. However, the IR spectra of these substances do not contain appreciable absorption bands of carbonyl groups [168, 169], and the high-resolution mass spectra of the products of their demetallization do not contain peaks of ions that contain any other elements than C, H, and N [157, 159]. The synthesis and investigation of authentic compounds are evidently necessary for the definitive identification of components of the M - 2, M - 4, and, particularly, the M - 6 and M - 8 series.

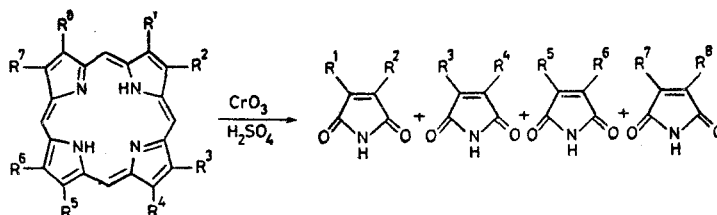
It has been pointed out [142, 145, 170, 171] that there are compounds that contain carboxyl and ester groups among petroleum porphyrins; however, a study [172] carried out especially to detect carboxyporphyrins and mass-spectrometric analyses [157, 158] did not confirm these conclusions. An attempt was made to explain these results by decarboxylation of the

pigments on contact with active sorbents in the course of separation or under the influence of electron impact [171]. It was assumed that carboxylated porphyrins do not get into petroleum because of selective sorption by rocks and can therefore be detected only by analysis of the core material [134]. The possibility of the presence of small amounts of carbonyl-containing porphyrins in the stratified petroleum system evidently cannot be completely repudiated.

All researchers postulate the allocation of alkyl substituents in the pyrrole rings; there is no direct evidence for the replacement of protons of the methylidyne bridges. Spectra of the phyllo type, which correspond to meso-alkylporphyrins, have often been observed [140, 152-158, 173], but this fact may also be associated with superimposition of the spectra of etio- and deoxophylloerythroetio types, which belong to the M and M - 2 series. Except for cases [162] in which spectra of the phyllo type were not observed, these series could not be separated by column [157, 158] or thin-layer chromatography [160, 161, 164-166, 168]. However, one of the authors of the present review observed the direct alkylation of etio-porphyrin-I in the meso position under the conditions of generation of alkyl radicals. It is possible that similar meso-alkylation processes may also occur in a petroleum medium. An indirect confirmation of the existence of meso-substituted porphyrins can evidently be obtained by destructive reduction and a study of the composition of the alkylpyrroles formed [174].

The lower members of the homologous series contain less than eight carbon atoms in the side chains [157, 158]; this indicates the presence of unsubstituted pyrrole protons in the molecules. It was found that there are also unsubstituted pyrrole positions in solid homologs containing up to 30-40 alkyl carbon atoms. The selective bromination of the pyrrole positions in petroleum porphyrins showed that 50-70% of the molecules present have one to two pyrrole protons and that the average number of protons of this type decrease as the molecular mass of the porphyrins increases [175].

It has been established that the products of the oxidative degradation of petroleum porphyrins include methyl- (citraconimide), ethyl-, methylethyl- (the major component), methylpropyl-, and ethylpropylmaleinimides [162, 176]. Unfortunately, porphyrins that were demetallated with methanesulfonic acid in an overall yield of 60% were oxidized in these studies [162]; the loss (decomposition) of a portion of the porphyrins during demetallation could distort the initial proportions of the individual structural fragments of the molecules.



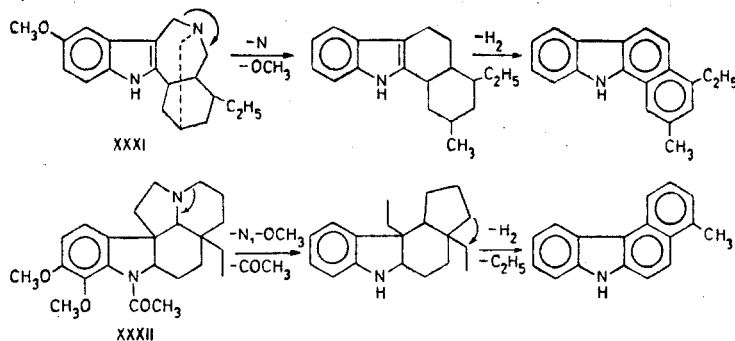
It has been shown that the molecules of the most chromatographically labile petroleum porphyrins contain substituents that have no less than 11-12 methyl groups in the chain [177]. The presence of alkyl chains 12-13-carbon atoms long in petroleum porphyrins was recently revealed by means of mass spectrometry of the metastable ions, and the possibility of the existence of branched substituents was observed [161, 177, 178]. Homologs with long side chains are even encountered among relatively low-molecular-weight porphyrins.

Thus petroleum porphyrins are complex mixtures of alkylated compounds. The total number of homologs contained in measurable amounts in oil exceeds 100; with allowance for possible isomerism, this may correspond to thousands of individual components.

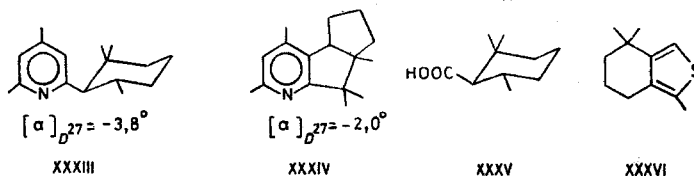
The detection of amino acid residues in the composition of the porphyrin fractions of oil is of exceptional interest [179-181]. Glycine, alanine, glutamic and aspartic acids, serine, and threonine were found in the acid hydrolyzate of concentrates of VO complexes; these acids are absent in Ni porphyrin concentrates. No information on the structure of the peptide portion and the character of its bonding with porphyrins is yet available; it is possible that the bond is a chemical bond, since after hydrolysis the specific retention volumes of porphyrins increase during gel chromatography [180], and their mobilities during thin-layer chromatography and their IR spectra change somewhat. The average molar ratio of amino acids (with respect to the amine nitrogen) to the porphyrins in the isolated fractions is 3.0-3.5 : 1 [179-181].

Origin of Petroleum Nitrogen Compounds

The genesis of petroleum nitrogen-containing substances is one of the most complex problems of the modern theory of the origin of petroleum. Evidence that the nitrogen compounds of petroleum were formed from the same petroleum parent substances as the other petroleum components and were not acquired by the oil during its migration and accumulation is presented in most papers. A reliable biological precursor has not yet been found for any of the individual nitrogen compounds detected in petroleum, although assumptions that they were formed from protein substances [26], nucleic bases [5] (purines and pyrimidines), and plant alkaloids [70, 117, 118, 182] have been expressed. Snyder [70, 118] links the observed peculiarities of the structures of petroleum benzocarbazoles (angular but not linear ring fusion) with the structures of typical plant alkaloids — ibogaine (XXXI) and aspidospermine (XXXII) — which are hypothetically transformed after burial via the following schemes:



Nitrogen compounds that have optical activity — an inherent property of biogenic material — were not identified in oils until relatively recently, when pyridine derivatives XXXIII and XXXIV, which appreciably rotate the plane of polarization to the left, were isolated from California oil in 1968 [28].



Attempts have been made to arrive at a solution of the problem under consideration by uncovering the features of the structural similarity between the nitrogen components and other components of petroleum. Thus there are obvious analogies in the structures of the carbon skeletons of XXXIII, 2,2,6-trimethylcyclohexylcarboxylic acid (XXXV), which was identified in the same oil [183], and cycloalkanothiophene XXXVI isolated from Middle-Eastern oil [184]. Ney and co-workers [184] regard the carotinoid pigments that are widely distributed in organisms are likely precursors of compounds of the XXXIII-XXXVI type. The number of such precursors should evidently be increased due to such polyunsaturated natural compounds as isoprenoids, sterols, acids, etc. It has been shown [185-188] that the latter are converted to aromatic hydrocarbons in early diagenesis. The idea [4, 125, 126] that there is a genetic relationship between the sulfur, oxygen, and nitrogen compounds of petroleum, which is based on the research of Yur'ev [189] on the interconversions of thiophene, furan, and pyrrole rings, has been expressed. A thorough study of diagenetic processes in systems that include heteroorganic substances may shed some light on the reasons for the most intimate analogies in the structures of the rings of native polycyclic hydrocarbons and heteroatomic compounds and provide keys to the decoding of the structures of many new petroleum components.

The problem of the origin of porphyrins somewhat is distinct from the general problem of the genesis of nitrogen compounds of petroleum. The formation of a porphyrin ring by condensation of pyrrole derivatives proceeds quite readily [190], particularly in the presence of metal ions, graphite [191], and rocks [192]. This is apparently the reason why porphyrins are detected in such clearly abiogenic objects as meteorites [193,194] and volcanic lavas and ashes [191]. Nevertheless, most researchers regard the prosthetic groups of biochromes — chlorophylls, hemoglobins, cytochromes, catalase, etc. — as the source of petroleum porphyrins

[5, 26, 130, 133, 134]. The study of the processes involving the conversion of the latter to petroleum pigments is far from complete. The presence of extensive homologous series in petroleum oils is explained [157] by trans-alkylation reactions; this is in agreement with the composition of the porphyrins from oils of different ages and the results of direct experiments [176]. A convincing explanation of the pathways of replacement of the Mg and Fe ions characteristic for biological complexes by VO and Ni ions has not yet been found; it is assumed [195, 196] that magnesium should be lost in the earliest stages of burial because of hydrolysis.

It is clear that nitrogen compounds have not received sufficient study and that in a genetic respect they constitute a much more mysterious group of petroleum components.

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