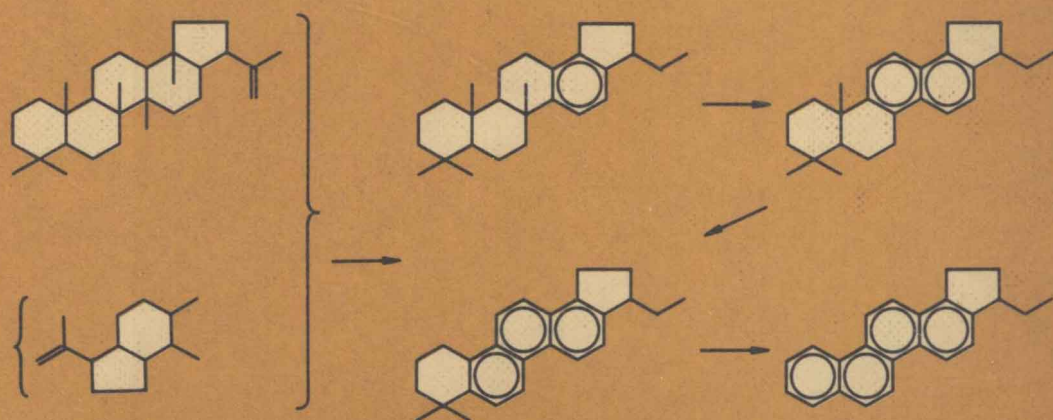


Alexander A. Petrov

Petroleum Hydrocarbons



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With 90 Figures

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Preface

The monograph analyzes contemporary data on the composition, structure and ways of formation of various petroleum hydrocarbons: alkanes, cyclanes and arenes. Special attention is paid to biological markers, compounds that could preserve main structural features of original biogenic molecules. Reviewed are modern concepts on chemical classification of crude oils based on molecular mass distribution of the principle biological markers. Certain matters pertaining to the genesis and chemical evolution of petroleum hydrocarbons are also discussed.

The book may be found helpful to a wide range of specialists: geochemists, chemists involved in petroleum industry, petroleum chemists, as well as graduate and postgraduate students and professorial staff.

The reviewing of the book by T.P. Zhuze, P.I. Sanin and J. Rullkötter is gratefully acknowledged.

ALEXANDER A. PETROV

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Introduction

This monograph is based on the research in the chemistry of petroleum hydrocarbons undertaken in the last 10–15 years by the Geochemical Laboratory of the Institute of Geology and Exploration of Combustible Fossiles (IG i GRI), although, naturally, full account was taken of the achievements of world science in this area.

Considerable success was registered in the last 15–20 years in elucidating the composition and structure of hydrocarbons in crude oils, coals and shales as well as dispersed organic matter. During this period, a new discipline evolved and obtained wide recognition, i.e. organic geochemistry, which entails the task of studying the composition and chemical evolution of organic molecules in the earth's crust. In effect, this field of science is a logical extension of the well-known chemistry of natural biological compounds.

Development of organic geochemistry proceeded on the basis of modern methodology, i.e. the application of molecular-level studies with the determination of both the structural and steric configuration of molecules, as well as the latest achievements of analytical and organic chemistry. Advancement of organic geochemistry is based on contemporary methods of analysis such as high resolution gas and liquid chromatography, gas chromatography-mass spectrometry with computerized data processing (including mass fragmentography) and ^{13}C NMR spectrometry.

However, the best research method in organic geochemistry is represented by the synthesis of standard samples. In effect, the majority of hydrocarbons to be discussed were first synthesized, then identified in crude oils. Naturally, initial evaluation of petroleum hydrocarbon. Structure can only be based on the analysis of crude oils.

As a result of investigations undertaken, over 700 individual $\text{C}_1 - \text{C}_{40}$ hydrocarbons of complex and unusual structure were identified in crudes. In the course of this research it was convincingly demonstrated that in their composition and structure petroleum hydrocarbons are complex and highly diversified organic molecules, which preserve information on the composition and construction of compounds comprising the lipid biosynthesis of ancient living organisms: algae, bacteria and higher plants. Of special significance was the discovery of the so-called relict hydrocarbons or biological markers (chemofossils), compounds which retained the basic structural features of the original biological molecules. Total concentrations of these compounds reach 35–40% in certain crudes, while their overall number exceeds 500. These biological markers are the focus of our attention.

Detailed information on crude oil composition is required not only in geochemical studies, but in petroleum chemistry as well. We could not completely agree with such a famous bio- and geochemist as Mr. Calvin who justly observed in his *Chemical Evolution* that "... petroleum composition should be established with great precision and in smallest details."¹

In fact, methods of petroleum hydrocarbon separation are being constantly refined and improved, thus practical applications of a much wider variety of individual hydrocarbons may be foreseen in the future.

The main thesis of the present monograph is that petroleum (its hydrocarbons) is not only a raw material for fuels and oils, but also a most valuable mixture of complex organic compounds, which is after all not limitless. Apparently, one of the best ways leading to a more rational use of this natural wealth is the ability to demonstrate the value of this gift of nature in the chemical versatility of petroleum hydrocarbons, presently extracted at a rate of over 2 billion tons a year.

The monograph consists of six chapters. The first one reviews certain general properties of petroleum hydrocarbons and presents examples of new classification schemes (chemical classification according to type), based on a combination of molecular and group-type methods in analyzing petroleum hydrocarbons. The homology of petroleum hydrocarbons is also discussed.

Chapter 2 is devoted to $C_5 - C_{40}$ petroleum alkanes of various structures. It also gives examples of GC (gas chromatography) analysis of different petroleum fractions and presents retention indices for a large number of branched alkanes.

Chapter 3 contains information on the composition, structure and regularities in the distribution of alicyclic hydrocarbons (cyclanes, naphthenes), which is a most interesting and characteristic class of petroleum hydrocarbons. Analysis of cyclanes begins with the simplest monocyclic hydrocarbons and ends with complex polycyclic molecular fossils – steranes and hopanes.

Chapter 4 reviews aromatic hydrocarbons with a varying number of aromatic nuclei in a molecule, as well as hydrocarbons of mixed (naphtheno-aromatic) type, which are known to be widely represented in crude oils. Of special significance in this respect are as yet marginally investigated aromatic hydrocarbons with a biogenic carbon skeleton.

The study of petroleum hydrocarbon composition and structure in Chapters 2–4 is based on contemporary perceptions as to the sources and ways of their formation in nature. At the same time, these issues are comprehensively treated in Chapter 5, which is specially devoted to the chemistry of petroleum formation. The latter chapter presents information on thermodynamic and kinetic control in reactions of certain petroleum hydrocarbon formations. Also reproduced are some experimental data on laboratory simulation of petroleum formation reactions.

Chapter 6 is devoted to the processes of chemical evolution of crude oils in sediments. Factors determining the composition of petroleum hydrocarbons, such as thermal transformations and biodegradation, are discussed and the results of laboratory experiments are presented.

¹ Calvin M. *Chemical Evolution*. M.:Mir, 1971, p 240 (in Russian).

Within his means, the author took scientific publications appearing between 1975 and 1984 into account. Earlier papers are quoted less extensively, since appropriate material was already reflected in a number of monographs and reviews mentioned in the text.

A particular feature of this publication is the frequent use of gas chromatograms, which allows the presentation of ample information on the composition of complex mixtures of petroleum hydrocarbons.

In presenting factual material, where possible, the author presents data not only on the structure, but also on the stereochemistry of petroleum hydrocarbons (mostly on the steric structure of epimers). More detailed information on the stereochemistry of these hydrocarbons is presented in a recently published monograph.²

Less attention is paid to the geochemical problems of petroleum formation, such as the original biomass composition, structure and transformation of kerogen, geological factors, etc., since these issues were exhaustively treated by Tissot and Welte in their monograph.³

In conclusion, the author wishes to express his gratitude to the staff and postgraduate students working in the Laboratory of Petroleum Geochemistry, who participated directly both in the experimental analysis of the composition of petroleum hydrocarbons and in the synthesis of standard hydrocarbons.

The author is also thankful to I. A. Matveeva and N. N. Abryutina who helped to prepare the graphic material for the publication.

² Petrov A. A. Stereochemistry of Saturated Hydrocarbons. M.: Nauka, 1981, 254 pp (in Russian).

³ Tissot B. P., Welte D. H. Petroleum Formation and Occurrence. Springer Verlag, Berlin, Heidelberg, New York, 2nd ed., 1984.

CHAPTER 1

General Characteristics of Petroleum Hydrocarbons Molecular and Group-Type Methods of Analysis and Classification

Hydrocarbons constitute the most important fraction in any crude oil. Although their proportion in different crudes varies significantly (e.g. from 30–40% to 100% in gas condensates), they comprise up to 70 mass % in all petroleum on the average. The history of petroleum chemistry, as a scientific discipline, is in effect the history of the chemistry of hydrocarbons. Research in petroleum chemistry was initiated in the 1860's by the well-known German chemist K. Shorlemmer, who discovered n-butane, n-pentane and n-hexane in crude oils from Pennsylvania (USA). Shorlemmer's success was due largely to his prior involvement in the synthesis of normal alkanes, conducted in the laboratory of his mentor, A. Würz. The Russian chemist, V. V. Markovnikov, while studying local crude oils from the Baku region 20–25 years later, concluded that it is not aliphatic, but alicyclic hydrocarbons, i.e. saturated hydrocarbons of the cyclopentane and cyclohexane series, which he called naphthenes, that prevail in crudes. And again this discovery was aided by Markovnikov's previous engagement in the synthesis and research of cycloalkane properties, undertaken in the laboratory of A. M. Butlerov. Thus, by the end of the 19th century, the methodological foundations for petroleum chemistry were already established, i.e. the synthesis of model hydrocarbons with their further identification in crudes. It was also then that original concepts on the chemical classification of oils emerged, suggesting their division into two main classes: paraffinic and naphthenic oils.

The “individual compound” (molecular) approach in the study of crude oil continued in the 20th century, though it was slowed down by the compositional complexity of petroleum hydrocarbons and inadequate analytical techniques. However, by the end of the 1950's investigations within Project 6 of the American Petroleum Institute, headed by F. D. Rossini, allowed the identification of over 150 hydrocarbons in a standard petroleum, belonging mostly to the light boiling fraction.

At the same time, the growing importance of oil in the world economy and the rapid development of oil processing necessitated at least some general knowledge of the chemical composition of a large number of crudes. Therefore, together with research on the molecular level, another avenue was explored, that of group-type analysis, based on the relative proportions of three different classes of petroleum hydrocarbons: alkanes, cyclanes and arenes.

Classification proceeded on the basis of information on the content of these three main classes of hydrocarbons, as well as the particulars of technological processes, such as the contents of resins, asphaltenes, sulfur, solid paraffins, etc.

In the 1940's, Nametkin (1950) and Dobryansky (1961) proposed a classification scheme of crude oils based on their group composition. Crudes were grouped in accordance with 14 indicators into 7 classes, varying in concentrations of aliphatic series hydrocarbons. Later, these schemes became more sophisticated. For example, the comprehensive formal-logical system of Kontorovitch (Kontorovitch and Stasova 1978) included 180 (!) classes of oils, varying in physical and chemical characteristics. Similar classification schemes were proposed by Vassoevitch (Vassoevitch and Berger 1968). An obvious methodological advantage of these classification schemes was that they were based on the analysis of all petroleum properties and not just those of light-boiling fractions, as often done before. However, only few of these classes actually exist in nature. Moreover, it is next to impossible to use these cumbersome schemes in their entirety. Therefore, Kontorovitch suggested only four basic types of crudes: (1) aliphatic, paraffinic; (2) aliphatic, low-paraffinic; (3) alicyclic-aliphatic; and (4) alicyclic. In a recently published comprehensive monograph, Tissot and Welte (1981) identified six different crude oil types: paraffinic, paraffinic-naphthenic, naphthenic, aromatic-intermediate, aromatic-naphthenic and aromatic-asphaltic. Various classification arrangements are reviewed in the monograph of Sokolov (1965). All the above classification schemes may apply to crudes as sources of fuels and lubricants, but may only partially be used in geochemistry, where the most important data can only be obtained by a classification based on the distribution of individual (primarily biological) hydrocarbons.

In the early 1960's new powerful analytical methods were elaborated (GC, gas chromatography-mass spectrometry) which completely revised our views on the composition and structure of petroleum hydrocarbons, hence, on the principles and methods of crude classification. The identification of a large number of biological markers (chemofossils) was an indisputable "discovery of the century". We include all hydrocarbons which retained specific structural features or the original biological molecules into this group, regardless of whether they were present in the initial biomass as hydrocarbons or were formed later from other compounds with functional groups (the chemistry of petroleum formation is analyzed in Chap. 5).

Biological Markers and Transformed Hydrocarbons

Hypothetically, all petroleum hydrocarbons can be subdivided into two main groups: (1) transformed hydrocarbons which have lost the structural features of the original biological molecules and (2) biological markers of chemofossils. Among the most important biomarkers we find: normal and isoprenoid alkanes and cyclic isoprenoids, e.g. steranes, triterpanes, etc.

Furthermore, all relict petroleum hydrocarbons can be subdivided into two main groups:

1. Biomarkers of isoprenoid type, both aliphatic and alicyclic, with one to five cycles per molecule.
2. Biomarkers of non-isoprenoid type represented mostly by aliphatic compounds with n-alkyl or slightly branched chains.

Biological markers of isoprenoid type are mostly represented by regular "head-to-tail" structures, although some hydrocarbons were found in crude oils with a "head-to-head" or "tail-to-tail" combination of isoprenoid units. Isoprenoid biomarkers are represented by a much greater variety of compounds than the non-isoprenoids.

Curiously, even in the early 1960's, a fairly pessimistic view was taken of the possibility of discovering biological markers in crudes. Thus, a well-known expert in petroleum chemistry, Dobryanskii (1961), wrote in his *Petroleum Chemistry*: " . . . V. I. Vernadskii, speaking of petroleum properties conceived in organisms, was correct only as far as a limited quantity of highly stable compounds, such as porphyrins, is concerned. It its turn, the hydrocarbon material was reprocessed to such an extent, that it lost all inherited traces of the original matter."

However, already in 1962 aliphatic isoprenoids were discovered in petroleum, followed by steranes, hopanes, and other biomarkers.

Since then, biological markers of crudes, coals, shales and dispersed organic matter continue their virtually triumphant march on the pages of science magazines, monographs and congressional papers. As was mentioned, over 500 such hydrocarbons have been discovered, their number increasing annually.

Homology of Biological Markers

Homology is the most important property of biological markers. Homology depends on the fact that these hydrocarbons are usually present in series of homologs having a common structural moiety. It should be stressed that we regard homology from a wider angle, as compared to ordinary study courses in organic chemistry. Thus, apart from homologous series of normal alkanes, we can identify homologous series of 2-methylalkanes, 3-methylalkanes, 4-methylalkanes, etc. Homologous series of 1-methyl-2-alkylcyclohexanes, 1-methyl-3-alkylcyclohexanes, etc. can also be isolated. In all cases, a homologous series is formed by a common structural group, with an additional alkyl chain of varying length. The homology of petroleum biomarkers is explained by the peculiarities of their formation by the destruction of aliphatic chains at different positions in appropriate geopolymers (kerogen). Details of this reaction will be reviewed later (see Chap. 5). From this viewpoint it becomes clear why pseudo-homologous series of isoprenoid compounds are usually characterized by concentrational "dips" of each fifth homolog, since simultaneous rupture of two bonds is obviously impossible at the branching point (see Chaps. 2 and 3).

Another important property of biological markers is represented by their relatively high concentration in crudes, usually exceeding equilibrium concentrations of similarly structured isomers.

Biological markers are also important, since they serve as a source in the formation of a certain portion of severely transformed petroleum hydrocarbons, and hence, facilitate the analysis of this intricate part of petroleum.

As was mentioned, biological markers are closely connected to original biological molecules. This connection helps to elucidate the structures of petroleum hydrocarbons, because homologous series usually possess structural properties

typical of the original material, reproduced later in petroleum derivatives. Earlier, this principle was applied in establishing the structures of isoprenoid compounds in accordance to different biogenic schemes (Waisberger 1967). Examples of such reconstructions are reviewed in Chapter 3.

The role of biological markers, especially in petroleum geochemistry, can hardly be overestimated. Firstly, their high concentration proves the biogenic nature of crude oils. Secondly, chemofossils are used as indicators of sedimentation conditions (Tissot and Welte 1981) in order to determine hydrocarbon source rocks, to reconstruct various oil-oil and oil-source rock relationships and to evaluate the thermal maturity of dispersed organic material. These compounds are also widely used in exploration in order to appraise the oil-bearing properties of various regions. A comprehensive review of the application of petroleum biomarkers for geochemical purposes was recently published by Mackenzie (1984).

Advances in organic and petroleum geochemistry created preconditions for the elaboration of new classification schemes of crude oils (according to chemical types), based on the molecular-level analysis of crude oils. Optimal results were achieved by combining molecular and group-type methods. One of these classification schemes was designed in the Laboratory of Petroleum Geochemistry (IG i RGI) and is based on a combination of GC data on the distribution of the most important alkane biomarkers, with MS (mass spectrometric) information on the quantitative distribution of saturated molecules, depending on the number of cycles per molecule (Zabrodina et al. 1978). The classification scheme proposed below is a refinement of our scheme suggested in the *Chemistry of Alkanes* (Petrov 1974).

Chemical Classification of Crude Oils

As was already mentioned, chemical classification is based on gas chromatography of whole oils using capillary columns with $25-30 \times 10^3$ theoretical plates and operating in the linear temperature programming mode. Experimental details have been presented (Zabrodina et al. 1978). Analysis of the bulk of a petroleum allows one to avoid quantitative errors often appearing in the separation of individual fractions, and helps to establish undistorted parameters of the relative concentrations of the most important biological markers: normal ($C_{12}-C_{35}$ range) and isoprenoid alkanes ($C_{14}-C_{25}$ range). Additionally, the group composition of the main fraction (the so-called petroleum body), i.e. a fraction boiling between 200° and 430°C ($n-C_{11}-n-C_{27}$) can be determined.

The distribution of saturated molecules as a function of the number of cycles per molecule (0–5 cycles), determined by Polyakova (1973), gives a detailed characterization of saturated hydrocarbons in the crudes under investigation. If necessary, an appropriate MS analysis of aromatic hydrocarbons may also be conducted (see Chap. 4). Moreover, mass spectrometry helps to determine the total contents of both normal and branched alkanes separately. A similar scheme of analysis was applied by the French Institute of Petroleum in its studies of numerous crudes (Tissot and Welte 1981).

Table 1. The composition of the 200°–430°C boiling fraction in crudes of different chemical types

Oil Field	Depth (m)	Crude type	Fractional composition (%)			Alkanes (%)			Pristane/ phytane	C ₁ ^a	Σn-C ₁₃ -n-C ₁₅	Naphthenic fingerprint rel. %					
			Paraf-fins	Naph-thenes	Aroma-tics	Nor-mal	Iso-prenoid	Iso-alkane				Σn-C ₂₅ -n-C ₂₇	Mono-cyclic	Bi-cyclic	Tri-cyclic	Tetra-cyclic	Penta-cyclic
Timano-Pechora Oil and Gas Basin																	
Solyukskoe	1603	A ¹	32.1	28.9	39.0	29.9	11.8	58.3	1.0	0.8	1.8	27.3	32.2	20.4	13.5	6.6	
Djiverskoe	800	A ²	9.9	22.1	68.0	15.2	22.2	62.6	1.1	3.3	0.8	39.6	28.6	15.9	8.7	7.2	
Varandeiskoe	—	A ¹	19.6	44.5	35.9	25.0	10.7	64.3	1.1	0.6	2.6	23.9	30.4	23.8	14.3	7.6	
Yaregskoe	200	B ²	4.6	17.0	78.4	—	5.5	94.5	1.4	—	—	24.0	30.1	21.1	16.3	8.5	
W. Tebuk	1943	A ¹	33.0	32.2	34.8	28.5	9.4	62.1	1.1	0.7	1.1	31.5	30.9	17.4	13.2	7.0	
—	—	A ²	26.4	33.8	39.8	21.6	23.5	54.9	1.2	3.1	0.7	33.9	32.5	18.8	10.2	4.6	
Vozeiskoe	1612	A ¹	48.7	33.4	17.9	33.3	4.1	62.6	0.91	0.4	1.5	39.4	30.7	12.5	11.1	6.3	
—	1627	A ¹	33.3	35.0	31.7	25.8	6.9	67.3	1.2	0.5	3.1	27.7	30.7	21.3	13.1	7.2	
E. Grubeshor	3675	A ¹	36.8	44.7	18.5	19.8	6.1	74.1	2.5	0.5	3.2	34.5	30.0	17.3	11.1	7.1	
Shapkinskoe	1714	A ¹	35.6	33.9	30.5	30.9	8.1	61.0	1.7	0.5	1.6	30.0	28.1	20.6	13.2	8.1	
Pashninskoe	2742	A ¹	32.9	28.9	38.2	24.0	5.8	70.2	1.0	0.8	1.0	31.0	32.1	20.3	12.9	3.7	
Usinskoe	2300	A ¹	42.2	28.9	28.9	25.2	5.9	68.9	0.8	0.6	2.2	34.6	29.8	16.3	13.4	5.9	
Volga-Urals Oil and Gas Basin																	
—	—	B ²	9.6	44.9	45.5	—	12.5	87.5	1.2	—	—	25.0	27.1	19.2	17.3	11.4	
Zhirnovskoe	1750	A ¹	32.6	44.4	23.0	29.5	10.7	59.8	1.7	0.7	1.7	36.5	26.7	14.2	13.5	9.1	
—	—	A ¹	32.5	23.5	44.0	25.9	6.4	67.7	0.8	0.4	3.1	31.8	29.0	18.7	13.0	7.5	
Tuyimazinskoe	1880	A ¹	35.0	30.2	34.8	32.6	6.6	60.8	0.6	0.4	3.1	34.3	31.0	16.9	11.2	6.6	
Bavinskoe	1165	A ¹	30.4	19.6	50.0	37.2	8.9	53.9	0.5	0.6	0.8	30.5	31.6	20.9	10.2	6.8	
Enarusinskoe	1356	A ¹	30.9	21.9	47.2	23.6	5.8	70.6	0.5	0.5	1.3	27.9	42.8	15.5	9.4	4.4	
Stepnozerskoe	—	A ¹	30.9	21.9	47.2	23.6	5.8	70.6	0.5	0.5	1.3	27.9	42.8	15.5	9.4	4.4	
Mordovo-	80	B ²	20.1	34.5	45.4	—	24.9	75.1	0.6	—	—	29.9	31.5	21.3	11.9	5.4	
Karnalskoe	—	A ¹	27.8	35.0	37.2	43.2	8.6	48.2	1.4	0.4	1.5	30.6	28.4	17.9	15.0	8.1	
Kasibskoe	—	A ¹	27.8	35.0	37.2	43.2	8.6	48.2	1.4	0.4	1.5	30.6	28.4	17.9	15.0	8.1	
Durinskoe	1870	A ²	7.2	20.8	72.0	13.9	11.1	75.0	1.1	1.5	1.4	28.5	32.1	20.9	13.1	5.4	
—	2012	A ¹	41.7	24.6	33.7	28.8	5.0	66.2	1.4	0.3	1.3	31.0	30.4	18.3	12.3	8.0	
Tikhovskoe	800	A ¹	16.2	15.6	68.2	40.1	8.0	51.9	0.71	0.3	1.5	31.1	25.5	19.7	16.9	6.8	

Sivinski	2806	B ²	9.2	53.3	37.5	—	19.6	80.4	1.0	—	—	13.5	30.3	28.1	18.9	9.2
Novo-Elkhovskoe	1618	A ¹	25.6	22.4	52.0	29.3	9.0	61.7	0.5	1.6	2.4	28.3	31.0	19.6	12.8	8.3
Tchapaevskoe	—	A ¹	50.9	26.4	22.7	25.7	13.8	60.5	0.55	0.5	6.5	39.5	29.6	14.3	11.2	5.4
Near-Caspian Oil and Gas Basin																
Kursaiskoe	4410	B ¹	7.6	67.7	24.7	—	—	—	—	—	—	16.3	29.1	25.3	18.5	10.8
Sagizskoe	800	B ¹	7.9	66.4	25.7	—	—	—	—	—	—	17.8	28.2	25.5	17.8	10.7
Karajانبas	300	A ²	16.6	44.4	39.0	12.9	25.7	61.4	0.91	3.8	1.5	24.4	29.8	22.8	14.0	9.0
Koshkar	—	A ¹	26.3	53.7	20.0	13.7	6.1	80.2	1.4	0.7	2.4	28.3	27.6	21.0	13.8	9.3
Kalamkas	847	A ²	25.2	44.1	30.7	13.0	8.3	78.7	1.0	1.6	0.5	30.4	29.8	20.8	13.3	5.7
N. Buzatchi	440	A ²	19.2	46.2	34.6	12.0	18.8	69.2	1.1	3.5	0.8	27.3	29.0	21.9	13.8	8.0
E. Prorva	3179	A ¹	30.8	44.7	24.5	26.0	5.2	68.8	0.91	0.3	0.9	24.3	26.3	22.2	17.1	10.1
Bilkan	5712	A ¹	27.0	40.6	32.4	18.1	5.2	76.7	1.6	0.6	3.0	31.9	28.4	18.6	13.7	7.4
Bekturly	2410	A ¹	51.0	36.5	12.5	46.9	4.5	48.6	1.07	0.2	1.0	31.6	26.4	17.0	16.9	8.1
Kenkiyak	330	B ¹	8.7	58.2	33.1	—	—	100	—	—	—	19.1	30.1	23.7	17.0	10.1
Dnepr-Donetsk-Privyat Oil and Gas Basin																
Sagaidakskoe	4600	A ¹	49.9	36.6	13.5	38.1	10.2	51.7	0.91	0.6	2.0	30.4	28.5	15.0	17.5	8.6
Prilukskoe	—	A ¹	38.1	35.9	26.0	28.4	8.9	62.7	0.83	0.7	1.1	31.0	27.9	17.0	14.2	9.9
Retschitskoe	2193	A ¹	31.1	23.1	45.8	28.6	5.5	65.9	1.0	0.4	2.0	24.7	34.0	20.4	14.6	6.3
Tishkovskoe	3688	A ¹	41.0	28.9	30.1	29.0	7.8	63.2	0.83	0.6	1.8	26.8	29.0	16.9	21.5	5.8
Ostashkovitchi	2750	A ¹	33.6	24.9	41.5	31.0	10.1	58.9	0.55	0.7	1.5	21.6	25.2	21.9	23.3	8.0
Ostashkovitchi	3663	A ¹	35.3	25.6	39.1	26.6	8.2	65.2	0.77	0.6	1.2	27.4	30.2	17.6	19.3	5.5
Barsukovskoe	3504	A ¹	38.8	21.6	39.6	32.5	4.6	62.9	1.25	0.3	1.1	27.0	27.9	19.8	17.3	8.0
Mozyrskoe	3350	A ²	31.2	30.8	38.0	18.6	10.3	71.1	1.0	1.4	5.4	24.8	23.3	24.9	16.5	10.5
Zavodya	3425	A ¹	42.7	30.4	26.9	34.9	9.6	55.5	1.67	0.9	0.5	23.3	20.1	22.0	24.3	10.3
South Caspian Oil and Gas Basin																
a) Azerbaijan																
Balakhanskoe	—	B ²	17.4	59.6	23.0	—	16.4	83.6	1.1	—	—	20.6	26.5	21.6	21.2	10.1
(Oleaginous)	1302	B ²	10.2	69.8	20.0	—	20.4	79.6	1.25	—	—	22.9	26.8	18.6	21.1	10.6
(Heavy)	1400	A ²	20.0	48.0	32.0	15.4	65.2	19.4	1.1	14.6	1.0	24.9	29.9	20.6	16.3	8.3
Neftyanje	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
Kamni	2574	B ²	14.3	44.7	41.0	—	15.0	85.0	1.0	—	—	24.4	26.6	19.5	19.9	9.6
Surakhanskoe	867	A ²	26.8	37.2	36.0	21.6	20.5	57.9	1.43	2.1	0.4	25.8	27.3	18.7	18.8	9.4
Sangatchaly	4782	A ¹	35.4	40.2	24.4	31.6	8.8	59.6	1.67	0.7	1.4	22.6	26.6	20.7	20.3	9.8

Table 1 (continued)

Oil Field	Depth (m)	Crude type	Fractional composition (%)			Alkanes (%)		Pristane/phytane	C_i^a	$\Sigma n-C_{13}$ - $n-C_{15}$	Naphthenic fingerprint rel. %			
			Paraffins	Naphthenes	Aromatics	Normal	Iso-prenoid				Mono-cyclic	Bi-cyclic	Tri-cyclic	Tetra-cyclic
Duvannyi-more	3440	A ¹	24.1	36.9	39.0	32.4	13.3	1.43	1.3	0.9	21.2	25.9	21.5	21.0
	3500	A ²	17.2	50.8	32.0	23.8	61.6	1.43	6.6	1.5	19.4	24.6	21.4	23.5
	3904	A ²	23.3	51.5	25.2	23.0	22.1	1.67	2.7	0.9	19.4	22.8	20.2	23.6
	4594	A ¹	28.8	37.7	33.5	38.9	12.5	1.43	0.8	1.0	20.2	25.8	20.6	22.1
	5203	A ¹	44.2	31.8	24.0	25.9	7.2	1.67	0.6	4.8	21.9	27.5	20.5	20.4
Isl. Garasu	—	A ¹	25.9	37.7	36.4	42.8	13.7	1.25	0.5	0.4	15.9	21.1	20.0	27.8
Gryazevaya Sopka	1006	B ¹	9.1	53.9	37.0	—	—	—	—	—	23.4	29.5	21.8	17.2
Surakhany	1674	B ¹	6.9	43.1	50.0	—	—	—	—	—	23.0	27.6	21.3	19.4
b) Turkmenistan														
Kotur-Tepe	1700	A ²	22.7	52.3	25.0	18.1	13.7	1.25	2.1	0.9	22.9	26.6	19.7	20.6
	2500	A ¹	30.9	40.1	29.0	27.8	12.3	1.25	1.0	1.6	25.9	27.1	19.2	18.6
Dagadjikskoe	900	B ²	23.7	50.3	26.0	—	14.8	1.25	—	—	24.5	28.0	19.7	19.6
	1000	A ²	9.6	30.4	60.0	11.5	26.0	1.25	13.9	3.5	25.6	27.9	20.3	18.6
Oval-Toval	1951	A ¹	41.9	33.1	25.0	42.2	8.6	1.43	0.5	1.2	24.3	28.3	19.6	19.1
	1100	A ²	28.5	52.2	19.3	12.8	18.3	1.43	3.4	1.6	24.9	25.8	17.2	22.6
Kamishldja	1000	B ²	32.2	45.3	22.5	—	8.2	1.25	—	—	34.6	33.6	18.0	9.0
West Siberian Oil and Gas Basin														
Russkoye	837	B ¹	6.8	49.1	44.1	—	—	—	—	—	15.9	26.8	26.1	21.0
N. Kom-somolskoe	1000	B ¹	9.1	49.2	41.7	—	—	—	—	—	21.7	29.2	21.4	19.1
Novoportovskoe	987	B ¹	8.0	47.0	45.0	—	—	—	—	—	18.4	24.1	25.1	21.8
	1828	A ²	21.9	28.1	50.0	16.9	13.2	2.5	7.1	0.2	31.3	30.2	15.8	15.4
	1973	A ¹	31.1	28.0	40.9	36.3	10.0	2.0	0.5	1.4	31.5	27.1	19.1	15.7
	1870	A ¹	36.9	21.2	41.9	28.9	4.4	2.5	0.3	1.7	31.3	29.8	20.1	13.3
Taitymskoe	2600	A ¹	60.8	25.7	13.5	60.9	9.0	0.77	0.4	0.6	27.8	33.6	18.0	13.5