

Composition of the dewaxed medium-viscous Romashkino-Mukhanovo lubricating oil distillate

Š. HOLOTÍK, M. KURAŠ, and V. VESELÝ

^a*Department of Chemistry and Technology of Petroleum, Slovak Technical University, 880 37 Bratislava*

^b*Department of Petroleum and Petrochemistry, Institute of Chemical Technology, 166 28 Prague*

Received 30 September 1971

Accepted for publication 3 March 1972

Fractions of the title lubricating oil distillate obtained by chromatography have been analyzed by mass spectrometry and the suitability of the method in group-type analysis has been verified. The occurrence of certain types of compounds in the petroleum under investigation has been examined.

The early methods used in structural group analysis were based on physical properties of the petroleum [1, 2]. Later on infrared spectrometry [3, 4] and nuclear magnetic resonance spectrometry [3, 5] was adapted for this purpose. In contrast to the above-mentioned methods, certain types of hydrocarbons can be determined using ultraviolet spectrometry [6]. Mass spectrometry offers far better possibilities for determination of major types (more frequently groups of types) of hydrocarbons, sulfur-, nitrogen-, and oxygen-containing compounds of petroleum. Great progress in the analysis of petroleum has been achieved by the application of high resolution mass spectrometry. These kinds of instruments make it possible, after a thorough fractionation of petroleum, to determine the individual members of certain homologous series of hydrocarbons or other types of compounds. The number of components measured quantitatively by mass spectrometry in combination with certain separation procedures and other spectral methods approaches one thousand [7]. In this work we deal with the problems related to the low resolution analysis of lubricating oils.

Experimental

The investigated substrate was a dewaxed medium-viscous oil distillate obtained from a mixture of Romashkino-Mukhanovo crude oil. The mixture was fractionated on silica gel (0.05–0.15 mm). Four metal columns (3 m long) with diminishing diameter, each containing 16.5 kg of packing were used. On the whole 40 kg of oil was fractionated in 2 kg runs per column. The packed column was first washed with 4 l of petroleum ether (b.p. 50–70°C) and then 2 kg of petroleum in 2 l of petroleum ether was pressed into the column which was then washed successively with 5 l of petroleum ether, petroleum ether containing 10, 20, 33, 50, and 66 volume % of benzene (3 l of each) and finally with 3 l of benzene. The flow rate was 0.1 l/min. Asphalts were eluted with benzene–ethanol (1 : 1), ethanol, and finally with water. The fractions were combined according to the increasing refractive index (in approximately 0.01 increments), and rechromatographed in a similar manner. The separation achieved was such that a fraction of saturat-

ted hydrocarbons free of aromatics and their mixture and several relatively homogeneous fractions of aromatic hydrocarbons were obtained.

Mass spectra were obtained with an LKB-9000 spectrometer having a maximum resolution of $M/\Delta M$ equal to 1000 at 70 eV. The individual chromatographic fractions were analyzed directly except the very viscous ones which were diluted with benzene. The first two fractions were analyzed as saturated hydrocarbons which may contain monoaromatics according to Hood and O'Neal [8]. A C_{32} matrix for isoalkanes was used for the calculation of the spectra. The aromatic concentrates were analyzed using the method of Hastings *et al.* [9].

Results and discussion

Chromatographic separation of the starting oil afforded 16 fractions [10]. Their characteristics are summarized in Table 1.

Table 1
Characteristics of the investigated fractions

Fraction	Weight %	M [g mol ⁻¹]		ρ [g cm ⁻³]	% S
Crude oil	—	373	1.5175	0.9274	2.25
1	33.16	406	1.4715	0.8567	0
2	4.19	405	1.4927	0.8880	1.10
3	5.18	388	1.5041	0.9046	1.25
4	10.80	375	1.5136	0.9212	1.80
5	3.08	372	1.5226	0.9431	2.55
6	3.24	368	1.5380	0.9602	3.40
7	3.09	364	1.5458	0.9703	3.80
8	5.35	362	1.5560	0.9844	4.30
9	3.75	353	1.5640	0.9989	4.70
10	3.63	349	1.5738	1.0077	4.90
11	2.93	330	1.5850	1.0226	4.95
12	1.65	328	1.6023	1.0424	5.30
13	1.04	324	1.6115	1.0597	5.57
14	1.31	319	1.6243	1.0718	5.80
15	1.49	323	1.6353	1.0874	5.90
16	0.86	323	1.6510	1.1020	5.70

M — Average-molecular weight determined ebullioscopically.

% S — Determined using the method of Grotte and Krekeler.

The mass spectra were evaluated by the two most commonly used methods. Applying the procedure of Hood and O'Neal [8] only the spectra of the first two fractions, containing but admissible amounts of monocyclic aromatic hydrocarbons, could be evaluated. The results of the analysis of these fractions are in Table 2.

The analysis showed that the investigated oil contained alkanes, monocycloalkanes, and condensed di-, tri-, tetra-, and pentacycloalkanes. Condensed hexacycloalkanes were not found. The first two fractions were rich in alkanes. Unexpectedly, the content of these was even higher in the second fraction. However, based upon the content of sulfur in this fraction (1.1%), it contains about 14% of sulfur-containing compounds. As the method of evaluation does not take into account the contribution of sulfur-containing components to the mass summation characteristic of alkanes, these com-

Table 2

Group-type analysis of saturated hydrocarbons-rich fraction of oil

Type	Fraction [weight %]	
	1	2
Alkanes	36.4	46.6
Monocycloalkanes	22.0	17.1
Dicycloalkanes	16.0	7.7
Tricycloalkanes	14.7	7.9
Tetracycloalkanes	8.7	7.5
Pentacycloalkanes	1.4	1.0
Hexacycloalkanes	0	0
Alkylbenzenes, benzocycloalkanes	0.8	12.2

pounds may seemingly increase the content of alkanes in the second fraction. This assumption needs further investigation.

Fractions 3, 4, and 5 are mixtures of saturated and aromatic hydrocarbons the mass spectra of which could not be reliably evaluated using the methods applied. The data deduced from the spectra are merely of qualitative importance.

Subsequently eluted fractions contain but negligible quantity of alkanes and cycloalkanes. Thus, starting with fraction 6, the spectra of the following fractions could be evaluated using the method of *Hastings et al.* [9]. The results of the analysis of fractions 6–15 are summarized in Table 3.

All of the twelve groups of types of compounds determinable in the aromatic concentrates by the group-type analysis, except chrysenes, were found. Seven groups of types, *i.e.* alkylbenzenes, benzomonocycloalkanes, benzodicycloalkanes, benzotricycloalkanes, with alkylnaphthalenes, naphthomonocycloalkanes with biphenyls, naphthodicycloalkanes with fluorenes and acenaphthylenes, as well as benzothiophenes, were found in all aromatic fractions.

Since the content of some of the types of compounds in consecutive chromatographic fractions was found to vary irregularly, their changing content was evaluated graphically. It can be seen that only benzothiophenes have a simple elution curve (Figs. 1 and 2), which has a shape of a striking elution zone. The peak of the zone is in the eighth fraction after which the content of benzothiophenes decreases.

Monocyclic aromatic hydrocarbons have a completely different elution curves. It can be assumed, from the graphical dependence of the content of alkylbenzenes, benzomonocycloalkanes, and benzodicycloalkanes, that these types of compounds have the peak of the elution zone in the fifth or sixth fraction. Starting with the sixth up to the ninth fraction the content of these substances decreases, whereafter it does not change significantly. In this part of the elution curves some poorly pronounced maxima were observed (Fig. 1).

Different shape of the elution curves of alkylbenzenes, benzomonocycloalkanes, and benzodicycloalkanes on the one hand and those of benzothiophenes on the other, points out that fractions 10–13 contain different types of compounds the elution zones of which overlap those of monocyclic aromatic hydrocarbons. Compounds, which would be probably identified by mass spectrometry as alkylbenzenes, benzomonocycloalkanes, and benzodicycloalkanes are alkyl arylalkyl sulfides and alkanes containing two benzene or benzocycloalkane residues.

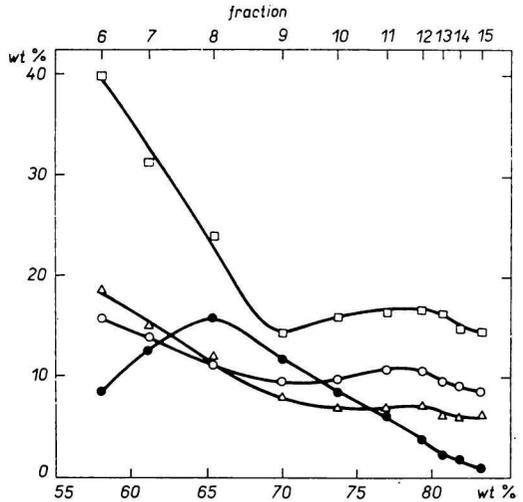
It follows from the works of *Snyder* [11, 12] that, on silica gel, diphenylalkanes and

Table 3
Group-type analysis of aromatics-rich fractions of oil

Type	Fraction [weight %]										
	6	7	8	9	10	11	12	13	14	15	
Alkylbenzenes	40.0	31.3	24.0	14.4	16.1	16.4	16.6	16.3	14.8	14.6	
Benzomonocycloalkanes	18.5	15.1	12.0	8.0	7.0	7.0	7.2	6.2	5.9	6.3	
Benzodicycloalkanes	15.7	13.9	11.2	9.6	9.8	10.7	10.7	9.5	9.2	8.6	
Benzotricycloalkanes, alkylnaphthalenes	5.7	7.3	6.7	5.7	4.8	4.5	4.1	3.8	3.8	4.0	
Naphthomonocycloalkanes, biphenyls	6.0	10.0	13.5	14.0	12.6	10.9	10.2	8.7	7.0	7.8	
Naphthodicycloalkanes, fluorenes, acenaphthylenes	3.3	9.9	16.7	19.0	19.4	20.5	25.4	25.3	20.6	17.2	
Naphthotricycloalkanes, phenanthrenes, nthalacenes	0	0	0	0	0	0	0	3.7	10.1	4.7	
Pyrenes	0	0	0	0	0	0	0	0	0	10.1	
Chrysenes	0	0	0	0	0	0	0	0	0	0	
Benzothiophenes	8.5	12.5	15.7	11.6	8.6	6.1	3.8	2.2	1.9	0.8	
Dibenzothiophenes	0	0	0	13.8	21.7	23.9	22.0	17.1	15.9	8.3	
Naphthobenzothiophenes	.3	0	0	0	0	0	0	7.2	10.8	19.6	

Fig. 1. Dependence of the content of the major compound types upon the amount of the eluted oil off column.

□ alkylbenzenes; △ benzomonocycloalkanes; ○ benzodicycloalkanes; ● benzothiophenes.



dialkyl sulfides are eluted after alkyl naphthalenes. Since alkyl arylalkyl sulfides, due to the effect of the aromatic system, are more strongly held on silica gel, they are eluted together with alkylphenanthrenes or even later (fractions 14, 15). The gradual increase of the sulfur content in the fractions 9, 10, and 11 disagrees with the expected occurrence of alkyl arylalkyl sulfides in the fractions 10–13. On the other hand, the assumption that alkanes bearing two benzene, benzomonocycloalkane or benzodicycloalkane residues occur in the fractions 10–13 is in agreement with Snyder's results. Accordingly, the main portion of alkyl naphthalenes is contained in the fractions 6–8. From the above-mentioned facts it can be concluded that alkanes containing two benzene or benzocycloalkane residues are the probable types of compounds in fractions 10–13 which are analyzed by mass spectrometry as alkylbenzenes or benzocycloalkanes. The occurrence of these types of compounds in petroleum was denied until recently [8, 13]. In a recent work [14], however, diphenylmethane structure in carboxylic acids isolated from petroleum, was proved. The occurrence of diphenylalkanes and related hydrocarbons in the investigated oil will be discussed in a subsequent paper.

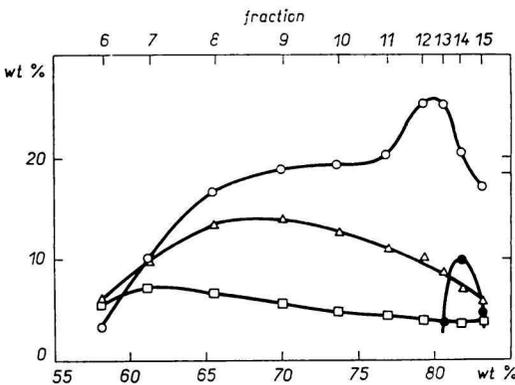


Fig. 2. Dependence of the content of the major compound types upon the amount of the eluted oil off column.

□ benzotricycloalkanes and alkyl naphthalenes; △ naphthomonocycloalkanes and biphenyls; ○ naphthodicycloalkanes, fluorenes, and acenaphthylenes; ● naphthotricycloalkanes, phenanthrenes, and anthracenes.

The elution curves of the dicyclic aromatic hydrocarbons have little pronounced peaks (Fig. 2). From the graphical dependence of the content of alkyl-naphthalenes with benzotricycloalkanes and of naphthomonocycloalkanes with biphenyls upon the amount of the eluted material it could not be concluded, however, whether the elution curves consist of one or two peaks.

The graphical dependence of the content of naphthodicycloalkanes, fluorenes, and acenaphthylenes upon the amount of the effluent shows that the elution curve of these represents two elution zones. The peak of one of them is in the fractions 9 and 10 and the other in the fractions 12 and 13.

As showed by Fig. 2, the group of phenanthrenes, anthracenes, and naphthotricycloalkanes, in contrast to dicyclic aromatic hydrocarbons, are eluted only in three fractions and form only one elution zone. Since these types of compounds were not found in fractions where naphthomonocycloalkanes and naphthodicycloalkanes normally occur (fractions 6–12), it indicates that naphthotricycloalkanes are, in the oil under investigation, present in a negligible amount, or are not present at all.

Naphthobenzothiophenes were, unexpectedly, found in fraction 6. The masses of the fragments on the basis of which the amount of naphthobenzothiophenes is normally calculated, are identical with the masses of fragments of tricycloalkanes. Since the content of tricycloalkanes in the preceding fractions was estimated to be 10–15% it is quite likely that they are present also in fraction 6 where these substances are evaluated as naphthobenzothiophenes.

When analyzing a sample of oil one has to take into consideration the fact that the absolute amount of a certain type of compounds may be determined inaccurately. Analyzing all the fractions under identical conditions the content of individual types of compounds will be proportional to their real content in the sample.

References

1. Van Nes, K. and Van Westen, H. A., *Aspects of the Constitution of Mineral Oils*. Elsevier, Amsterdam, 1951.
2. Hazelwood, R. N., *Anal. Chem.* **26**, 1073 (1954).
3. Oelert, H. H., *Ropa a Uhlie* **8**, 135 (1966).
4. Jogansen, A. V. and Brown, E. V., *Trudy komisii po analiticheskoi khimii*, Tom XIII. *Organicheskiy analiz*, p. 367. Izd. Akad. Nauk SSSR, Moscow, 1963.
5. Knight, S. A., *Chem. Ind.* (London) **1967**, 1920.
6. Siryuk, A. G. and Zimina, K. I., *Khim. Tekhnol. Topl. Masel* **8**, 52 (1963).
7. Aczel, T. and Johnson, B. H., *ACS Div. Petrol. Chem. Preprints* **12**, No 2, B-83 (1967).
8. Hood, A. and O'Neal, M. J., Jr., *Proceedings of Joint Conference Organized by Hydrocarbon Research Group*. Inst. of Petroleum and ASTM Committee E-14, University of London, September 24–26, 1958.
9. Hastings, S. H., Johnson, B. H., and Lumpkin, H. E., *Anal. Chem.* **28**, 1243 (1956).
10. Prikryl, R., Miglieriniová, K., Holotík, Š., and Pacigová, D., *Ropa a Uhlie* **11**, 238 (1969).
11. Snyder, L. R., *Advan. Anal. Chem. Instrum.* **3**, 251. (C. N. Reilley, Editor.) J. Wiley, New York, 1964.
12. Snyder, L. R., *Anal. Chem.* **33**, 1527 (1961).
13. Hood, A., Clerc, R. J., and O'Neal, M. J., *J. Inst. Petrol.* **45**, 168 (1959).
14. Seifert, W. K. and Teeter, R. M., *Anal. Chem.* **42**, 180 (1970).

Translated by P. Kováč