UDC 665.61

Organosulphur Compounds in High-Sulphur Petroleum from the Nizhne-Pervomayskoye Deposit (Tomsk Region)

V. P. SERGUN[1], I. S. KOROL[2] and R. S. MIN[1]

[1]*Institute of Petroleum Chemistry, Siberian Branch of the Russian Academy of Sciences, Pr. Akademicheskiy 4, Tomsk 634021 (Russia)*

E-mail: sergun@ipc.tsc.ru

[2]*Trofimuk Institute of Petroleum Geology and Geophysics, Siberian Branch of the Russian Academy of Sciences, Pr. Koptyuga 3, Novosibirsk 630090 (Russia)*

E-mail: KorolIS@ipgg.sbras.ru

(Recieved October 7, 2013)

Abstract

The structure and composition of organic sulphur compounds in high-sulphur petroleum from Nizhne-Pervomayskoye deposit (Tomsk Region) have been studied. Sulphur compounds have been shown to be represented by a mixture of isomers of dialkylthiacyclopentanes, alkyl- and methylalkylthiacyclohexanes, bicyclic sulphides, alkyl-homologues of benzothiophene, dibenzothiophenes and benzonaphthothiophenes and their alkyl-substituted.

Keywords: high-sulphur petroleum, composition, distribution, organosulphur compounds

INTRODUCTION

Sulphur compounds (SC) are a part of practically all petroleum and petroleum products and complicate significantly the technology of petroleum refining, reduce the quality of petroleum products, accelerates corrosive wear of the technological equipment, have an adverse impact on the environment due to the formation of sulphur oxides during fuel combustion. For these reasons, hydrocarbon raw materials entering the processing companies are increasingly made stringent requirements for the sulphur content. Studies on the composition and the structure of the SC of petroleum are required for a targeted search of optimal processes of their processing.

Petroleum widespread on the territory of the Tomsk region are localized mainly in the Upper Jurassic sedimentations, their SC are mainly represented by thiophenes and sulphides, there are almost no mercaptans in them, disulfides were not detected. In works [1, 2] data on the distribution and composition of low molecular mass SC in petroleum of the Upper Jurassic Complex of the West Siberia were given. It has been established that the content of total and sulphide sulphur changes in boundaries of 0.05–1.14 and 0.007–0.400 mass %, in average, 0.46 and 0.12 mass %, respectively. The share of sulphides is from 8 to 35 rel. %.

The successful solution of scientific problems associated with the study of petroleum components depends primarily on the availability of the extraction methods directly from petroleum. The method of liquid-adsorption chromatography (LAC) is usually used to separate oil systems, since the former allows to vary adsorbents, solvents and chromatography conditions. It has been shown in works [3, 4] that the differentiation of components of petroleum

can be achieved by the use of adsorbents modified with metal chlorides. Nickel-containing sorbent [5] possesses a greater efficiency of the separation of petroleum components. In the present work, to separate SC, the method LAC with the use of silica gel modified with nickel chloride is applied in this work.

The present work is devoted to the study of the composition of low molecular mass SC of high sulphur petroleum from the Nizhne-Pervomayskoye deposit.

EXPERIMENTAL

Deasphalted and deresined highly resinous high-sulphur petroleum from the Nizhne-Pervomayskoye deposit (Tomsk Region) was selected as the research object. Sulphur compounds were isolated from deasphalted petroleum by the method of LAC on silica gel modified with 5 % $NiCl_2$ [2]. Benzene and *n*-hexane were used as eluents. The total content of sulphur was defined according to the method given in [6].

The chromato-mass spectrometry (CMS) was performed on a Hewlett Packard Aglient/HP 6890/5973 spectrometer. Conditions of the CMS analysis are given in the work [2]. The identification of SC was carried out, according to the retention time by comparison of mass fragmentograms obtained with mass spectra present in the library of the system NIST 02 and published data.

RESULTS AND DICSUSSION

The Nizhne-Pervomayskoye petroleum is characterized by a high content of resin-asphaltene compounds (19.42 mass %) and total sulphur (2.16 mass %), at that sulphides (52 rel. %) predominate in SC compositions. Hexane and benzene fractions with the content of total sulphur of 0.68 and 4.68 mass %, respectively, of 0.26 and 2.82 mass %, respectively, have been obtained from petroleum using LAC on silica gel modified with $NiCl_2$.

According to data of CMS analysis, at the chromatographic separation of deasphalted petroleum saturated carbohydrates (CH), highly-alkylated naphthenes, mono- and diaromatic CH are separated into the *hexane fraction*. Isoalkanes and *n*-alkanes of the composition C_9–C_{35} and C_{12}–C_{27}, respectively, cyclopentanes from C_{10} to C_{28}, cyclohexanes from C_{10} to C_{31}, decalins C_{11}–C_{17}, steranes C_{21}–C_{30} and terpanes from C_{27} to C_{35}, *n*-alkylbenzenes from C_{10} to C_{32}, phytanylbenzene, alkyltoluenes C_7–C_{24} and

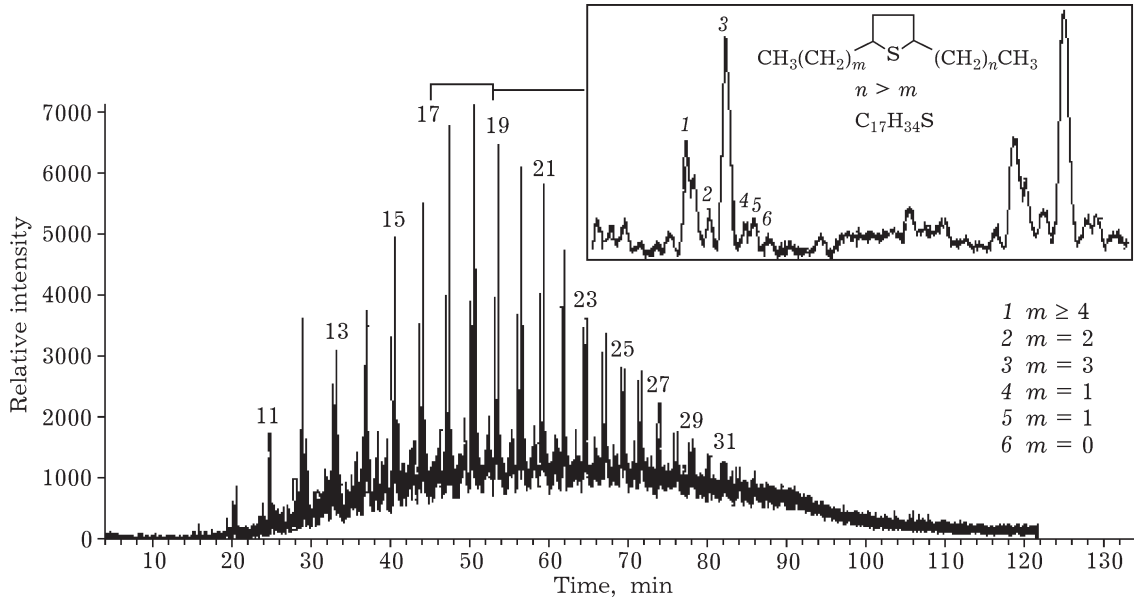

Fig. 1. Mass-fragmentogram for the ion m/z 87 of the benzene fraction of petroleum.

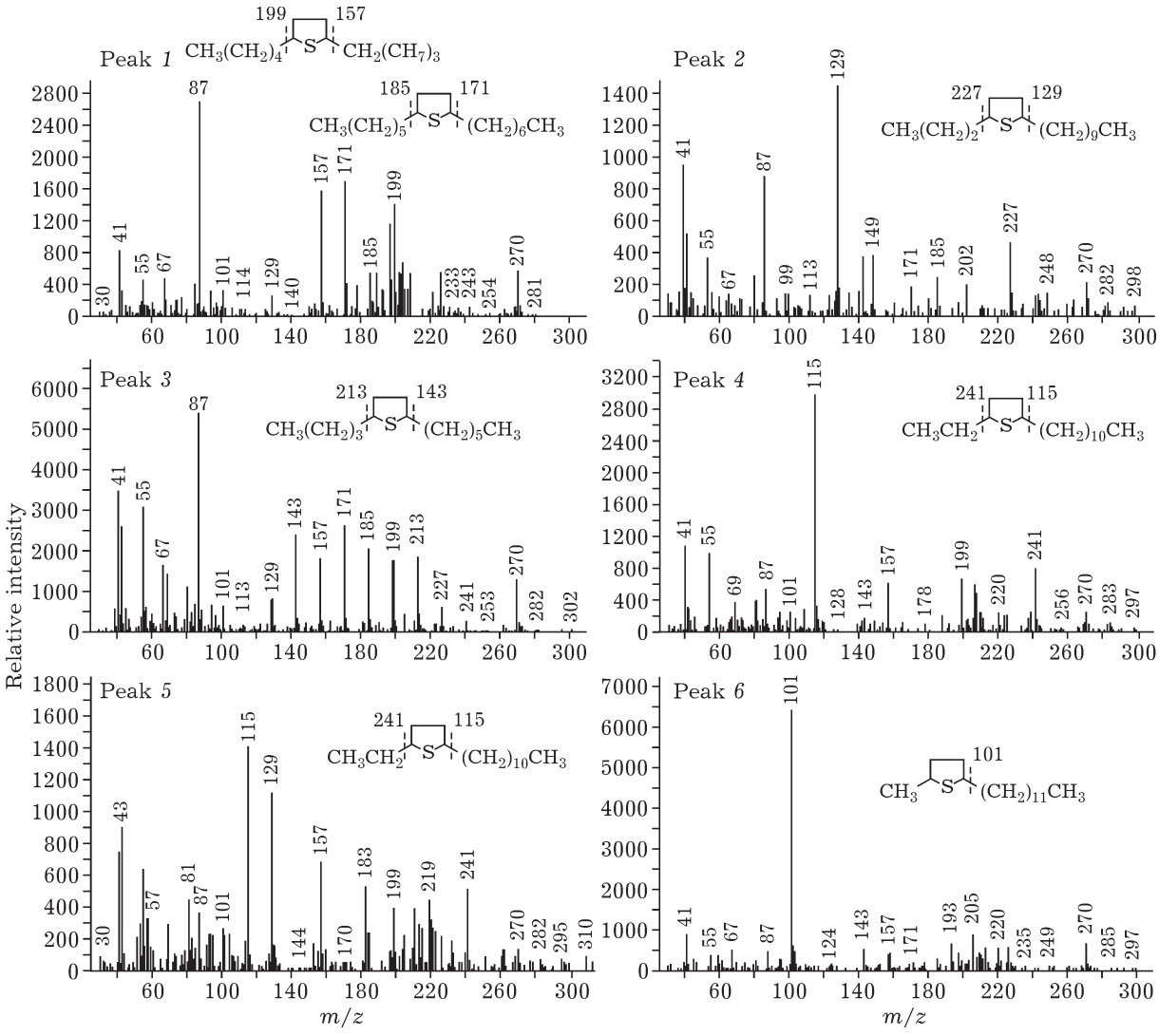

Fig. 2. Mass spectra of 2,5-dialkylcyclopentanes (see numbers of peaks on the insert).

1-methyl-3-phitanylbenzene, alkylxylenes C_7–C_{23} and dimethylphytanylbenzene, alkylnaphthalenes C_{11}–C_{23} and alkylindanes C_9–C_{26} have been identified as a part of CH.

In the hexane fraction, one did not manage to identify SC because of their low concentration in the sample.

In the benzene fraction (BF), there are polycyclic aromatic hydrocarbons (AH), cyclic sulphides, thiaarene and their alkyl derivatives.

Di- and tricyclic AH are represented by naphthalene, phenanthrene and their C_1–C_4 homologues. The maximum in the distribution of naphthalenes corresponds to homologues of C_3, in the distribution of phenanthrenes it does to C_1. Phenyl-substituted structures, viz, diphenyl, their C_1–C_3 alkyl derivatives, phenylnaphthalenes and phenylphenanthrenes have also been defined. Among naphthenoaromatic CH, the presence of acenaphthene, their C_1–C_2 alkyl homologues, fluorene and its monomethyl derivatives, 1,2,3,4-tetrahydroanthracene has been established.

In the composition of tetracyclic AH, there are fluoranthene, pyrene, triphenylene, chrysene, 4H-cyclopenta[def]phenanthrene, 7H-benzo[de]anthracene, 11H-benzo[b]fluorene, 11H-benzo[a]fluorene, 7H-benzo[c]fluorene, 1,2,3,4-tetrahydrobenzo[a]anthracene, among pentacyclic – perene, benzofluoranthenes, benzo[e]chrysene are presented in the composition of AH.

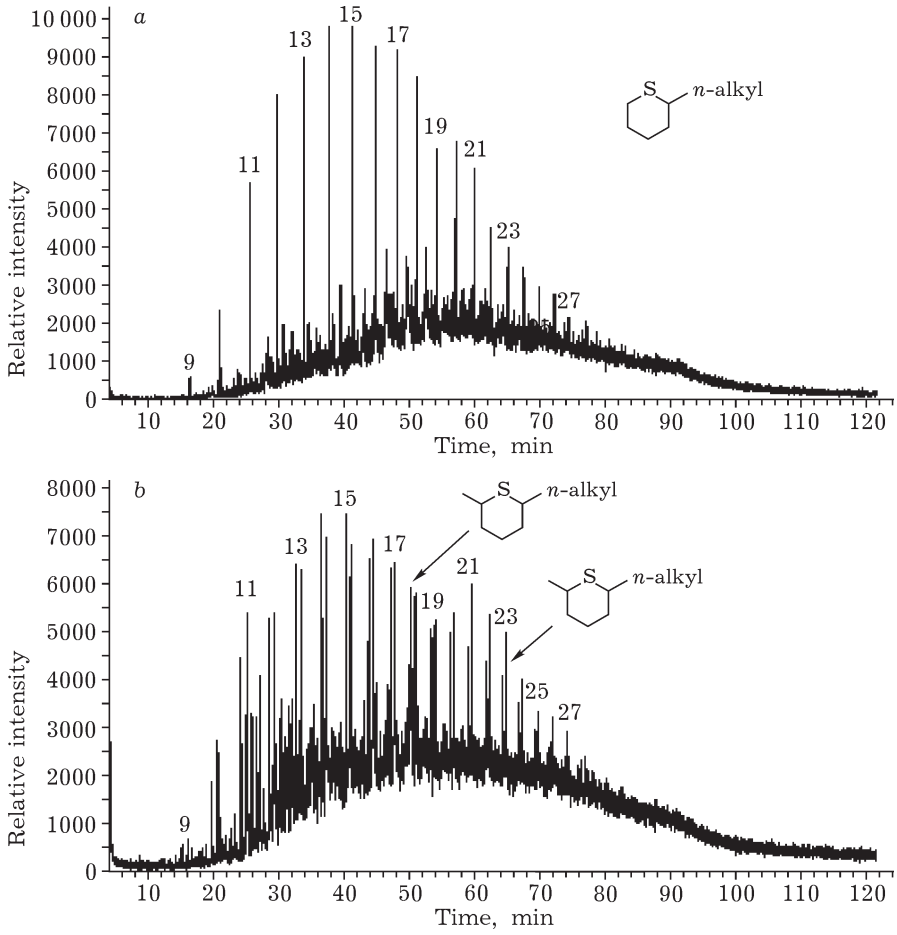

Fig. 3. Mass-fragmentogram for ions m/z 101 (*a*) and 115 (*b*) of the benzene fraction of petroleum.

Sulphur compounds of the benzene fraction are represented by a complex mixture of components of sulphide and thiophene rows, in the compositions of which sulphides (602 rel. %) predominate.

Sulphides

Scanning on the fragment ion m/z 87 has shown the presence of BF of thiolanes with 2,5-substitution, *viz.*, so called linear sulphides. They are represented by a mixture of *cis*- and *trans*-isomers of dialkylthiacyclopentanes with the composition of C_{10}–C_{31} (Fig. 1) with a different length of the alkyl chain at 2- and 5-positions of the ring. Mass-spectra of thiolanes identified on the example of the sulphide $C_{17}H_{34}S$ (see Fig. 1 on the insert) are presented on Fig. 2. They are identified by us as 2-octyl-5-pentyl- and 2-heptyl-5-hexyl- (peak 1), 2-nonyl-5-butyl- (peak 2), 2-decyl-5-propyl- (peak 3), 2-undecyl-5-ethyl- (peaks 4, 5) and 2-dodecyl-2-methylthiolanes (peak 6) [6–8]. The maximum in the distribution of thiacycloalkanes with the composition $C_{17}H_{34}S$ corresponds to 2-decyl-5-propylthiolane (peak 3).

Alkyl-substituted thiacyclohexanes are identified on mass-fragmentograms m/z 101 and 115. 2-*n*-alkylthianes (Fig. 3), *cis*- and *trans*-isomers of 5-methyl-2-*n*-alkylthianes (see Fig. 3, *b*) are present in their composition. 5-Methyl-2-alkyl-substituted structures prevail in the composition of thiacyclohexanes.

Mass-fragmentogram of BF for ion m/z 183 is presented in Fig. 4. Peaks A and B are assigned by us to alkyl-substituted thiabicyclo[4,4,0]decanes.

Linear dialkylthiacyclopentanes, alkyl- and methylalkylthiacyclohexanes, alkylthiadecalines

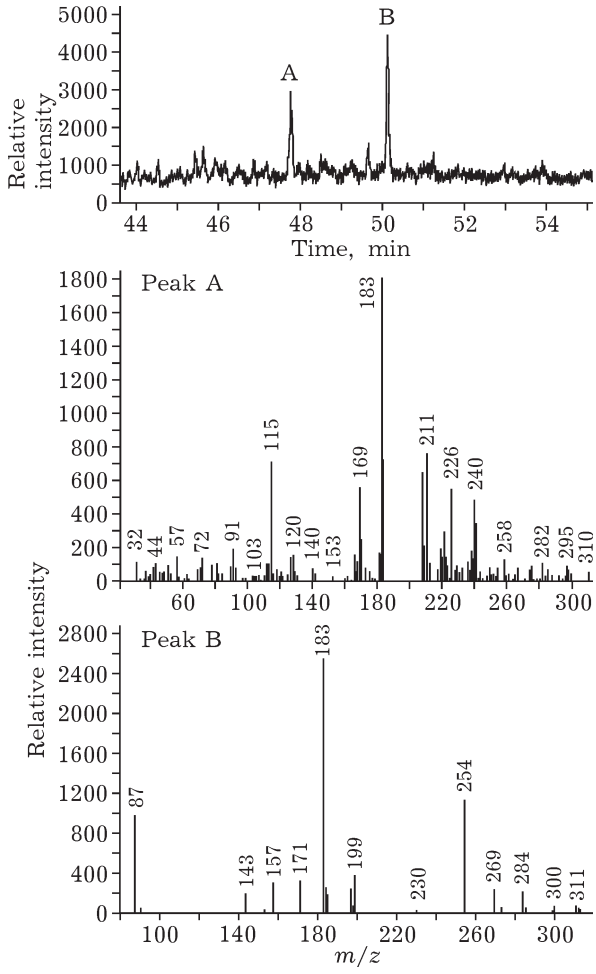

Fig. 4. Mass-fragmentogram for the ion of m/z 183 of benzene fraction of petroleum and mass spectra of thiabicyclo[4,4,0]decanes.

in oils of the West Siberia have been identified by us for the first time.

Aromatic sulphur compounds

According to data of the CMS analysis bi-, tri- and tetracyclic aromatic compounds have been identified. Dibenzothiophene compounds prevail.

Benzothiophenes (BT) are represented by (C_2–C_4)-BT, in the composition of which dimethyl-, ethyl- (m/z 161), trimethyl- (m/z 175), ethyldimethyl-, diethyl-BT (m/z 190) with the prevalence of C_3-homologues have been established.

Dibenzothiophene (DBT) (m/z 184) and its alkyl homologues from C_1- to C_{15}-DBT (Figs. 5, 6) are identified in the compositions of dibenzothiophenes (DBT). Alkyl derivatives of DBT prevail, the maximum in the distribution of which corresponds to homologues C_2–C_3. Among C_1-DBT (m/z 198), 1-, 2-, 3- and 4-methyl-substituted structures are identified, 1-methyl-DBT prevails. In the composition of C_2-DBT (m/z 212) 4-, 2- and 3-ethyl-, 4,6-, 2,4-, 1,3-, (2,6+3,6)-, (2,7+2,8+3,7)-, (1,4+1,6+1,8)-, (1,7+/1,9+/3,4)-dimethyl-substituted DBT are identified. C_3-DBT (m/z 226) and C_4-DBT (m/z 240) are represented by trimethyl-, ethylmethyl-, 4-propyl-, ethyldimethyl-, diethyl-, propylmethyl- and butyl-substituted DBT [10]. In the composition of (C_5–C_{15})-DBT 4-alkyl-substituted structures (Fig. 7) are identified [11].

Benzonaphthothiophenes are presented by isomers of benzo[b]naphtho[2,1-b]-, benzo[b]-naphtho[1,2-b]-, benzo[b]naphtho[2,3-d]thio-

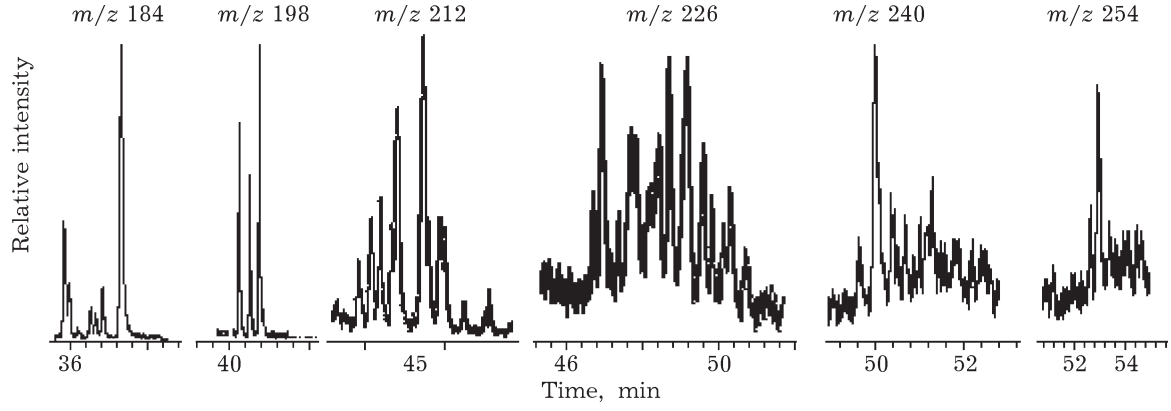

Fig. 5. Mass-fragmentograms of dibenzothiophenes for ions m/z of 184, 198, 212, 226, 240 and 254 of benzene fraction of petroleum.

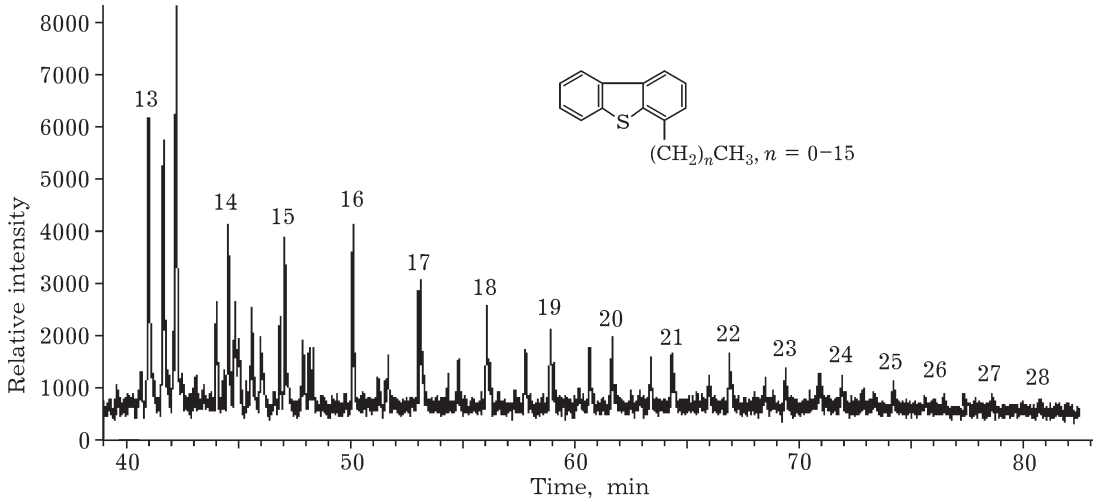

Fig. 6. Mass-fragmentogram of alkylated dibenzothiophenes for the ion of m/z 197 in benzene fraction of petroleum.

phene and their C_1- and C_2-alkyl homologues, in the compositions of which [2,1-b]benzonaphthothiophenes [12] prevails.

CONCLUSION

Therefore, the method of the isolation of SC with the use of silica gel modified by nickel chloride developed by us allows concentrating them in a more polar chromatographic fraction and studying their compositions. SC in the highly resinous, high-sulphur petroleum from Nizhne-Pervomayskoye deposit (Tomsk Region) have been shown to be represented by thiaarenes and sulphides with the predominance of the latter. Aromatic SC are represented by alkyl homologues benzothiophene, dibenzothiophene and benzonaphthothiophenes and their alkyl-substituted. Dibenzothiophene compounds prevail. Basic representatives of SC of the sulphide type are thiacycloalkanes. For the first time in the composition of sulphur compounds of high-sulphur petroleum of the West Siberia, *cis*- and *trans*-isomers of dialkylthiacyclopentanes of the linear structure, different by the length of the alkyl chain, 2-*n*-alkylthiacyclohexanes and bicyclic sulphides represented by *cis*- and *trans*-isomers of 5-methyl-2-*n*-alkylthianes and alkyl-substituted thiabicyclo[4,4,0]decanes, respectively, have been identified.

REFERENCES

1 Gerasimova N. N., Kovalenko E. Yu., Sergun V. P., Sagachenko T. A., Min R. S., *Neftekhim.*, 45, 4 (2005) 243.
2 Sergun V. P., Min R. S., *Neftekhim.*, 52, 2 (2012) 86.
3 Kuz'menko I., Min R., *Khim. Ust. Razv.*, 7, 2 (1999) 169.
4 Kuz'menko I. S., Nikolaeva T. L., Bauer L. N., Min R. S.,*Neftekhim.*, 39, 2 (1999) 124.
5 Kuz'menko I., Min R. in: Progress in Oilfield Chemistry. Managing Matured Fields and Wells, in Istvan Lakatos (Ed.), Akademiai Kiado, Budapest, 2005, vol. 6, pp. 285–292.
6 Klimova V. A., Osnovnye Mikrometody Analiza Organicheskikh Soyedineniy, Khimiya, Moscow, 1975, pp. 104–110.
7 Sinninghe Damste J. S., Organically-Bound Sulphur in Geosphere: a Molecular Approach, Delf University of Technology, Ablasserdam, 1988.
8 Schmid J. C., Сопиап J., Albrecht P., *Nature*, 329 (1987) 54.
9 Payzant J. D., McIntyre D. D., Mojelsky T. W., Torres M., Montgomery D. S. and Strausz O. P., *Org. Geochem.*, 14, 4 (1989) 461.
10 Payzant J. D., Lom E. M. and Strausz O. P., *Energy & Fuels*, 5 (1991) 445.
11 Mossner Stephanie G., Lopez de Alda Maria J., Sander Lane C., Lee Milton L., Wise Stephen A., *J. Chromatogr. A*, 841 (1999) 207.