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New Approach towards Structure Determination of Fragments Coupled *via* Ether/Ester Bridges in Petroleum and Natural Bitumen Oils

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Abstract

A new approach towards determination of structure and composition of fragments coupled *via* a C–O bond in ethers and esters of petroleum and natural bitumen oils is developed. It is based on the use of the known chemical reaction of selective cleavage of ether/ester bridges in petroleum oil components using BBr_3 . Unlike the known approach involving the stage for reduction of products of chemical modification of oils with lithium aluminium hydride, it is proposed to analyse the composition of the resulting organic bromides by the GC-MS method. Mono- and dibromo derivatives of C_{13} – C_{22} alkyltrimethylbenzenes are identified in chemical modification products on an example of natural bitumen oils from the Ashalchinsk field (Tatarstan). Unlike C_{18} – C_{22} compounds, C_{13} – C_{17} homologues are not detected in initial oils, therefore they are entirely coupled to other fragments of complex high molecular mass formations by one or two ester-ether bridges. Furthermore, as established during analysis of GC-MS results, there are ions corresponding to monobromides of characteristic fragment ions of *n*-alkanes, and also to mono- and dibromides of characteristic molecular ions of naphthalene, phenanthrene, dibenzothiophene, and their homologues. Hence, in complex high molecular mass formations of the studied oils, some of the listed compounds are linked *via* one or two ether/ester bridges.

Keywords: natural bitumen, oils, composition, analysis, new approach

INTRODUCTION

The information about the components (oils, resins, and asphaltenes) of heavy high-viscosity oils and natural bitumens, the majority of which are biodegraded, is required to detect ways of their genesis, solve the issues of their extraction, transportation, processing, and

rational use [1]. Several foreign [2–4] and domestic publications [5–8] using selective chemical reactions found that some structural fragments in asphaltene and resin species were interconnected *via* sulphide and ether/ester bridges. A combination of selective chemical reaction to tear apart ether/ester bridges and analysis of the resulting products

by gas chromatography-mass spectrometry (GC-MS) allowed establishing for the first time [9] that alkanes, alkyltrimethylbenzenes, alkylcyclohexanes, cheilanthanes, hopanes, phenanthrenes, benzo- and dibenzothiophenes were present in petroleum and natural bitumen oils not only in the molecular form but also as chemically bound structural fragments in complex high molecular mass formations.

The presence of bound forms of some compounds types in petroleum and natural bitumen oils follows from the results of thermal decomposition of oils under two-stage flash pyrolysis conditions (300, 600 °C, 15 s) combined with analysis of the obtained products by GC-MS in on-line mode [10]. However, it is worth noting that cleavage of ether/ester bridges in the presence of BBr_3 is accompanied by the formation of bromo derivatives of organic compounds that are reduced with lithium aluminium hydride prior to GS-MS analysis. Herewith, the bromine

atom in the molecule is replaced by hydrogen [2–4, 9]. Variations in the composition of the analysed types of compounds during comparative GC-MS analysis of initial oils and products of their chemical modification may remain unnoticed with low relative content of the bound structural fragments in oils. In addition, the information about the number of ether/ester bridges that connect the above structural fragments is lost during the reduction of bromides.

The present work proposes an alternative procedure option deprived of the above disadvantages that excludes the stage of reduction of bromo derivatives. Bromo-substituted structural fragments that were present in initial oils in the bound form *via* ether/ester bridges were readily determined in a mixture of other organic compounds by GC-MS analysis of selective reaction products according to the presence of characteristic doublets and triplets determined by approximately

TABLE 1

List of m/z values for ions characteristic of “pure” compounds, their mono- and dibromo derivatives

Compound	“Pure”	Monobromide	Dibromide
Alkanes	57	135, 137	213, 215, 217
Alkyltrimethylbenzenes	133	211, 213	289, 291, 293
<i>n</i> -Alkylbenzenes	91	169, 171	247, 249, 251
Alkylmethylbenzenes	105	183, 185	261, 263, 265
Alkyldimethylbenzenes	119	197, 199	275, 277, 279
Alkylcyclohexanes	83	161, 163	239, 241, 243
Cheilanthanes and hopanes	191	269, 271	347, 349, 351
Pregnanes and steranes	217	295, 297	373, 375, 377
Naphthalene	128	206, 208	284, 286, 288
Methylnaphthalenes	142	220, 222	298, 300, 302
C_2 -naphthalenes	156	234, 236	312, 314, 316
C_3 -naphthalenes	170	248, 250	326, 328, 330
C_4 -naphthalenes	184	262, 264	340, 342, 344
Phenanthrene	178	256, 258	334, 336, 338
Methylphenanthrenes	192	270, 272	348, 350, 352
C_2 -phenanthrenes	206	284, 286	362, 364, 366
C_3 -phenanthrenes	220	298, 300	376, 378, 380
C_4 -phenanthrenes	234	312, 314	390, 392, 394
Dibenzothiophene	184	262, 264	340, 342, 344
Methyldibenzothiophenes	198	276, 278	354, 356, 358
C_2 -dibenzothiophenes	212	290, 292	368, 370, 372
C_3 -dibenzothiophenes	226	304, 306	382, 384, 386
C_4 -dibenzothiophenes	240	318, 320	396, 398, 400

the same identical relative content of stable bromine isotopes (^{79}Br and ^{81}Br). Table 1 gives a list of characteristic ions, according to which reconstruction of the molecular-mass distribution of various compounds, and also their mono- and dibromo derivatives was carried out.

EXPERIMENTAL

The studies were carried out for oils of natural bitumen from the Ashalchinsk field (OAB) located in the territory of the Volga-Ural Oil and Gas Province [1]. Paper [9] sets out methods of isolation of OAB from natural bitumen. The technique of the selective rupture of a C-O bond of ether/ester bridges in OAB components consisted in the following. To a sample of oils (0.3 g) pre-dissolved in the minimum volume of chloroform, 8 cm³ of a 1.6 M solution of BBr_3 in chloroform was added. The mixture was refluxed with stirring with a magnetic stirrer for 48 h, then, cooled, and 16 cm³ of ether and 8 cm³ of distilled water were sequentially added. The organic layer was separated and the aqueous phase was extracted with chloroform. The extract and organic layer were combined and rinsed with a saturated aqueous solution of

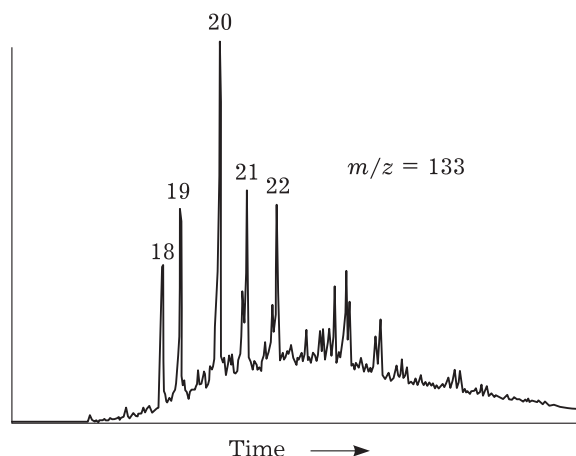


Fig. 1. Mass-chromatograms of OAB according to characteristic ions of alkyltrimethylbenzenes ($m/z = 133$). Numbers correspond to the total number of carbon atoms in species.

potassium chloride; the solvent was evaporated using a rotary evaporator. The resulting bromination products were purified from oxygen-containing polar impurities using liquid-adsorption chromatography on silica gel. The initial oils and purified bromination products were analysed by the GC-MS method using Thermo Scientific DFS instrument. A TR5MS capillary column with a 30 m length and a 0.25 mm internal diameter was used in the gas chromatograph. Chromato-

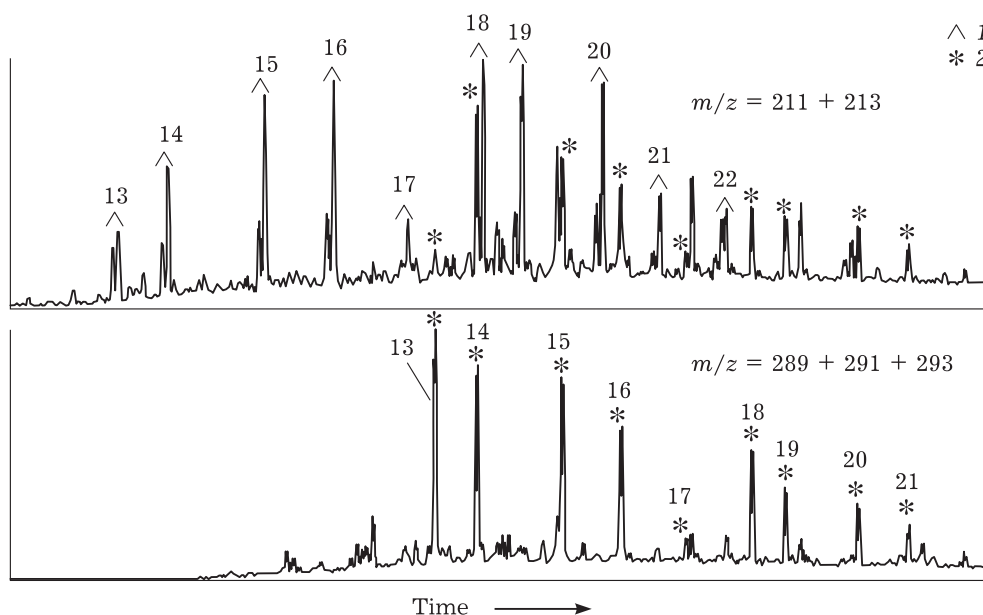


Fig. 2. Mass-chromatograms of OAB-Br-NF according to characteristic ions of mono- (1) and dibromo (2) derivatives of alkyltrimethylbenzenes. Numbers correspond to the total number of carbon atoms in species.

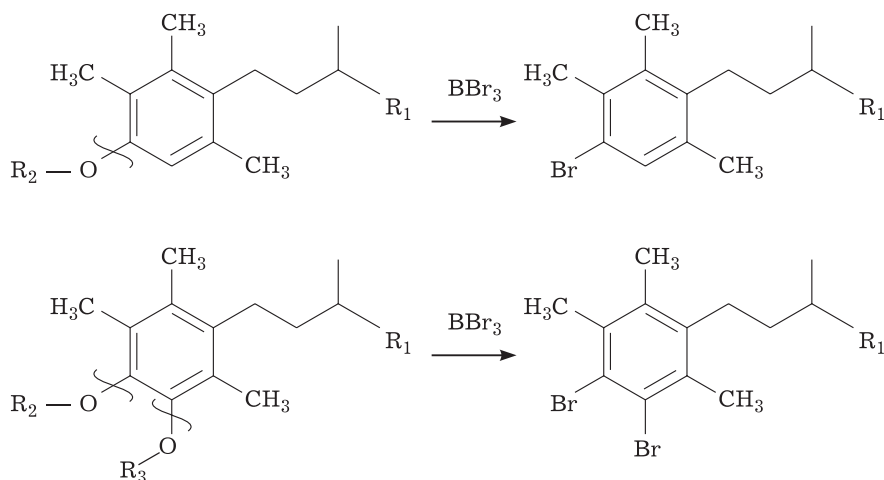


Fig. 3. Scheme of cleavage of ether/ester bridges in coupled alkyltrimethylbenzene species with the formation of their mono- and dibromo derivatives.

graphing was carried out in the mode of programmed temperature rise from 80 to 300 °C at a rate of 4 °C/min and then for 30 min at the final temperature with helium as a carrier gas. Scanning of mass-spectra was carried out every second in a mass range to 500 amu.

The reconstruction of the molecular mass distribution of compounds of different types was carried out using characteristic ions based on chromatograms of the total ion current using

the Xcalibur program. Compounds were identified with the involvement of published data and NIST 02 mass spectral library.

RESULTS AND DISCUSSION

In initial OAB, alkyltrimethylbenzene (ATMB) homologues from ATMB-C₁₈ to ATMB-C₂₂ were identified (Fig. 1). At the same time, mono- and dibromo derivatives of the

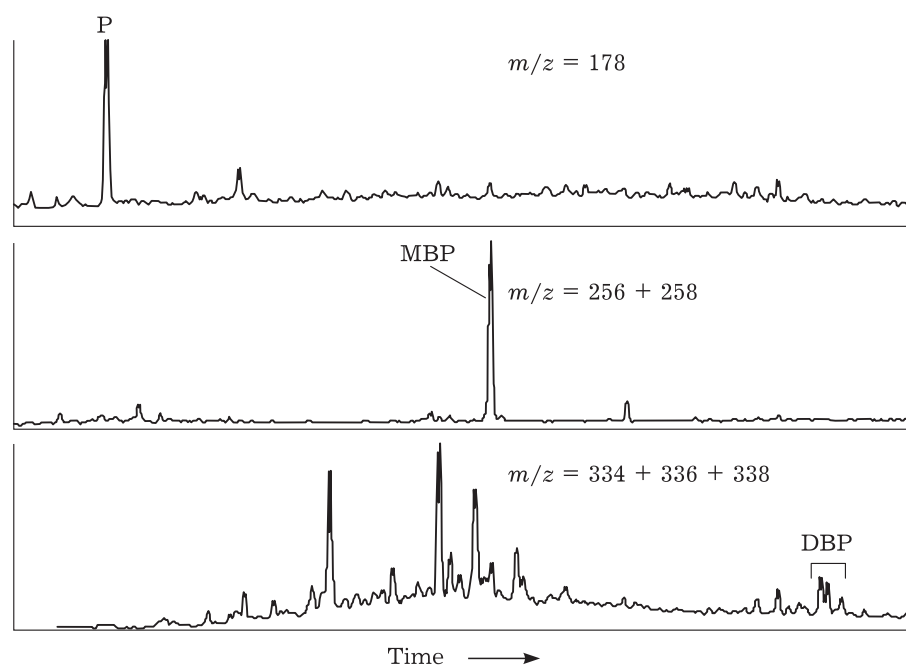


Fig. 4. Mass-chromatograms of OAB-Br-NF according to characteristic ions of phenanthrene ($m/z = 178$), its monobromo- ($m/z = 256$, and 258) and dibromo derivatives ($m/z = 334$, 336 , and 338). P - Phenanthrene; MBP - monobromo derivative of phenanthrene; DBP - dibromo- derivatives of phenanthrene.

homological ATMB series from ATMB-C₁₃ to ATMB-C₂₂ were found in a nonpolar fraction of bromination products (Oils of Ashalcha Bitumen-Bromide-Nonpolar Fraction, OAB-Br-NF) using GC-MS (Fig. 2). Two neighboring peaks in the mass-chromatogram on characteristic ions with $m/z = 211 + 213$ are most likely driven by the presence of two bromide isomers of ATMB homologues with different positions of bromine atoms in a species. Importantly, among mono- and dibromo derivatives, there are derivatives of ATMB homologues with a composition of C₁₃–C₁₇ that were absent in the initial OAB [9] (see Fig. 1). Thereby, in initial oils, these homologues, unlike a composition of C₁₈–C₂₂, were entirely coupled with other fragments of complex high molecular mass formations *via* one or two ether/ester bridges.

TABLE 2

The presence of mono- and dibromides of various compounds in OAB-Br-NF

Compounds	Monobromides	Dibromides
Alkanes	Yes	No
Alkylcyclohexanes	No	No
Cheilanthanes	No	No
Hopanes	No	No
Steranes	No	No
Pregnanes	No	No
Alkyltrimethylbenzenes	Yes	Yes
<i>n</i> -Alkylbenzenes	Yes	Yes
Alkylmethylbenzenes	Yes	Yes
Алкилдиметилбензолы	Yes	Yes
Naphtalene	Yes	Yes
Methylnapthalenes	No	Yes
C ₂ -napthalenes	No	Yes
C ₃ -napthalenes	Yes	Yes
C ₄ -napthalenes	Yes	Yes
Phenanthrene	Yes	Yes
Methylphenanthrenes	Yes	Yes
C ₂ -phenanthrenes	Yes	Yes
C ₃ -phenanthrenes	Yes	Yes
C ₄ -phenanthrenes	Yes	Yes
Dibenzothiophene	Yes	Yes
Methyl dibenzothiophenes	Yes	Yes
C ₂ -dibenzothiophenes	Yes	Yes
C ₃ -dibenzothiophenes	Yes	Yes
C ₄ -dibenzothiophenes	Yes	Yes

Figure 3 presents examples of the formation of mono- and dibromo derivatives of ATMB with selective cleavage of ether/ester bridges in complex high molecular mass formations of OAB.

Furthermore, as established during the analysis of GC-MS results, mass chromatograms constructed according to characteristic ions presented in Table 1 prove the presence of monobromo derivatives of *n*-alkanes, and also mono- and dibromo-substituted naphthalene, phenanthrene (Figure 4), dibenzothiophene, and their homologues. Hence, in complex high molecular mass formations of the studied oils, some of the listed compounds are linked *via* one or two ether/ester bridges.

It is worth noting that monobromo derivatives of phenanthrene (see Fig. 4) and dibenzothiophene are presented by only one isomer. This attests to the fact that ether/ester bridge that binds the listed structural fragments with other units in complex high molecular mass formations of the studied oils is present in the strictly defined position of the tricyclic aromatic compounds.

The results for the detection of mono- and dibromo derivatives of various compounds in OAB-Br-NF are presented in Table 2. From its data, it follows that there are no forms of alkylcyclohexanes, cheilanthanes, hopanes, and steranes linked *via* ether/ester bridges in OAB. Alkanes in the composition of complex high molecular mass formations are linked with other structural fragments *via* only one, while C₁- and C₂-naphthalenes – *via* only two ether/ester bridges. For other compounds listed in Table 2, both options are typical. The relative content of monobromo derivatives is always higher than that of dibromo ones.

CONCLUSION

It has been demonstrated that GC-MS analysis of organic bromo derivatives compounds generated by C–O bond cleavage in ethers/esters of components of oils and bitumens during the reaction with BBr₃ allows obtaining the information about the composition of structural fragments that are linked *via* one or two ether/ester bridges in the composition of complex high molecular mass formations contained in oils. Alk-

yltrimethylbenzene, *n*-alkanes, and also naphthalene, phenanthrene, dibenzothiophene, and their homologues are present in oils of natural bitumen in both molecular forms and as structural fragments bound *via* one or two ether/ester bridges in complex high molecular mass formations. In initial oils, C₁₃–C₁₇ alkyltrimethylbenzenes, unlike C₁₈–C₂₂ homologues, are entirely linked to other fragments of high molecular mass formations *via* one or two ether/ester bridges.

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