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Investigation of the Composition of *n*-Heptane and Ethanol-Benzene Extracts of Brown Coal for the Isolation of Biologically Active Substances

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Abstract

The group and component composition of *n*-heptane and alcohol-benzene extracts of bitumen obtained from the brown coal of the Tyulgan deposit was investigated. Application of ¹³C NMR spectroscopy (CPMAS) and IR Fourier spectroscopy, gas chromatography – mass spectrometry, liquid chromatography allowed us to determine that *n*-heptane and alcohol-benzene extracts are represented by similar groups of substances: alcohols, phenols, alkanes, small amounts of carboxylic acids and aromatic compounds, esters, unsaturated hydrocarbons. The substances of these groups are distributed in these extracts to different extents, with the prevalence of the compounds of aliphatic nature. A number of biologically active substances were identified in the extracts: tetra-, hexa-, octadecanoic acids, butylparabene, ferruginol, eicosane.

Keywords: Bitumen of brown coal, biologically active substances, component composition

INTRODUCTION

One of the essential issues to be solved within the problem of integrated coal processing is brown coal processing. At present, the most promising method in this respect is the extraction of bitumen (mineral wax). Bitumen and the products of its processing are in demand at the world market and are used in more than 200 branches of industry. The cost of 1 t of rough mineral wax reaches 3000 euros on the world market, and its price increases substantially after further processing [1–5].

Brown coal is distinguished by high bituminosity [6]. The yield and composition of bitumen from extraction may vary within broad ranges depending on initial raw material, extraction method, chemical nature of the organic

solvent used as extractant, and process parameters – temperature, pressure, process duration. Bitumen extraction with solvents boiling below the temperature of decomposition of the organic substance allows extracting compounds in the initial form avoiding their thermal destruction. This is a key factor in the investigation of the organic composition and structure of brown coal. The wax and resin components are distinguished in extracted bitumen [7].

Substantial amounts of compounds characteristic of vegetation, namely terpenoids, hopanes, sterols, some vitamins and other biologically active substances (BAS) are present in bitumen extracted from brown coal, especially in the resinous part, which is today considered to be waste. The possibility to extract BAS in the pure form or in the form of narrow cuts opens

the outlooks for their application in medicine, cosmetics, agriculture, *etc.* [7–9].

The present work is a continuation of the studies of bitumen extracted from brown coal of the Tyulgan deposit in The South Ural basin [9] and deals with a more detailed investigation of the composition of bitumen fractions extracted with *n*-heptane and with ethanol – benzene.

EXPERIMENTAL

By means of consecutive extraction according to Graefe's method [6], *n*-heptane (ENH) and ethanol-benzene (EEB, ethanol/benzene = 1 : 1) extracts were obtained from the brown coal of the Tyulgan deposit of the South Ural basin. The yield of ENH was 1.2 %, EEB – 2.6 %. Then these extracts were separated into saponifiable and non-saponifiable fractions [9]. The data of technical and elemental analysis of the samples of initial and debituminized coal are presented in Table 1.

The initial extracts and their saponifiable and non-saponifiable fractions were separated into narrower fractions with the help of liquid column chromatography (LC), which was carried out in glass columns 10 mm in diameter and 500 mm long, filled with silica gel with the grain size of 0.2–0.5 mm (GOST 3956–76). Chromatographic separation was carried out with the consecutive use of eluents: toluene, ethylacetate, butanol, ethanol, a mixture of ethanol/formic acid (1 : 1). The fraction that remained on silica gel was washed after elution using hot butanol. The yield of fractions was controlled relying on the refractive index of the eluent used [10].

The composition of initial extracts and the obtained fractions was studied by means of IR (FTIR), ¹³C NMR (CPMAS) and gas chromatography – mass spectrometry (GC-MS).

IR spectra were recorded with an Infracum-FT 801 IR Fourier spectrophotometer (Russia) with the resolution of 4 cm⁻¹, with the

accumulation of 16 scans within the range 4000–550 cm⁻¹ in dry KBr.

High-resolution NMR spectra in solid were recorded with a Bruker Physik AG WP-200 instrument (Germany) at the frequency of 75 MHz using a standard procedure of cross-polarization with the suppression of signals from protons and with magic angle spinning (CPMAS). Accumulation of 1024 scans was carried out at room temperature. The chemical shift was measured with respect to the signal from tetramethylsilane.

Analysis by means of gas chromatography – mass spectrometry was carried out with an Agilent 6890N instrument (USA) with mass selective detector Agilent 5973: capillary column HP-5ms; evaporator temperature 290 °C; evaporation of the solvent for 4 min; flow partitioning 50 : 1; flow rate of helium as carrier gas 1 mL/min; sample volume for analysis 5.0 mL; the programmable rise of column temperature from 50 °C with exposure for 3 min to 280 °C at a rate of 5 °C min with exposure at 280 °C for 60 min. The content of individual compounds was recorded on the basis of full ion current. Identification of the component composition was carried out using the spectral library NIST-8 and Wiley. For chromatographic separation, the obtained fractions were additionally esterified with butanol.

RESULTS AND DISCUSSION

The IR spectra of ENH sample and its saponifiable (ENHS) and non-saponifiable (ENHN) fractions are shown in Fig. 1, *a*, while the spectra of EEB and its saponifiable (EEBS) and non-saponifiable (EEBN) fractions are shown in Fig. 1, *b*. These IR spectra were analyzed on the basis of literature data [11–15].

It was revealed that ENH is a multicomponent mixture of alcohols, phenols, alkanes, a small

TABLE 1

Data of technical and elemental analysis of coal samples

Coal sample	W ^a , %	A ^d , %	V ^{daf} , %	C ^{daf} , %	H ^{daf} , %	H/C atomic ratio	(O + N + S), % from difference	E ^{daf} , %
Initial	9.1	21.5	65.9	57.3	6.3	1.3	36.4	3.8
Debituminized	7.5	27.0	64.4	63.6	5.9	1.1	30.5	–

Note. 1. W^a is analytical moisture; A^d is ash content per dry sample; V^{daf} is the yield of volatile components; C^{daf}, H^{daf} are carbon and hydrogen content, respectively; E^{daf} is total yield of *n*-heptane and ethanol-benzene extract; daf is dry ash-free sample. 2. Dash means absence.

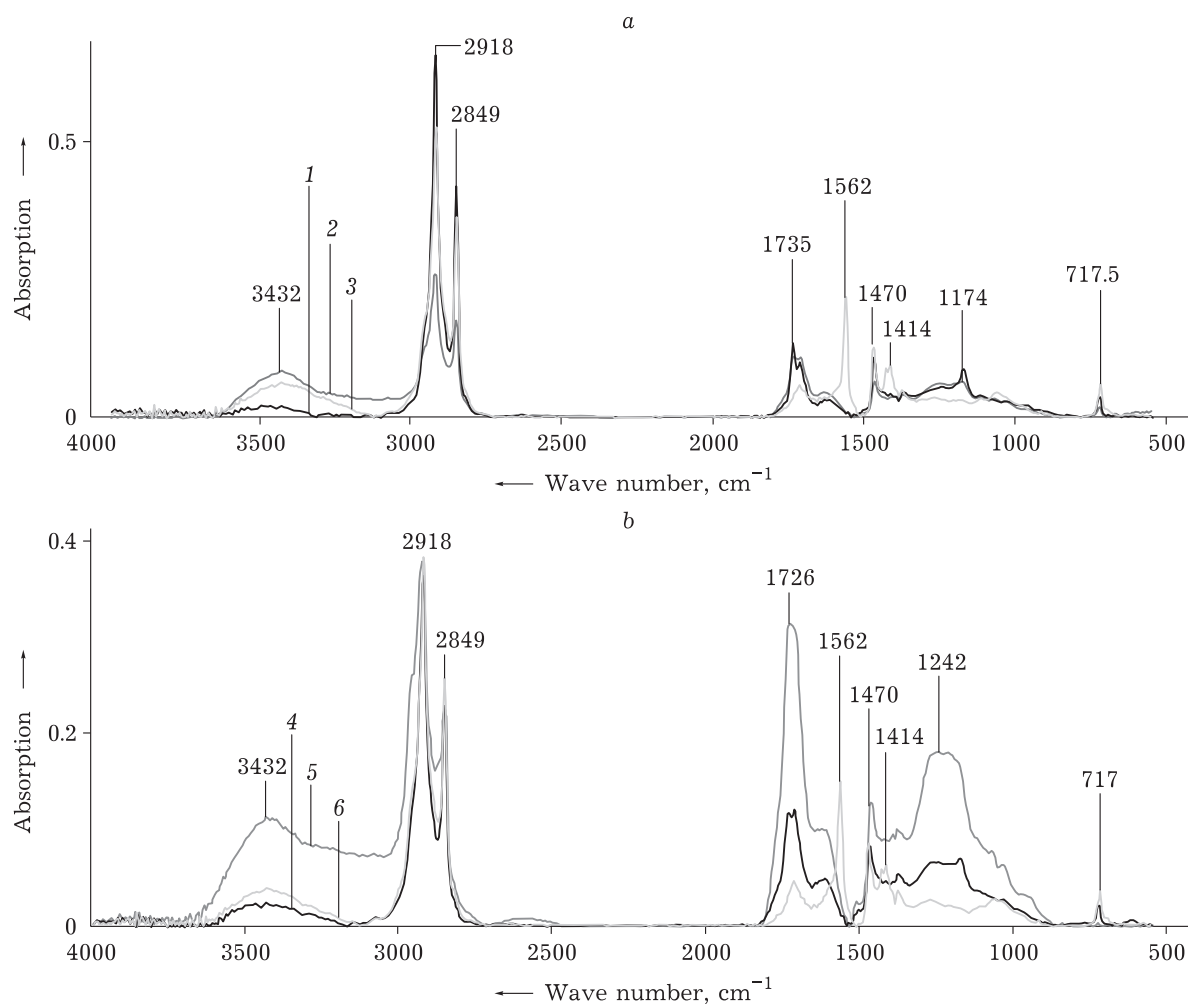


Fig. 1. IR spectra of: *a* – *n*-heptane extract (1) and its saponifiable (2) and non-saponifiable (3) fractions; *b* – ethanol-benzene extract (4) and its saponifiable (5) and non-saponifiable (6) fractions.

amount of carboxylic acids and aromatic compounds, esters, unsaturated hydrocarbons. Alkanes and alcohols predominate in the sample.

After fractionation, ENHS contains mainly alkanes and carboxylic acids, while ENHN contains alkanes and alcohols, carboxylic acids.

TABLE 2

Integral intensities of the signals of functional groups in ^{13}C NMR (CPMAS) spectra of the extracts, %

Sample	Range of chemical shifts of functional groups, ppm							Structural parameters	
	220–187	187–165	165–145	145–108	108–90	90–48	48–5	f_a	f_{al}
	C=O	COOH	C _{ar-O}	C _{ar}	C _{O-alk-O}	C _{alk-O}	C _{alk}		
ENH	1.5	2.2	1.3	4.3	2.5	8.1	80.0	5.6	90.5
ENHS	1.7	2.6	1.7	5.1	2.6	7.9	77.8	6.8	88.3
ENHN	1.4	2.3	1.1	3.7	2.1	8.0	81.3	4.8	91.3
EEB	3.0	3.6	2.7	8.7	3.1	12.8	64.6	11.4	80.4
EEBS	3.1	4.2	3.0	10.3	2.9	13.5	62.2	13.3	78.6
EEBN	1.3	1.7	1.1	4.1	2.2	8.7	79.8	5.2	90.7

Note. f_a is the degree of aromaticity, f_{al} is the degree of aliphaticity.

TABLE 3

Group composition of *n*-heptane and ethanol-benzene extracts according to GC-MS data, relative content in sample, % (coincidence with NIST databases more than 70 %)

Sample	Group of substances											
	Alkanes	Alkenes	Carboxylic acids*	Ketones	Natural esters	Alcohols	Sterols	Phenols	Terpenes	Aldehydes	Amines	Other
ENH	2.2	3.1	1.6	1.4	2.5	9.5	0.2	0.8	0.4	–	0.2	0.2
ENHS	1.0	0.9	9.1	0.1	2.6	1.2	0.4	1.1	0.3	0.2	–	1.0
ENHN	1.9	2.0	2.9	1.3	0.2	17.7	1.2	1.4	1.3	0.3	0.1	0.7
EEB	0.1	4.4	6.3	0.9	0.2	9.5	–	1.2	1.3	0.3	–	0.5
EEBS	1.2	–	14.4	–	2.9	–	0.3	0.8	0.7	–	–	0.6
EENB	1.2	4.0	4.1	1.2	0.6	10.7	–	0.2	1.2	0.5	0.4	0.9

* Detected in the form of butyl esters.

Alcohols present in ENHS in small amounts are the product of saponification (alkaline hydrolysis of esters). Carboxylic acids present in the ENHN fraction are the products of decomposition of natural esters.

It follows from the data of IR spectroscopy that EEB is a multicomponent mixture of compounds: alkanes, carboxylic acids, unsaturated hydrocarbons, normal saturated esters and a small amount of aromatic compounds. The distribution of the groups of substances in saponifiable and non-saponifiable fractions is similar to their distribution in EEBS and ENHN.

The data of ^{13}C NMR (CPMAS) analysis agree with the data of IR spectroscopy. The results of ^{13}C NMR (CPMAS) show (Table 2) that the samples under study are represented by similar compounds: alkanes, alcohols, phenols, carboxylic acids, unsaturated hydrocarbons, normal saturated esters, aromatic substances. During fractionation, the compounds dominating in saponifiable fractions (ENHS, EEBS) were carboxylic acids and alkanes, while the compounds dominating in non-saponifiable fractions (ENHN, EENB) were alkanes and alcohols. Aromatic substances were concentrated in ENHS and EEBS. The signal assignment was carried out on the basis of literature sources [14–17].

The structural group parameters [18] for the samples under investigation were calculated according to the data of ^{13}C NMR (CPMAS): the degree of aromaticity (f_a) and the degree of aliphaticity (f_{al}), %: $f_a = \frac{C_{ar-O} + C_{ar}}{C_{ar-O} + C_{ar} + C_{alk-O} + C_{alk}}$ (see Table 2), here C means carbon

atoms of aryl (ar) and alkyl (alk) functional groups. One can see that the substances of aliphatic structure dominate in the samples.

The group and component composition of the obtained bitumen and its fractions ENH, ENHS, ENHN, EEB, EEBS, EENB were studied by means of GC-MS. According to the results, ENH is a multicomponent mixture of alcohols, alkanes, alkenes, ketones and esters of natural origin (Table 3). The compounds prevailing in EEB are: alcohols, acids, alkenes, phenols and terpenes.

Further on, for narrower fractionation, ENH and EEB were separated with the help of LC. The resulting fractions were then studied by means of GC-MS. The group attribution of the compounds detected in the fractions after the separations of extracts is presented in Table 4. All carboxylic acids identified in the extracts are represented as esters formed as a result of esterification of carboxylic acids with butanol, which was carried out as sample pretreatment for GC-MS studies.

Separation of ENH by means of LC by toluene resulted in the elution of the fraction containing mainly carboxylic acids, alcohols, a small amount of ketones and sterols, represented mainly by butyl-9-hexadecenate (10.5 %), lignoceryl alcohol (7.6 %), begenyl alcohol (5.3 %), 1-heptacosanol (5.2 %). These compounds were previously detected in ENHN. The compounds identified in the fraction eluted with ethylacetate include butyl esters of hexadecanoic and octadecanoic acids, and butyloleate. The fraction eluted with butanol was composed only of three carboxylic acids, with the highest relative content of

TABLE 4

Group composition of *n*-heptane and ethanol-benzene extracts according to the data of LC and GC-MS, relative content, % (coincidence with NIST databases more than 70 %)

Eluent	Groups of substances								
	Alkanes	Carboxylic acids*	Natural esters	Alcohols	Sterols	Terpenes	Alkenes	Ketones	Non-identified
<i>n</i> -Heptane extract									
Toluene	–	28.1	–	25.0	1.3	–	–	0.9	44.7
Ethylacetate	–	16.6	–	–	–	–	–	–	83.4
Butanol	–	100	–	–	–	–	–	–	–
Ethanol	–	97.2	–	–	–	–	2.8	–	–
Ethanol/formic acid (1 : 1)									
Fraction 1	–	78.7	–	–	–	–	–	–	21.3
Fraction 2	–	25.1	–	–	–	–	–	–	74.9
Butanol (<i>T</i> = 118 °C)	–	20.4	–	–	–	–	–	–	79.6
Ethanol-benzene extract									
Toluene	0.4	18.4	1.0	10.6	0.9	0.5	3.9	–	64.3
Ethylacetate	–	62.0	–	–	–	–	–	–	38.0
Butanol	–	86.8	13.2	–	–	–	–	–	–
Ethanol	–	96.9	–	–	–	–	3.1	–	–
Et hanol/formic acid(1 : 1)									
Fraction 1	–	59.7	8.0	–	–	–	–	–	32.3
Fraction 2	–	38.7	–	–	–	–	–	–	61.3
Butanol (<i>T</i> = 118 °C)	–	34.1	7.9	–	–	–	–	–	58.0

* Detected in the form of butyl esters.

hexadecanoic acid (41.3 %). Elution with ethanol allowed us to obtain the fraction composed mainly of carboxylic acids, with the highest relative content of butyloleate (74 %). A mixture of ethanol/formic acid (1 : 1) eluted two fractions. Fraction 1 is composed mainly of carboxylic acids, with the highest relative content of butyloleate (69 %). Only carboxylic acids were identified in fraction 2. Hot butanol eluted the fraction in which only carboxylic acids were identified, mainly *n*-butylmyristate (6.6 %) and the butyl ester of hexadecanoic acid (6.4 %).

Separation of EEB by means of LC also allowed obtaining several fractions. Toluene eluted the fraction with prevailing content of butyloleate (8.6 %), *n*-tetracosanol-1 (4.2 %), 1-hexacosanol (3.4 %). Ethylacetate eluted the fraction composed of two substances: butyl ester of hexadecanoic acid (62 %), the second component was not identified. Butanol eluted the fraction composed mainly of carboxylic acids, with the highest relative content of the butyl ester of hexadecanoic acid (33 %) and butyl-9-hexadecenate (30 %). Ethanol eluted the

fraction with the highest relative content of butyloleate (76 %). A mixture of ethanol/formic acid (1 : 1) eluted two fractions containing butyloleate in substantial amount – 51 % in fraction 1 and 38.7 % in fraction 2. A high content of butyloleate (14.9 %) and butyl ester of hexadecanoic acid (10.2 %) was detected in the residual fraction eluted from the column by hot butanol.

A series of BAS detected in the extracts of ENH, EEB and their saponifiable and non-saponifiable fractions were present in substantial concentrations (Table 5). A homologous series of aliphatic carboxylic acids discovered in the samples under study include: C₁₈, C₂₀, C₂₂, C₂₄, C₂₆, C₂₈, C₃₀, C₃₂, C₃₄, C₃₆. One can see that acids with an even number of carbon atoms are predominant.

CONCLUSION

The studied extracts from the brown coal of the Tyulgan deposit in the South Ural basin are complicated multicomponent mixtures of alcohols,

TABLE 5

Biologically active substances (BAS) detected in the fractions of *n*-heptane and ethanol-benzene extracts with the help of GC-MS

Substance [19]	Relative content in the sample, %	Coincidence with NIST database, %
Saponifiable fraction of <i>n</i> -heptane extract		
Butyl ester of oleic acid	1.0	99
Ceryl alcohol	1.0	99
β -Tocopherol	0.1	89
13-Hydroxy-14-isopropylpodocarpa-8,11,13-trien-3-on	0.3	90
Ferruginol	0.2	87
Butylmyristate	0.7	99
Butyl ester of hexadecanoic acid	2.13	99
Butyl ester of octadecanoic acid	0.6	91
Non-saponifiable fraction of <i>n</i> -heptane extract		
Ferruginol	0.4	87
Butyl ester of oleic acid	0.3	96
Ceryl alcohol	3.8	99
Begenyl alcohol	2,0	99
Lignoceryl alcohol	4.2	99
γ -Tokopherol	0.1	98
β -Amirin	0.3	99
1-Octacosanol	4.0	99
<i>n</i> -Tetracosanol-1	0,2	93
Butylmyristate	0.4	99
Saponifiable fraction of ethanol-benzene extract		
Sugiol	0.7	99
Butyl ester of octadecanoic acid	0.8	99
Butylmyristate	0.4	99
Butylparabene	0.8	99
Butyl ester of hexadecanoic acid	1.5	99
Butyl ester of sebacinic acid	1.7	91
Non-saponifiable fraction of ethanol-benzene extract		
Lignoceryl alcohol	3.55	99
β -Amyrine	0.1	97
Begenyl alcohol	2.0	99
Ceryl alcohol	3.0	99
γ -Tocopherol	0.2	99
Sugiol	0.5	99
Butyl ester of octadecanoic acid	0.4	99
Butylpalmitate	0.9	99
1-Triacontanol	2.0	95

phenols, alkanes, a small amount of carboxylic acids and aromatic compounds, esters, unsaturated hydrocarbons. The compounds with aliphatic structure prevail in the extracts under investigation.

The use of LC allowed us to carry out narrower fractionation of ENH and EEB. A number of fractions with the high relative content of definite substances were obtained, in particular, butyloleate with relative content in some fractions

up to 76 %; butyl ester of hexadecanoic acid with relative content in some fractions up to 62 %.

A series of BAS were identified in bitumen extracted with *n*-heptane and with an alcohol-benzene mixture (ethanol/benzene (1 : 1)) from the brown coal of the Tyulgan deposit, as well as in its saponifiable and non-saponifiable fractions. These BAS include sugiol, β - and γ -tocopherols; β -amyrine; begenyl, ceryl and lignoceryl alcohols;

n-tetracosanol-1; hexa- and octadecanoic acid; butylmyristate; butylparaben; ferruginol; eicosane. The major part of BAS was concentrated in non-saponifiable part of *n*-heptane and ethanol-benzene extracts. A homologous series of aliphatic carboxylic acids were detected in the samples under study: C₁₈, C₂₀, C₂₂, C₂₄, C₂₆, C₂₈, C₃₀, C₃₂, C₃₄, C₃₆. Acids with an even number of carbon atoms are prevailing.

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REFERENCES

- Zherebtsov S. I. Alkylation of solid fossil fuel of low coalification degree with alcohols (Thesis. ... Dr. Sci. in Chemistry). D. I. Mendeleev Russian Chemical and Technological University, Moscow, 2017.
- Zherebtsov S. I. Extraction technologies and products of processing brown and nonstandard coal, *Ugol'*. 2009. No. 7. P. 63–66.
- Zherebtsov S. I. Non-fuel use of brown coal from the Itatskoe deposit, in: Experience and outlooks of science-intensive technologies in the coal industry of the Kuzbass. Proceedings of scientific-technological conference. Kemerovo: Institute of Coal and Coal Chemistry SB RAS, 1998. P. 258–262.
- Zherebtsov S. I., Moiseev A. I. Composition of the wax fraction of bitumen from methylated brown coals, *Solid Fuel Chemistry*. 2009. Vol. 43, No. 2. P. 71–79.
- Zherebtsov S. I., Moiseev A. I. Integrated technologies and products of processing peat, brown and nonstandard coal of the Kuzbass, *Gor. Inform.-Analit. Bul.* 2008. No. S7. P. 114–124.
- Aronov S. G., Nesterenko L. L. Chemistry of solid fossil fuel. Kharkov: Izd-vo Khark. Gos. Un-ta, 1960. 371 p.
- Belkevich P. I., Golovanov N. G., Dolidovich E. F. Butimen of peat and brown coal. Minsk: Nauka i Tekhnika, 1989. 125 p.
- Shpakodraev K. M., Zherebtsov S. I., Ismagilov Z. R. Extraction and component composition of bitumoids of solid fossil fuel (a review), *Vestn. Kuzbas. Gos. Tekhn. Un-ta*. 2018. No. 1. P. 169–180.
- Shpakodraev K. M., Zherebtsov S. I., Smotrina O. V., Ismagilov Z. R. Structural-group and component composition of the fractions of bitumen of brown coal from the Tyulgan deposit, *Chemistry for Sustainable Development*. 2018. Vol. 26, No. 6. P. 707–715.
- Ayvazov B. V. Practical handbook on chromatography. Moscow: Vyssh. Shk., 1968. 279 p.
- Nakanisi K. Infrared spectra and structure of organic compounds. Moscow: Mir, 1965. 219 p.
- Bellami L. D. New data on IR spectra of complicated molecules. Moscow: Mir, 1971. 318 p.
- Pretsch E., Bühlmann P., Affolter C. Structure Determination of Organic Compounds: Tables of Spectral Data, 3rd ed. Berlin, Heidelberg, New York, Barcelona, Hong Kong, London, Milan, Paris, Singapore, Tokyo: Springer, 2000. 404 p.
- Nyquist R. A. Interpreting Infrared, Raman, and NMR Spectra. Vol. 1. San Diego: Acad. press, 2001. 448 p.
- Silverstein R. M., Webster F. X., Kiemle D. J. Spectrometric Identification of Organic Compounds, 7th ed. Hoboken: John Wiley & Sons. Inc., 2005. 502 p.
- Kalaitzidis S., Georgakopoulos A., Christanis K., Iordanidis A. Early coalification features as approached by solid state ¹³C CPMAS NMR spectroscopy, *Geochim. Cosmochim. Acta*. 2006. Vol. 70. P. 947–959.
- Mao J.-D., Schimmelmann A., Mastalerz M., Hatcher P. G., Li Y. Structural features of a bituminous coal and their changes during low-temperature oxidation and loss of volatiles investigated by advanced solid-state NMR spectroscopy, *Energy & Fuels*. 2010. No. 24. P. 2536–2544.
- Kalabin G. A., Kanitskaya L. V., Kushnarev D. F. Quantitative NMR spectroscopy of natural organic raw material and the products of its processing. Moscow: Khimiya, 2000. 408 p.
- PubChem [Electronic resource]: [scientific database]. Chemical compounds and mixtures. USA: National Center for Biotechnology Information, 2004. URL: <https://pubchem.ncbi.nlm.nih.gov>, free (accessed: 30.08.2019).