ISSN 1068-364X, Coke and Chemistry, 2022, Vol. 65, No. 9, pp. 386–391. © Allerton Press, Inc., 2022.
Russian Text © The Author(s), 2022, published in Koks i Khimiya, 2022, No. 9, pp. 15–21.

CHEMISTRY

Physicochemical and Antioxidant Properties of Humic Acids from Low-Sulfur Kazakhstan Shales

S. M. Suimbayeva[a, *], **Zh. K. Kairbekov**[a, **], **A. S. Maloletnev**[b, ***], **K. O. Kishibayev**[c, ****], and **I. M. Dzheldybaeva**[a, *****]

[a] *Scientific Research Institute for New Chemical Technologies and Materials, al-Farabi Kazakh National University, Almaty, Kazakhstan*

[b] *Mining Institute, Moscow Institute of Steel and Alloys, Moscow, Russia*

[c] *Kazakh National Women's Pedagogical University, Almaty, Kazakhstan*

**e-mail: saltanat_suimbayeva@mail.ru*
***e-mail: zh_kairbekov@mail.ru*
****e-mail: anstanmal@mail.ru*
*****e-mail: kishibaev64@gmail.com*
******e-mail: indiko_87@mail.ru*

Received June 23, 2022; revised June 23, 2022; accepted July 25, 2022

Abstract—The structural, chemical, and physicochemical characteristics and antioxidant properties of humic acids isolated from shale in the Kenderlyk and Kiin fields are determined. Negative values of the acids' oxidation are found: –3.62 and –4.06 for Kenderlyk and Kiin shale, respectively. Thus, the shale-based humic acids are reducing agents. IR spectroscopic data show clear absorption bands of hydroxyl, functional, and carbonyl groups. ESR spectroscopy indicates a high content of paramagnetic centers in the humic acids: 9.3×10^{17} and 9.5×10^{17} spin/g for Kenderlyk and Kiin shale, respectively. The paramagnetic centers in the molecular structure of the humic acids indicate that they are promising as antioxidants.

Keywords: fuel shales, humic acids, functional groups, physicochemical characteristics, antioxidant properties, IR spectroscopic data, ESR spectroscopy

DOI: 10.3103/S1068364X2270003X

INTRODUCTION

In Kazakhstan today, coal and shale processing is of great interest, and researchers are seeking to identify the basis for the development of a coal and shale industry. The nation has more than 400 basins and fields containing coal and lignite (particularly promising are the Oi-Qaragai, Maikubinsk, Alakol, and Mamytsk fields), as well as fuel shales (in particular, the Kenderlyk, Baikozhinsk, and Priural'sk fields, as well as a group of deposits in the west). Their industrial reserves amount to billions of tons [1, 2].

The highest quality shales are low-sulfur shales from the Kenderlyk field (eastern Kazakhstan), where they are extracted along with coal. D coal (size class ≤300 mm) is open-pit mined for domestic use and also for bed and dust combustion and for brick, cement, and lime production. Extraction at a rate of 300000 t/yr is planned.

The total reserves of Kenderlyk shale are estimated at 4075 million t, with readily available reserves of 708 million. The coal reserves are 55.2 million t. The shale may be divided into three suites: Kenderlyk (medium–late Carboniferous) and also Karaungursk and Saikansk (Taranchinsk) from the early Permian age. In the upper part of the Kenderlyk suite (the coal-bearing subsuite), two beds are of industrial value: Kalyn-Kara and Luchshii. The tar yield in the pyrolysis of Luchshii shale exceeds 10%; in some cases, it may be 27%. The yield of distillate fractions in the tar is 20.7 wt % gasoline fraction, 0.5 wt % ligroin fraction, and 20.4% diesel fraction.

The Kiin shale deposit within the Priural'sk group of fields is in the Stepnyi region of the Aktyubinsk Oblast (western Kazakhstan) in the upper reaches of the Kiya River and the left branch of the Ural River. The total reserves amount to 10 million t. Within the geological cross section of the Kiin suite, we find ~55 beds and intercalations of bituminous and fuel shales (height 0.1–20 m) [3].

In studying fuel shales, the elemental composition of its organic matter is usually determined, as well as the composition and properties of the bitumen, the products of hydrogenation, oxidation, thermal decomposition, hydrolysis, the reduction of kerogen, and so on. However, only a few studies of humic matter as a component of shale's organic mass are known. By contrast, humic matter has been studied in peat, lignite, oxidized coal, sapropels, soils, peloids, and elsewhere. Humic acids from Kazakhstan coal were investigated in [4]. Such coal and the corresponding humic acids contain paramagnetic centers. That indicates the presence of free radicals in the molecules of the coal and humic acids. Research shows that humic acids have antioxidant activity [4].

The antioxidant activity of humic acids from Aleksandriisk lignite (Ukraine) in radical-chain oxidation of model aromatic hydrocarbons was studied in [5]. It was found that the presence of oxygen-bearing functional groups (–COOH, –OH) in the macromolecules of humic acids is associated with antioxidant activity.

There is almost no information regarding the structural, chemical, and physicochemical characteristics and antioxidant properties of humic acids isolated from shale. That prevents the appropriate use of such humic acids in the chemical industry and also prevents the formulation of biogeochemical laws describing humification, as noted in [6, 7]. Researchers expect that analysis of the physicochemical properties of humic acids derived from shale and the determination of their functional, amino-acid, and hydrocarbon composition will permit their use in the production of pharmaceuticals or soil conditioners [6].

In the present work, we isolate humic acids from Kenderlyk and Kiin fuel shales; and determine their functional and hydrocarbon compositions. By IR and ESR spectroscopy, we investigate their structural, chemical, and physicochemical characteristics and their antioxidant properties.

EXPERIMENTAL

In the experiments, the shale samples are crushed in air for 30 min. We use a laboratory ball mill, in which steel balls are sealed within a steel vessel (vibrational frequency 3000 rpm).

The humic acids are extracted by decalcifying the shale using a 0.1 N solution of hydrochloric acid (with 1 : 20 dilution); by exhaustive extraction using dilute NaOH solution at room temperature (20°C); and by deposition of the humic acids as a result of acidification by the methods in [6, 7]. The residues are washed with dilute 0.1 N hydrochloric acid. After mixing, they are left to stand for 10–12 h. Acidic treatment of the shales continues until a negative response for the calcium content is obtained.

The deposits after standing are washed with distilled water until neutral and the humic acids are extracted by means of 0.1 N NaOH solution, over the course of days. The liquid is run off, and the residue is again washed with alkaline solution. Extraction continues until the alkaline solution is markedly clarified. Then coagulant (NaCl to concentrations of 0.8 g/L) is added to the alkaline extract so as to precipitate mineral colloids. The next step is centrifuging. After acidification of the fugate to pH 1–2, the humic acid flakes that form are separated by centrifuging. For purification purposes, the humic acids undergo repeated solution in alkali, deposition, and centrifuging. The purified humates are dried at 50–60°C and ground in an agate mortar.

The elemental composition of the humic acids is determined in accordance with State Standard GOST R 54221–2010 [8]. Their yield is determined in accordance with State Standard GOST 9517–94 (ISO 5073–85) [9]. The specific surface (m^2/g) is determined by the method in [10]; and the monolayer volume (m^2/g) is determined by the method in [11]. We find that the yield of humic acids is 9.8% for regular Kenderlyk shale and 7.2% for the corresponding Kiin shale. The carbon content in the humic acids is 62.02–62.47 wt % and the hydrogen content is 6.07–6.21 wt %. Those results are consistent with the range in the literature [3]. The nitrogen content in the humic acids is 2.35–2.75 wt %; the oxygen content is 28.33–28.57 wt %; and the sulfur content is 0.59–0.64 wt %.

The IR spectra of the humic acids are recorded on a Bruker Tensor II instrument (United States), using a diffraction grating. In preparing the samples for IR spectroscopy, we use the standard method [12]: they are mixed with 500 mg KBr and then ground for 0.5 h; the mixture obtained is dried for 1 h at 90°C, with subsequent pressing into 200-mg tablets. In the IR spectra, the intensity of the absorption band in the range 600–3600 cm^{-1} is recorded. The spectrograms are analyzed by the method in [13, 14].

The presence of paramagnetic centers is determined by means of a JEOL JES-FA 200 ESR spectrometer, in normal conditions ($T = 26°C$, atmospheric pressure), with a working frequency of 9.3 GHz when the modulation current is 0.10 A. We use a modulation current of 0.75 A. The concentration of paramagnetic centers corresponding to free radicals is determined by comparing the area of the spectrum for the given sample with that for a point standard graduated in accordance with the DPPH standard. The standard sample chosen is 2,2-diphenyl-1-picrylhydrazyl $(CH_6H_5)_2–N–N–C_6H_5(NO_3)_2$, which consists entirely of radicals. At 3.5 VE^2, the standard sample has 4.8×10^{15} paramagnetic centers. The intensity of the resonant line is determined from the area under the absorption curve.

Table 1 presents the characteristics of the Kenderlyk and Kiin shales. We see that the moisture content is 1.86% for the Kenderlyk shale, while its ash content is 64.5%; the corresponding figures for the Kiin shale are 2.25% and 70.5%. The carbon content in the organic matter of the shales is 74.5 and 74.10 wt %, respectively. The concentrations of other components in the Kenderlyk and Kiin shale, respectively, are as follows (wt %): 70.05 and 71.30 SiO_2; 15.57 and 16.40 $Al_2O_3 + TiO_3$; 7.05 and 8.01 Fe_2O_3; 1.39 and 1.45 CaO; 1.47 and 1.51 MgO; 3.85 and 5.66 $Na_2O + K_2O$; and 0.62 and 0.65 SO_3. Note that the K_2O content is higher for the Kiin shale than for the Kenderlyk shale; in addition, its SiO_2 and Fe_2O_3 concentrations are higher. The calorific value is 14.46 and 18.12 MJ/kg for the Kenderlyk and Kiin shale, respectively (bomb tests). In semicoking, the tar yield is 5.9 and 6.5% (dry samples) for Kenderlyk and Kiin shale, respectively.

RESULTS AND DISCUSSION

We know that the functional composition of humic matter is represented by characteristic polar functional groups –COOH, –OH, –CO, and $-NH_2$, as well as long alkyl side chains of fatty acid residues [15]. Therefore, we determine the content of carboxyl, phenol, and carbonyl groups in the humic acids. The sum of acidic functional groups –COOH and $-OH_{phen}$ is determined by the barite method; the content of carboxyl groups by chemisorption using calcium acetate; and the quantity of $-OH_{phen}$ groups by calculating the difference between the total acidity and the quantity of –COOH groups. Carbonyl groups are determined on the basis of phenylhydrazine ($C_6H_5NHNH_2$).

The dissociation constants pK_α of the acidic groups are determined as follows [16, 17]. A 0.1 N aqueous solution of NaCl is poured over weighed humic acid samples (1 g) in 50-mL vessels. After some time, titrated alkali is added. Constant pH is restored after the addition of each portion and held for 15 min. To prevent dilution of the salt in titration, the alkali for titration is prepared in 0.1 N NaCl solution. The dissociation constants of the acidic groups in the humic acids are calculated by means of the modified Henderson–Hasselbach equation

$$pK = pH + n\log\frac{1-\alpha}{\alpha}, \qquad (1)$$

where α is the degree of neutralization of the polymeric acid.

Table 2 presents the results of functional analysis of the humic acids. We see that the overall acidity of the humic acids is 6.46 and 6.51 for the samples from Kenderlyk and Kiin shale, respectively. The total content of acidic groups in the humic acids is 1.78 and 1.81 mg-eq/g for the Kenderlyk and Kiin shale, respectively. That includes 1.29 and 1.31 mg-eq/g for carboxyl groups, 0.49 and 0.50 mg-eq/g for phenol hydroxides, and no carbonyl groups.

In addition to the properties in Table 2, we also calculate the degree of association cA and degree of oxidation cO of the humic acids (Table 3). In calculating the degree of association, we take account of the number of carbon bonds per atomic unit that remain free, if we assume that all the other elements are bound with carbon. (In other words, this index characterizes the

Table 1. Characteristics of shales and humic acids

Characteristic	Field	
	Kenderlyk	Kiin
Shale properties		
Moisture content W^a, %	1.86	2.25
Ash content of regular shale A^a, %	64.50	70.50
Yield of volatiles V^{daf}, %	78.74	81.50
Elemental composition, wt %:		
C^{daf}	74.45	74.10
H^{daf}	8.95	7.60
N^{daf}	0.45	0.50
S_t^d	0.70	0.65
O^{daf} (calculated as the difference)	15.45	17.75
Calorific value (bomb tests) Q_b^a, MJ/kg	14.46	18.12
Chemical composition of mineral component, %:		
SiO_2	70.05	71.30
$Al_2O_3 + TiO_3$	15.57	16.40
Fe_2O_3	7.05	8.01
CaO	1.39	1.45
MgO	1.47	1.51
SO_3	0.62	0.65
Na_2O	2.25	2.31
K_2O	1.60	3.35
Yield of semicoking products (dry samples), %:		
tar	5.9	6.5
semicoke	89	93
pyrogenetic water	3.5	3.7
gas + losses	3.6	4.3
Yield $(HA)^{daf}$ of humic acids (dry, ash-free samples), %	9.8	7.2
Properties of humic acids		
Elemental composition, wt %:		
C^{daf}	62.47	62.02
H^{daf}	6.21	6.07
N^{daf}	2.35	2.75
S_t^d	0.64	0.59
O^{daf} (calculated as the difference)	28.33	28.57
Specific surface, m^2/g	23.10	22.80
Monolayer volume, m^2/g	4.80	4.63

Table 2. Acidic properties of humic acids and content of functional groups

Source of humic acids	Acidic properties pK_α	Content of functional groups, mg-eq/g			
		$COOH + OH_{phen}$	COOH	OH	C=O
Kenderlyk shale	6.46	1.78	1.29	0.49	None
Kiin shale	6.51	1.81	1.31	0.50	None

number of C–C bonds.). We calculate this index on the basis of the elemental composition (in wt %) for dry ash-free samples, in accordance with [18]

$$cA = \frac{4/12\,C - H - 2/16\,O - 3/14\,N - 2/32\,S}{4/12\,C}. \quad (2)$$

The degree of oxidation, which characterizes the proportion of carbon bonds with oxygen, is calculated analogously from the elemental composition, as follows

$$cO = 2/16\,O - H + 3/14\,N + 3/32\,S. \quad (3)$$

For humic acids from Kenderlyk and Kiin shale, cA = –2.77 and –3.18, respectively, on the basis of Eq. (2). In other words, around half the carbon bonds are of C–C type.

The degree of oxidation permits more precise estimation of the electronegative and electropositive atoms per carbon atom. According to Eq. (3), the degree of oxidation of the Kenderlyk and Kiin shale humic acids is –3.62 and –4.06, respectively. Thus, the humic acids are reduced compounds.

IR Spectroscopy of Humic Acids

The humic acids have few bands in their IR spectra (Table 4), as is clear from analysis on the basis of [19]. We observe absorption bands at 3299 and 3300 cm^{-1}, due to hydroxyl groups of different types with hydrogen bonds. In addition, absorption by NH groups is possible in that region. We also see bands at 2946 and 2948 cm^{-1} due to valence vibrations of methyl and methylene groups. The intensity of all these bands is considerable. The bands at 2946 and 2948 cm^{-1} are stronger, indicating a predominance of methylene groups. We also note an elevated H/C ratio. In the IR spectra of the Kenderlyk samples, we see absorption bands of nitriles at 2342–2363 cm^{-1}; these are not seen in the spectra of the Kiin samples.

Table 3. Degree of association (cA) and degree of oxidation (cO) of humic acids

Source of humic acids	cA	cO
Kenderlyk shale	–3.18	–4.06
Kiin shale	–2.77	–3.62

The absorption in this region may be attributed to valence vibrations of the carbonyl groups in the carboxyl grouping of the carbonic acids at around 1705 and 1708 cm^{-1}. When salts are formed, the carboxyl groups are restructured and the vibration frequency correspondingly. Thus, it is likely that the band of the carboxyl group may coalesce with the band of lower intensity centered at 1705 and 1708 cm^{-1}. In other words, the band is complex on account of the superposition of vibrations of different groups and bonds.

We should note the intense band around 1636–1653 cm^{-1} in the IR spectra of the Kenderlyk samples; these are not seen in the spectra of the Kiin samples. Note that the shale humic acids contain little nitrogen but have a high carbon content. As a result, their phenolic content is obviously low. Most likely, this complex band consists of several smaller bands.

The band at 1640 cm^{-1} corresponds to the complex absorption of C=O bonds in quinones and ketones (unsaturated and diacrylic ketones) and also of C–O bonds in the amide groups of proteins and peptides. The vibration of aromatic C=C bonds contributes to the 1650 cm^{-1} band and does not appear independently, e specially when their content is low. Thus, the intense band near 1650 cm^{-1} is complex.

In the IR spectra of the Kenderlyk samples, we see absorption bands of nitrogen-bearing compounds at 1558 cm^{-1}; these are not visible in the spectra of the Kiin samples. In all the humic acid samples, we note absorption bands of aliphatic amines at 1202 and 1200 cm^{-1}. In addition, we see intense bands corresponding to the deformational vibrations of CH in $-CH_2$ and $-CH_3$ groups, with peaks at 1456 and 1458 cm^{-1}.

For all the humic acid samples, we see relatively strong bands (comparable in intensity with the 3299 and 3300 cm^{-1} bands) at 1058 and 1060 cm^{-1}. These bands are usually attributed to the influence of alcoholic hydroxyl groups. The band around 1058 cm^{-1} is also complex: the absorption is due to both hydrocarbons and oxygen-bearing aliphatic groups.

In the IR spectra of all the samples, we see absorption bands at 852 and 860 cm^{-1} (nitrates $R-O-NO_2$), 795 and 797 cm^{-1} (*trans*-nitrites RO–N=O), and 624–690 and 625–695 cm^{-1} (*cis*-nitrites RO–N–O).

Thus, the IR spectra of all the shale humic acid samples have a small set of bands, with none in the

Table 4. IR spectral characteristics of humic acids

Compound	Field	
	Kenderlyk	Kiin
	absorption band, cm^{-1}	
Hydroxyl groups	3299	3300
Long methylene groups	2946	2948
Nitriles	2363–2342	–
Carbonyl groups	1705	1708
Unsaturated and diacrylic ketones	1653–1636	–
Nitrogen-bearing compounds	1558	–
Deformational vibrations of CH in $-CH_2$ and $-CH_3$ groups	1456	1458
Aliphatic amines	1202	1200
Alcoholic hydroxyl groupings	1058	1060
Nitrates $R-O-NO_2$	852	860
Nitrates *Trans*-nitrites RO–N–O	795	797
Nitrates *Cis*-nitrites RO–N–O	690–624	695–625

long-wave region. We see pronounced bands corresponding to hydroxyl groups, $-CH_2$ groups, $-CH_3$ groups, and carbonyl groups.

ESR Spectroscopy of Humic Acids

In Fig. 1, as an example, we show the ESR spectrum of humic acids from Kenderlyk shale. As we see, in the ESR spectra of humic acids, a single intense broad band, whose Lande spectroscopic splitting factor is $g = 2.003$, is identified. We know that the g factor is determined by the presence of free radicals due to the delocalized electron cloud on the molecule [17].

By ESR spectroscopy, we establish that the content of paramagnetic centers in the humic acids from Kenderlyk and Kiin shale, which determines the potential of those humic acids as antioxidants, is 3.66×10^{15} and 3.68×10^{15} spin/g, respectively. The high content of paramagnetic centers in the humic acids indicates the presence of free radicals, with concentrations of 9.3×10^{17} and 9.5×10^{17} spin/g, respectively.

Thus, after investigation of the physicochemical properties of the humic acids, determination of their structural and chemical characteristics, and analysis of spectral data, we may regard the humic acids from Kenderlyk and Kiin fuel shales as natural humic mate-

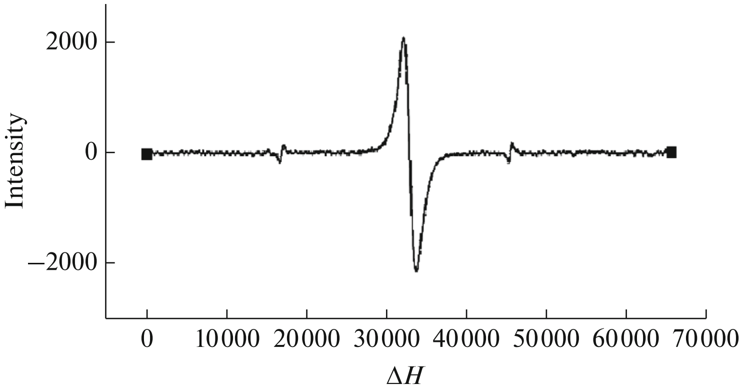

Fig. 1. ESR spectrum of humic acids from Kenderlyk shales.

rials. The high content of paramagnetic centers in the humic acids indicates that they are promising as antioxidants.

CONCLUSIONS

The structural and chemical characteristics of humic acids from Kenderlyk and Kiin fuel shales (Kazakhstan) may be determined by investigating their physicochemical and antioxidant properties using IR and ESR spectrometry.

In the shale humic acids, we note relatively high content of carbon (62.02–62.47%) and hydrogen (6.07–6.21%). The atomic ratio H/C is 1.10–1.13. That indicates that the aromatic rings are highly substituted and the periphery of the humic acid molecules is well developed.

Functional analysis shows that the total acidity of humic acids from the Kenderlyk and Kiin fuel shales is 6.46 and 6.51 mg-eq/g, respectively. The total content of acidic groups is 1.78 and 1.81 mg-eq/g, respectively, including 1.29 and 1.31 mg-eq/g carboxyl groups and 0.49 and 0.50 mg-eq/g phenol groups. There are no carbonyl groups.

Negative values are obtained for of the degree of oxidation of the Kenderlyk and Kiin humic acids: –3.62 and –4.06. That is typical of reduced compounds.

According to IR spectral data, the Kenderlyk and Kiin fuel shales have a similar molecular structure. The basic components are carbonyl, hydroxyl, and aliphatic functional groups of similar composition.

The ESR spectral data show that the content of paramagnetic centers is 3.66×10^{15} and 3.68×10^{15} spin/g, respectively, for the Kenderlyk and Kiin humic acids. The high content of paramagnetic centers in the humic acids indicates the presence of free radicals, with concentrations of 9.3×10^{17} and 9.5×10^{17} spin/g, respectively. The high content of paramagnetic centers in the humic acids indicates that they are promising as antioxidants.

FUNDING

Financial support was provided by the science committee of the Kazakhstan Ministry of Education and Science (grant AR09057905).

REFERENCES

1. Kairbekov, Zh.K., Toktamysov, M.T., Zhalgasuly, N., and Eshova, Zh.T., *Kompleksnaya pererabotka burykh uglei Tsentral'nogo Kazakhstana* (Complex Conversion of Lignites of Central Kazakhstan), Almaty: Izd-vo Kaz. Nats. Univ., 2014.
2. Kairbekov, Zh.K., Ermoldina, E.T., Kairbekov, A.Zh., and Dzheldybaeva, I.M., *Kompleksnaya pererabotka burykh uglei Yuzhnogo Kazakhstana* (Complex Conversion of Lignites of South Kazakhstan), Almaty: Izd-vo Kaz. Nats. Univ., 2018.
3. *Basseiny i mestorozhdeniya uglei i goryuchikh slantsev Kazakhstana. Spravochnik* (Basins and Fields of Coals and Oil Shales of Kazakhstan: Reference Book), Almaty: Izd-vo Komiteta Geologii i Prirodopol'zovaniya, 2013.
4. Jeldybayeva, I.M., Kairbekov, Zh.K., and Suimbayeva, S.M., Investigation of physico-chemical and antioxidant properties of humic acids isolated from coal, *Dokl. Nats. Akad. Nauk Resp. Kaz.*, 2021, no. 5, pp. 109–118. https://doi.org/10.32014/2021.2518-1483.89
5. Khil'ko, S.L., Efimova, I.V., and Smirnova, O.V., Antioxidant properties of humic acids from brown coal, *Solid Fuel Chem.*, 2011, vol. 45, no. 6, pp. 367–371. https://doi.org/10.3103/S036152191106005X
6. Krechetova, E.V., Humic acids of oil shales, their properties and structure: *Cand. Sci. (Biol.) Dissertation*, Moscow: Moscow State Univ., 1994.
7. Krechetova, E.V., Comparative characteristics of humic acids composition and properties in oil shales and soils, *Pochvovedenie*, 1994, no. 2, pp. 57–66.
8. *GOST R* (State Standard) *54221-2010: Humic substances from brown coals, lignites and oxidized coals. Test methods*, 2012.
9. *GOST* (State Standard) *9517-94 (ISO 5073-85): Solid fuel. Methods for determination of humic acids yield*, 1997.
10. Gregg, S.J. and Sing, K.S.W., *Adsorption, Surface Area and Porosity*, London: Academic Press, 1967.
11. Brunauer, S., Emmett, P.H., and Teller, E., Adsorbtion of gases in multimolecular layers, *J. Am. Chem. Soc.*, 1938, vol. 60, no. 2, pp. 309–319. https://doi.org/10.1021/ja01269a023
12. Egorova, T.F., Klinkova, V.V., and Skripchenko, G.B., Quantitative IR spectroscopy of brown coal from the Kansk-Achinsk basin, *Khim. Tverd. Tela*, 1985, no. 4, pp. 3–8.
13. Nakanishi, K., *Infrared Spectra and Structure of Organic Compounds*, Holden-Day, 1957.
14. Agapov, A.I. and Katunina, E.E., Paramagnetic properties and structure of the peloid humat substances, *Izv. Samar. Nauchn. Tsentra Ross. Akad. Nauk*, 2010, vol. 12, no. 1–8, pp. 2007–2010.
15. Rus'yanova, N.D., *Uglekhimiya* (Carbon Chemistry), Moscow: Nauka, 2003.
16. Lishtvan, I.I., Kruglitskii, N.N., and Tretinnik, V.Yu., *Fiziko-khimicheskaya mekhanika guminovykh veshchestv* (Physicochemical Mechanics of Humic Substances), Minsk: Nauka i Tekhnika, 1976.
17. Zhorabekova, Sh.Zh., *Makroligandnye svoistva guminovykh kislot* (Macroligand Properties of Humic Acids), Frunze: Ilim, 1987.
18. Veselovskii, V.S., *Ispytanie goryuchikh iskopaemykh* (Testing of Combustible Fossils), Moscow: Gostoptekhizdat, 1963.
19. Tarasevich, B.N., *IK spektry osnovnykh klassov organicheskikh soedinenii* (Infrared Spectra of Basic Classes of Organic Compounds), Moscow: Mosk. Gos. Univ., 2012.

Translated by B. Gilbert