Petroleum and Coal

Article **Open Access**

Electron Spin Resonance of Humic and Hymatomelanic Acids, Lipids and Initial Brown Coal of the Nether-Polar Urals

*Olga A. Gurova, Mikhail P. Sartakov, Evgeny M. Osnitsky**

Institute of Oil and Gas, Yugra State University, Khanty-Mansiysk, Russia

Received May 4, 2022, Accepted December 1, 2022

Abstract

This work presents the results of studying paramagnetic activity of humic and hymatomelanic acids, lipids and initial brown coal of the Otoryinsk field in the Nether-Polar Urals. Two methods were used for quantitative research: the method of ABS spins and the double resonator method relative to TEMPO. The two methods were compared. Concentrations of paramagnetic cents per gram and molecular weights of assumed paramagnetic molecules were calculated. Based on the results obtained, it was concluded that humic acids have higher paramagnetic activity than hymatomelanic acids. The differences in paramagnetic activity of the studied samples were identified.

Keywords: *Brown coal; Lipids; Humic acids; Hymatomelanic acids; Electron spin resonance; Nether-Polar Urals.*

1. Introduction

During the second half of the twentieth century eight deposits of brown coal were found and explored in the Berezovski district of the Khanty-Mansiysk Autonomous Okrug – Ugra (the Nether-Polar Urals). Three of the fields – Lyulyinsk, Tolyinsk, and Otoryinsk – are near the largest settlement in the north-western part of the Berezovski district – Saranpaul village [1-2].

Commercial coal mining was not carried out at these deposits. The basic idea of many reports and project documents is to provide local heat and electricity supply without bringing in hard coal and heavy fuel oil for local boiler houses. However, we suggest assessing the potential for advanced processing of brown coals based on studying their physic-chemical characteristics, particularly fundamental properties of humic acids, their paramagnetic activity.

Studying chemical nature of humic acids (HA) and hymatomelanic acids (HMA) of brown coals is connected with solving the fundamental problem related to coalification mechanism in the Nether-Polar Urals (the Khanty-Mansiysk Autonomous Okrug – Ugra), which is conditioned by the specific character of structural and molecular transformation of coal organic matter.

The electron paramagnetic resonance (EPR) method is widely used in the study of coals [3-7]. An advantage of EPR spectroscopy is the possibility to detect unpaired electrons even in case of their low concentration in any substance without changing its composition or structure. Free electrons have much energy and high activity in any system (chemical or biological). In humic substances, electrons are bound to the greater part of a molecule, hence they move in highly delocalized molecular orbitals and condition the activity of atom groups forming the molecule [8-10].

Electronic paramagnetism is the fundamental property of all humic substances. Their paramagnetic properties are connected with a peculiar redistribution of electron density in molecular p-orbitals. The more condensed the structure of macromolecules is, the stronger their paramagnetic properties are. For humic acids (HA) and hymatomelanic acids (HMA), paramagnetic activity increases in the series: sapropel, peat, soil, coal [11-13].

2. Experimental

The central part of the Otoryinsk field is eight kilometres east of Tolya village and 280 kilometres north in a straight line from the nearest railway station Polunochnoye. The winter

road from the field to the town of Ivdel is 370 kilometres. Geographical coordinates of the central part of the field are 63°14′ NL and 60°21′ EL. The Otoryinsk field is in the eastern part of the Otoryinsk anticline, and in the west it is limited to the axial part of the anticlinal structure, where it goes through the erosion section of the coal-bearing strata. In the east the field is limited either along the line where the coal-bearing strata of the main seam wedges out, or along a conventional line drawn at the depth of 300 metres in the main seam roof. The surface of the field is slightly hilly, higher in the north and in the south, dissected by numerous rivers and streams. Absolute heights in the valleys of large rivers, near the water's edge, range from 62.0 to 30.0 m, rising in the watersheds in the southern part of the field up to 180 m, in the northern part – up to 120 m. A significant part of the field area is swamped to one degree or another and covered with an oppressed fir-pine forest; a normal building spruce-fir-pine forest grows only along the valleys of the Volya, Tolya, Mauryngya and Otorya rivers, where these valleys are well drained [1-2].

The coal-bearing strata lie over dislocated rocks of the Paleozoic (presented in the area by diabases, diabase porphyrites with interlayers of clay shales and quartz sandstones) or over the products of their weathering. In some places, in the eastern part of the field, where the Paleozoic basement is somewhat elevated, the coal-bearing stratum wedges out, and coal argillites overlie the weathering crust. Everywhere, coal-bearing formations are covered by coal argillites mentioned above, as well as by clays along the section. In the western uplifted axial part of the anticline, where these sediments are eroded, coal-bearing deposits sometimes come to the surface or are covered by Quaternary glacial or interglacial deposits. According to the exploration data [1-2], the Otoryinsk formation contains eight seams of coal. The most mature of them is the "Main seam". Coal seams below the "Main seam" are generally poor in striking and depth and are located in small, limited areas (Table 1) [1-2].

Table 1. Structure and thickness of coal seams in the Otoryinsk field according to the exploration data

Formation	Thickness calculations from-to average (number of seam crossings)	No. and name of seam	Seam structure	Normal spacing between seams
Otoryinsk	1.8	Main «A»	Simple	3.0
	1.0-9.7 3.75 (16)	Main	Complex	7.0
	1.1-4.8 2.5 (8)	№14	Simple	8.0

The brown coal samples brought to the laboratory were made air-dry. The air-dried samples of brown coal were freed from lipids by extraction with benzene and decalcified with sulfuric acid for 12 hours until a negative reaction to calcium was reached. Excess sulfate ions were removed by distilled water washing. The HA were extracted from the decalcified samples using a decimolar sodium hydroxide solution for 12 hours, followed by two repeated treatments. An exhaustive extraction was not carried out.

The sodium humate solution was separated from the sludge by the centrifuge method. Sodium sulfate solution was added to separate the suspensoid of clay minerals. The HA were precipitated using a 0.25 M solution of H_2SO_4 at pH=1, then the samples were allowed to stand overnight for the precipitate to grow and mature, and were separated from the mother solution by centrifugation. The samples were dried at 40 degrees Celsius. The HMA were extracted from the HA using ethanol three times.

Thus, 8 samples were prepared for electron paramagnetic resonance (EPR) spectroscopy: initial brown coal, lipids, 3 samples of HA (HA 1, HA 2, HA 3) and three samples of HMA (HMA 1, HMA 2, HMA 3) corresponding to three successive extractions.

The EPR spectroscopy of the samples was carried out at the Novosibirsk Institute of Organic Chemistry, the Siberian Branch of the Russian Academy of Sciences (analyst L.A. Shundrin). Radio spectrometer Bruker ELEXSYS E-540 (X-band), with a high-quality cylindrical resonator. The research was carried out by two methods: the method of absolute spins (ABS Spins) and the double resonator method relative to TEMPO (2,2,6,6-tetramethyl-piperidine-1-oxyl). The

method of ABS Spins was developed by Bruker, and it is based on measuring the quality factor of a resonator at a microwave field power of 33 dB using an external standard.

3. Results and discussion

Figure 1 shows EPR spectra of brown coal and lipids extracted from it, HA and HMA on a double resonator relative to TEMPO. Figure 2 shows corresponding EPR spectra reflecting the full sweep of the field at 4000 G.

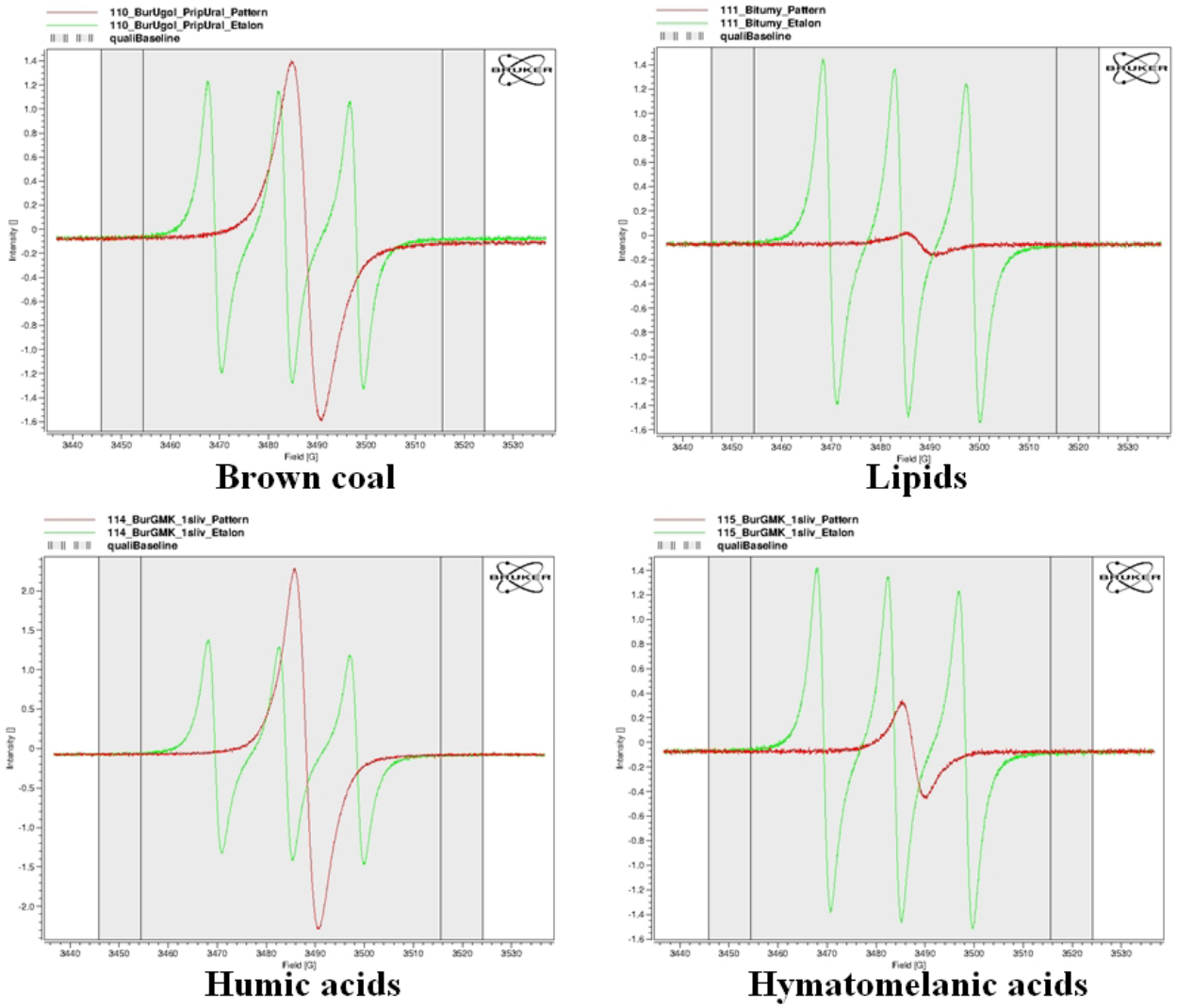

Figure 1.EPR spectra of brown coal and lipids extracted from it, HA and HMA on a double resonator relative to TEMPO

All spectra contain a singlet in the range of magnetic field H values of 3510 – 3515 G, which corresponds to free radicals of organic compounds. The spin content in the samples varies greatly.

Some spectra of a wide field sweep show broad impurity signals of paramagnetic inorganics. This is typical for HMA spectra. HA have a more intense signal than HMA, which corresponds to the nature of these substances, but the integrated observed signal intensity of the sample corresponds to its weight, for this reason there is no direct correspondence between the integrated signal intensity in the figures and the results of EPR spectroscopy.

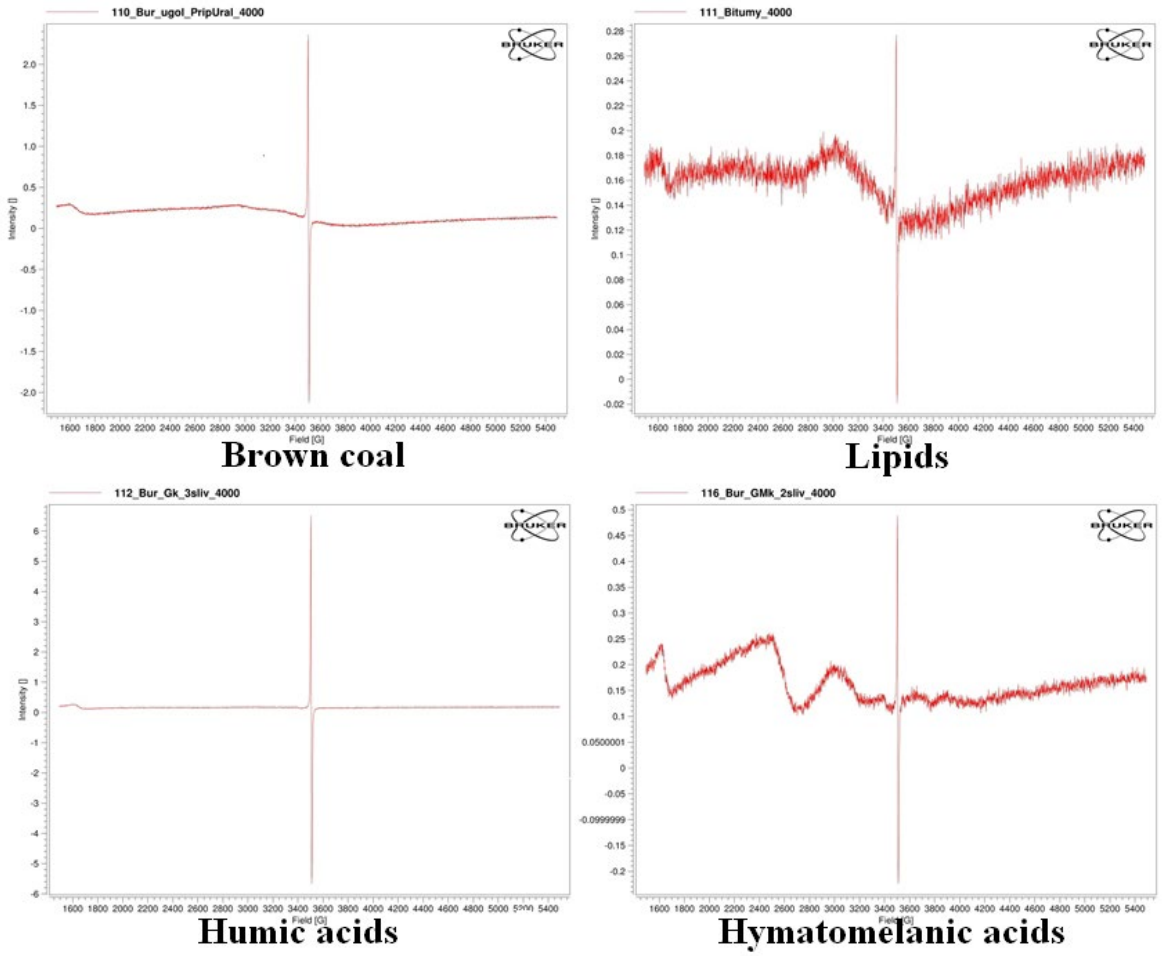

Figure 2. EPR spectra of brown coal and lipids extracted from it, HA and HMA reflecting the full sweep of the field at 4000 G

The results of EPR spectroscopy obtained by the two methods and the calculated concentration of paramagnetic centers in 1 mg are presented in Table 2. The method of ABS Spins systematically shows lower values compared to the results obtained with a double resonator. The error in the accumulation of measurement statistics ranges from 9 to 15%. The maximum error is observed in the samples with a low spin content. There is a strong correlation between the results obtained by the two different methods (Fig. 3).

Table 2. Results of quantitative EPR spectroscopy

Sample	m, mg	ABS spins method		Method of double resonator relative to TEMPO	
		Spin content	Concentration of paramagnetic centers, spin·mg^{-1}	Spin content	Concentration of paramagnetic centers, spin·mg^{-1}
Brown coal	58.2	8.517E+15	1.46E+14	1.5E+16	2.57E+14
Lipids	23.0	3.247E+14	1.41E+13	6.4E+14	2.79E+13
HA 1	32.7	5.951E+15	1.82E+14	1.3E+16	3.98E+14
HA 2	39.4	8.751E+15	2.22E+14	2.0E+16	5.16E+14
HA 3	38.8	1.066E+16	2.75E+14	2.7E+16	6.97E+14
HMA 1	32.8	6.608E+14	2.01E+13	2.0E+15	6.11E+13
HMA 2	33.5	7.252E+14	2.16E+13	1.8E+15	5.35E+13
HMA 3	36.8	5.210E+14	1.42E+13	1.5E+15	4.10E+13

(Numbering for HA and HMA samples corresponds to sequential extraction)

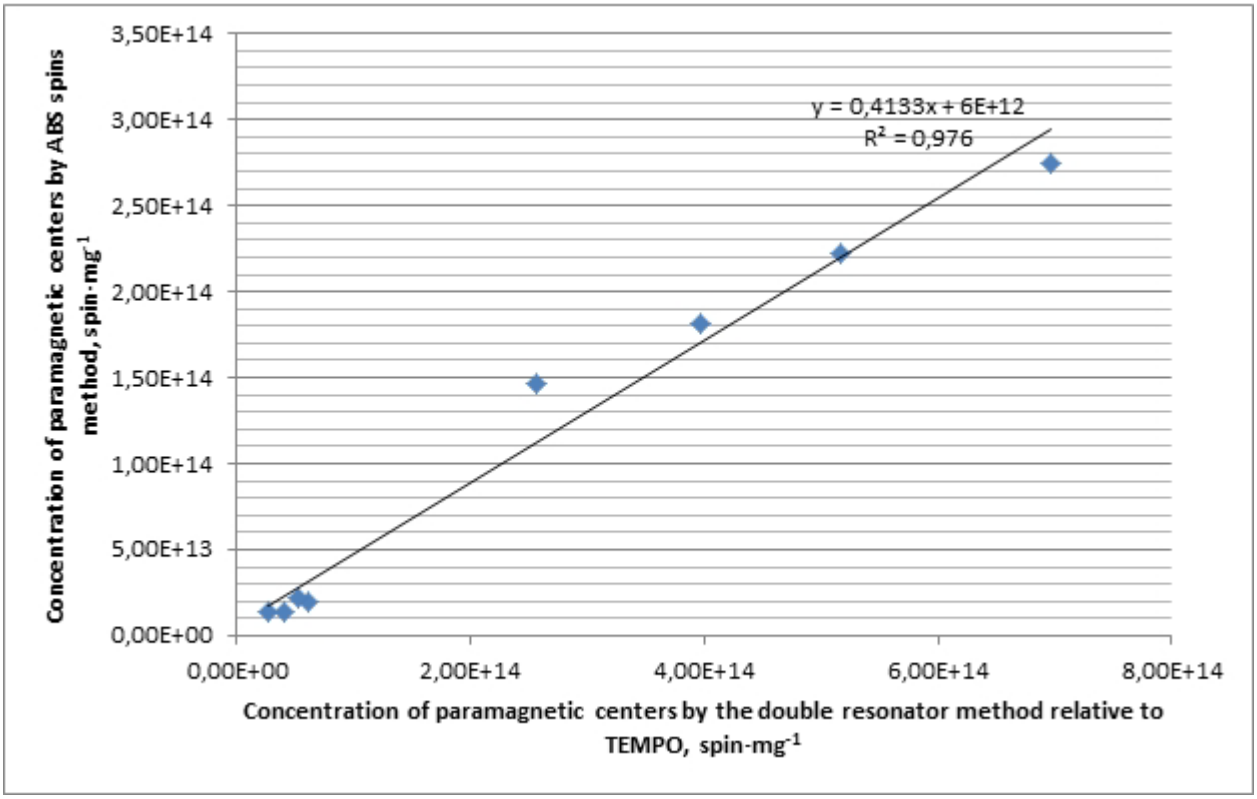

Figure 3. Correlation between the methods for determining spins

As the method of ABS Spins systematically shows lower values compared to the results obtained, further characterization of the samples was carried out based on the double resonator method relative to TEMPO.

The concentration of paramagnetic centers was recalculated per 1 gram of the substance (specific concentration of paramagnetic centers). The molecular weights of assumed paramagnetic molecules were calculated (Table 2). The calculation was made according to the following formula: $M = \frac{N_A}{N_S/g}$,

where: M molecular weight of an assumed paramagnetic molecule, g/mol; N_A – Avogadro constant $6{,}02 \cdot 10^{23}$, mol^{-1}; Ns/g specific concentration of paramagnetic centers, $spin \cdot g^{-1}$.

These molecular weights are not the molecular weights of HA and HMA. These are the molecular weights of assumed paramagnetic molecules obtained under the assumption that one molecule has one paramagnetic center. In essence, these molecular weights are an alternative representation of the specific concentration of paramagnetic cents. The larger the molecular weight is, the fewer paramagnetic centers are in 1 gram of the substance and the lower the paramagnetic activity of the samples is.

Table 3. Molecular masses of assumed paramagnetic molecules

Sample	Ns/g, $spin \cdot g^{-1}$	M, g/mol
Brown coal	2,57E+17	2,34E+06
Lipids	2,79E+16	2,16E+07
HA 1	3,98E+17	1,51E+06
HA 2	5,16E+17	1,17E+06
HA 3	6,97E+17	8,64E+05
HMA 1	6,11E+16	9,85E+06
HMA 2	5,35E+16	1,13E+07
HMA 3	4,10E+16	1,47E+07

The HA sample extracted in the third stage (HA 3) has the highest paramagnetic activity. For the studied HA, the paramagnetic activity increases in the successive extracts. The opposite is observed in HMA samples. The sample extracted first (HMA 1) has the highest paramagnetic activity. The paramagnetic activity decreases in the successive extracts. To compare the paramagnetic activity, it is convenient to use the ratio of the molecular masses of assumed paramagnetic molecules. The comparison was made with respect to the paramagnetic sample of HA 3 (Fig. 4).

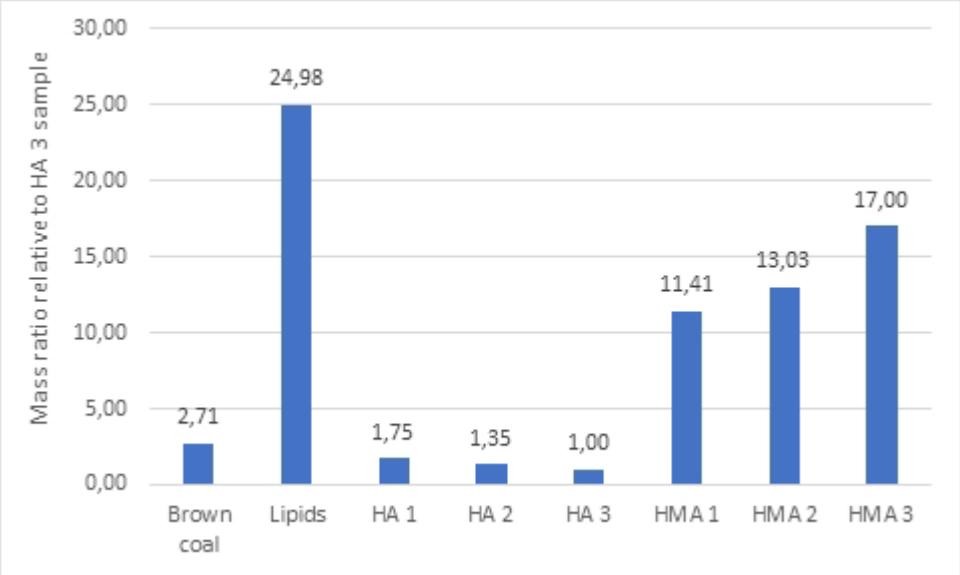

Figure 4. The ratio of the molecular masses of assumed paramagnetic molecules relative to HA 3 sample

The paramagnetic activity of the initial brown coal is quite high. This is due to the high content of HA, as well as the presence of paramagnetic inorganic molecules. The paramagnetic activity of the studied HA is an order of magnitude higher than that of HMA. Lipids have the lowest paramagnetic activity.

4. Conclusions

Among all the samples, those with HA have the highest paramagnetic activity. The specific concentration of paramagnetic centers in HA increases from the sample extracted first (HA 1 3.98E+17 spin·g^{-1}) to the third sample (HA 3 6.97E+17 spin·g^{-1}). Relative to the HA 3 sample, the molecular weights of the assumed paramagnetic molecules of the HA 2 and HA 3 samples are 1.35 and 1.75 times higher, respectively.

The paramagnetic activity of the initial brown coal is slightly lower than that of HA. The specific concentration of paramagnetic centers is 2.57E+17 spin·g^{-1}. Relative to the HA 3 sample, the molecular weight of assumed paramagnetic molecules of brown coal is 2.71 times

The paramagnetic activity of HMA samples is an order of magnitude lower than that of HA. The specific concentration of paramagnetic centers in HMA decreases from the sample extracted first (HMA 1 6.11E+16 spin·g^{-1}) to the third sample (HMA 3 4.10E+16 spin·g^{-1}). Relative to the HA 3 sample, the molecular weights of the assumed paramagnetic molecules of the HMA 1, HMA 2 and HMA 3 samples are 11.41, 13.03, and 17.00 times higher, respectively.

Lipids have the lowest paramagnetic activity. The specific concentration of paramagnetic centers is 2.79E+16 spin·g^{-1}. Relative to the HA 3 sample, the molecular weight of assumed paramagnetic lipid molecules is 24.98 times higher.

References

[1] Denisov VA, Koshevoy VN, Pershin AP. Report: Exploration work at the Lyulinsk deposit, general search for brown coal on its flanks and in the area. In 3 volumes - Saranpaul: Sosvinsk geological exploration expedition, 1986.

[2] Denisov VA, Koshevaya LA. Report: Prospecting and evaluation work on the flanks of the Tolya-Otoryinsk brown coal deposit with the purpose of increasing reserves for open mining. In 4 volumes - Saranpaul: 1993.

[3] Piawa B, Pusz S, Krzesińska M, Koszorek A, Kwiecińska B. Application of electron paramagnetic resonance spectroscopy to examination of carbonized coal blend. International Journal of Coal Geology, 2009; 77(3-4): 372-376.

[4] Stenberg VI, Jones MB, Suwarnasarn NJ. Radicals in coals during pyrolysis in relation to liquefaction conversion. Fuel, 1985; 64(4): 470-474.

[5] Petrakis L, Grandy DW. Formation and behavior of coal free radicals in pyrolysis and liquefaction conditions. Nature, 1981; 289: 476-477.

[6] Retcofsky HL. Magnetic resonance studies of coal. Coal Science, 1982; 1: 43-82.

[7] Adashkevich S. Role of coal structure in gasdynamic phenomena. Polish Journal of Applied Chemistry, 2000; 2−3: 139-144.

[8] Chukov SN. Structural and functional parameters of soil organic matter under anthropogenic impact. St. Petersburg: Publishing House of St. Petersburg University. 2001, p. 216.

[9] Komissarov ID, Loginov LF. Electron paramagnetic resonance in humic acids. Scientific papers of Tyumen Agricultural Institute, Tyumen. 1971; 14: 99-116.

[10] Lodygin ED, Beznosikov VA, Chukov SN. Paramagnetic properties of humic acids in podzolic and swamp-podzolic soils. Soil Science, 2007; 7: 807–810.

[11] Lodygin ED, Beznosikov VA, Vasilevich RS. Paramagnetic properties of humic substances in taiga and tundra soils of european northeast Russia. Soil science, 2018; 8: 985-993.

[12] Vasilevich RS, Lodygin ED, Beznosikov VA, Abakumov EV. Molecular composition of raw peat and humic substances from permafrost peat soils of european northeast Russia as climate change markers. The Science of the Total Environment, 2018; 615: 1229-1238.

[13] Chukov SN, Eharkyu E, Abakumov EV. Characterization of humic acids in the tundra zone of the north of Western Siberia by the method of paramagnetic resonance. Soil science; 2017; 1: 35-39.

To whom correspondence should be addressed: Dr. Evgeny M. Osnitsky, Institute of Oil and Gas, Yugra State University, Khanty-Mansiysk, Russia, E-mail: vg.osn@gmail.com