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Humic Substances of Brown Coal from the Sergeyev Coalfield

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Abstract

Using the methods of elemental analysis, IR spectrophotometry and ^{13}C NMR spectroscopy we have studied chemical structure of humic substances (HS) obtained from brown coals the Sergeyev coal field and carried comparative analysis of the fragmentary composition of their fractions. It has been demonstrated that the extraction of humic acids is accompanied by oxidation-reduction transformations. Data concerning the polyfunctional composition and the potential of HS physiological activity indicate the possibility of using the Sergeyev coal as a source of humic fertilizers.

Key words: humic acids, fulvo acids, brown coal, extraction, functional composition

INTRODUCTION

Being the major component of low-metamorphized and oxidized solid fuels, soils and sedimentary rocks, humic substances (HS) play an important role in vital functions of ecosystems. The HS exert physiological effect on plants and microorganisms and provide a number of important functions such as accumulating nutrition elements for living organisms, binding toxic and radioactive chemical elements into inactive compounds, regulating soil processes, preserving the soil biota and a vegetative cover under adverse conditions. Thus, HS promote the stabilization of ecological situation in the biosphere and determine the stability of soils, terraneous and aquatic landscapes [1].

The most large-scale direction of employing HS extracted from brown coal and peat consists in the obtaining of growth-promoting factor for plants. The Amur Region has rich raw materials sources for the manufacture of humic fertilizers, which sources are presented by low-caloric brown coals of the Svobodnoye, Nygda and Sergeyev deposits. The authors of [2] have demonstrated that the preliminary extraction of bitumen from the Sergeyev coal

promotes an increase in the yield of humic acids (HA) from 63 up to 74 %, with the aromaticity level and the contents of the phenolic and quinoid functional groups therein providing to a considerable extent the physiological activity of HA [3].

The present work is devoted to comparative studies on the chemical structure of the fractions of humic substances extracted from the Sergeyev coal. Employing ^{13}C NMR spectroscopy, a universal, actively developing technique for the analysis of multicomponent polyfunctional mixtures, we have quantitatively determined structural parameters describing the fragmentary composition of the compounds under investigation.

EXPERIMENTAL

Humic acids were extracted using the pyrophosphate technique according to the USSR State Standard GOST 9517–76. For the removal of the substances of nonspecific nature (wax, resins) the employing of benzene appeared unpractical since a part of acidic bitumen components insoluble in the mentioned extraction

TABLE 1

Characteristics of humic substances from the sample under investigation

| Substances | Yield, % | Elemental composition*, % daf | | | | Atomic ratio | | |
|-------------------|----------|-------------------------------|-----------|-----------|-------------|--------------|------|------|
| | | C | H | N | O + S | H/C | C/H | O/C |
| HA | 74.6 | 58.29/56.43 | 5.11/5.32 | 0.95/1.09 | 35.65/37.16 | 1.05 | 0.95 | 0.46 |
| HMA | 16.2 | 63.84 | 6.71 | 0.43 | 29.02 | 1.26 | 0.79 | 0.34 |
| FA-1 | 3.5 | 60.51 | 5.22 | 0.68 | 34.99 | 1.03 | 0.97 | 0.44 |
| FA-2 | 1.7 | 57.11 | 5.38 | 0.93 | 36.58 | 1.13 | 0.89 | 0.48 |
| HA without HMA | 58.4 | 54.38 | 4.94 | 1.27 | 39.41 | 1.09 | 0.92 | 0.54 |

* The first value is the content of the element in humic acids, the second value is the total content of the element in soluble and insoluble fractions taking into account the yield of the fractions (the calculation was carried out according to the formula [5]: $A = A_1X_1 + A_2X_2$, where A is the balance content of the element in HA; A_1 and A_2 stand for the content of the element in soluble and insoluble fractions, respectively; X_1 and X_2 are the mass fractions of soluble and insoluble fractions, respectively).

agent were extracted together with HA. For the preliminary treatment we have chosen hexane which does not cause any changes in the structure of HA [4]. In order to isolate humatomelanic acids (HMA) a fresh HA precipitate was triply treated by ethyl alcohol with triply subjecting an insoluble residue to reprecipitation from an alkaline solution prior to the extraction. The fractions of fulvo acids (FA-1 and FA-2) were consecutively extracted from acidic filtrates obtained in the course of HA precipitation with the use of diethyl ether and methylethylketone (MEK), respectively.

The elemental composition of the products obtained was determined employing EA 1110 elemental analyzer. IR spectra were registered with the help of a Perkin-Elmer Spectrum One FT-IR spectrometer using KBr pellets. Quantitative ^{13}C NMR spectra were registered with the help of a Varian-VXR500S NMR spectrometer with the operation frequency of 125.6 MHz using 1 % NaOD solution¹. The NMR spectra were registered employing an IGD (Inverse Gate Decoupling) technique that includes the irradiation of protons while reading free induction signal decay. The ranges have been selected those correspond to the resonant absorption of the following groups of carbon atoms: 220–186 ppm – carbon atoms of the carbonyl groups ($\text{C}=\text{O}$); 186–180 ppm – carbon atoms of the quinoid groups (C_Q); 180–168, 162–160 ppm – carbon atoms of the car-

boxyl, ester groups (COO); 160–140 ppm – aromatic carbon atoms bonded with oxygen atoms ($\text{C}_\text{ar}-\text{O}$); 140–106 ppm – C and the H-substituted aromatic carbon atoms ($\text{C}_\text{ar} + \text{CH}_\text{ar}$); 106–93, 80–58 ppm – carbon atoms of carbohydrate fragments ($\text{C}_\text{alk}\text{O}$); 58–54 ppm – carbon atoms of the methoxy groups (CH_3O); 54–0 ppm – carbon atoms of alkyl fragments (C_alk); 160–106 ppm – the aromaticity level $f_a(\text{C}_\text{ar}\text{O} + \text{C}_\text{ar}, \text{CH}_\text{ar})$.

RESULTS AND DISCUSSION

As a subject of inquiry we have chosen an averaged sample of oxidized brown coal from the Sergeyev coalfield, grinded to obtain grain size $<250\ \mu$. The sample exhibited the following characteristics: $W^a = 8.1\ \%$, $A^a = 22.3\ \%$, $V^{\text{daf}} = 60.3\ \%$; elemental composition (% daf): C 66.1, H 5.5, N 0.7, S 0.4, O 27.3; H/C = 1.00; the content of functional groups (mg-eq/g): peroxide groups 0.24, $\text{COOH} + \text{OH}$ groups ≈ 8.03 .

Table 1 demonstrates the results of HS extraction and fractionation. One can see that samples exhibit a high yield of HA, which is inherent in oxidized brown coals.

Using the methods of IR absorption and ^{13}C NMR spectroscopy we have established that the structure HA from the coal under investigation corresponds to the general structural type of HA extracted from various kinds of solid combustible minerals. Humic acids are presented by aliphatic and aromatic fragments as well as by compounds with functional groups. The analysis of the fragmentary composition determined according to ^{13}C NMR spectroscopy

¹The analysis by ^{13}C NMR spectroscopy method has been performed at the Institute of Petrochemical and Coal-Chemical Synthesis attached to the Irkutsk State University under the direction of Prof. A. V. Rokhin

TABLE 2

Parameters of fragmentary composition of humic substances determined according to the data of ^{13}C NMR spectra

| Substances | Carbon content in structural fragments, rel. % | | | | | | | | | Φ_1 |
|-------------------|--|-------------------|-----------|-------------------|------------------------------------|--------------------|-------------------|------------------|-------------|----------|
| | C=O | C _{quin} | COO | C _{ar} O | C _{ar} + CH _{ar} | C _{alk} O | CH ₃ O | C _{alk} | f_a | |
| HA | 3.91/1.90 | 1.44/2.03 | 5.03/4.80 | 5.85/7.46 | 27.78/23.05 | 8.56/4.87 | 2.92/1.18 | 44.51/50.56 | 33.64/30.51 | 0.27 |
| HMA | 1.72 | 1.90 | 4.28 | 6.09 | 20.36 | 6.61 | 3.18 | 54.85 | 26.45 | 0.23 |
| FA-1 | 6.96 | 2.17 | 6.26 | 5.15 | 23.12 | 5.21 | 2.31 | 48.82 | 28.27 | 0.23 |
| FA-2 | 2.36 | 1.85 | 6.01 | 4.94 | 21.29 | 10.02 | 4.11 | 49.43 | 26.23 | 0.30 |
| HA without HMA | 1.95 | 2.06 | 4.95 | 7.84 | 23.80 | 4.39 | 0.63 | 49.37 | 31.64 | 0.23 |

Note. For data concerning HA see Table 1.

py data (Table 2) demonstrates saturated structures to be prevailing in HA composition. At the same time the fraction of aromatic fragments therein characterized by the aromaticity level (f_a) is high. IR spectra exhibit absorption bands of 2980–2920, 2850, 1460, 1380 cm^{-1} those are corresponding to hydrocarbonic groups of aliphatic and alicyclic compounds. Aromatic structures are presented by substituted and condensed systems (IR absorption bands within the wave number range of 900–700 cm^{-1}), aromatic cycles enhanced by oxygen-containing, in particular, quinoid groups (an intense absorption band at 1615 cm^{-1}), and phenols (1257 cm^{-1}). Approximately 30 % of HA carbon is incorporated into various functional groups. The compounds containing C–O bonds (alcohols, phenols, carbonic acids, ethers, esters) are characterized with the absorption within the range of 1200–900 cm^{-1} wherein the bands of 1180, 1100, 1050, 1010 cm^{-1} are observed. A wide area with the maximum at 3420 cm^{-1} corresponds to the absorption of alcoholic (including carbohydrates), phenolic hydroxyls, as well as amino groups associated through hydrogen bonds. ^{13}C NMR spectra (within the range of 160–220 ppm) demonstrate well resolved signals related to carbonyl fragments (aliphatic aldehydes and ketones) corresponding to about 4 % of carbon. The bands at 1715, 920 cm^{-1} in the IR spectra correspond to the absorption of carbonyl-containing groups in the structure of acids, esters, aldehydes, ketones.

Fulvo acids isolated from hydrochloric acid solution filtrate are characterized by a low yield (see Table 1); in this case diethyl ether extracts twice more substances comparing to methyl-

ethylketone. As compared to HA, water-soluble acids contain more hydrogen, approximately the same amount of oxygen, whereas the most reduced level, as judged by the atomic ratio H/C, is exhibited by fraction FA-2. From data presented in Table 2 one can see that the aromaticity level of fulvo acids is lower, whereas the content of alkyl fragments and the saturation level of functional groups is higher comparing to HA. Fulvo acids are to a considerable extent enriched with the carbonyl, quinoid, methoxy groups and contain more COO fragments those could be a part of carboxyl, ester, lacton functional groups.

The method of IR spectroscopy applied to the fractions of water-soluble acids FA-1 and FA-2 has revealed identical absorption bands, though some differences in their configuration and intensity are observed. So, the absorption within a wide range of 3600–3100 cm^{-1} is inherent in both fractions (alcoholic and phenolic hydroxyls, amide and amino groups linked by hydrogen bonds), however there are two maxima (at 3430 and 3200 cm^{-1}) exhibited in the absorption spectrum of FA-2 as against the spectrum of FA-1 (3430 cm^{-1}). This fact indicates an increase in the contribution of phenolic hydroxyl groups involved in intermolecular hydrogen bond with the response within 3300–3150 cm^{-1} [6]. Aliphatic fragments are prevailing in the structure of FA, since they contain almost twice more carbon, than aromatic compounds (see Table 2). Saturated structures including naphtenes are presented by the absorption bands at 2960 (shoulder), 2920, 2850, 1460, 1380 cm^{-1} . One could assume that the presence of alicyclic compounds is more inherent in FA-1, since the intensity of the band

at 1460 cm^{-1} in the absorption spectrum of this fraction is higher comparing to the intensity of the band at 1380 cm^{-1} . To all appearance, this is caused by the fact that CH_3 groups are incorporated in cyclic or bridge-like structures of compounds from fraction FA-1. As far as fraction FA-2 is concerned, an inverse ratio of the mentioned bands is observed. The vibrations of aromatic bonds are exhibited within several regions of absorption spectra (at 1605 , 1510 , 1490 , 840 , 760 cm^{-1}). A higher aromaticity level is inherent in FA-1, wherein more carbon involved in ($\text{C}_{\text{ar}} + \text{CH}_{\text{ar}}$) fragments is contained, with the content of oxygen-bonded aromatic carbon ($\text{C}_{\text{ar}}\text{-O}$) being close to that for FA-2.

A considerable contribution of carbonyl-containing compounds (aldehydes, ketones, carbonic acids, esters) to the structure of FA is indicated by an intense band 1705 cm^{-1} and absorption at 1430 cm^{-1} . This is especially inherent in the IR spectrum of fraction FA-1 which contains three times greater amount of carbonyl carbon as compared to FA-2 (see Table 2). On the contrary, the amount of methoxy groups for FA-2 is higher as compared to that for FA-1. Moreover, the fraction FA-2, to all appearance, concentrates carbohydrate fragments, since the content of $\text{C}_{\text{alk}}\text{-O}$ groups therein belonging to oxygen-containing structures with ether bond is twice higher than that for FA-1.

The process of extraction by ethanol results in the separation of HA into the fractions those differ from each other in chemical composition and the oxidation level. As compared to HA and the HA insoluble fraction, HMA contain more hydrogen and carbon, but much less heteroelements (see Table 1). This fact indicates that the soluble state is observed for more reduced products with a higher H/C parameter, but a lower yield as compared to the insoluble part. The character of varying the H/C ratio allows us to hypothesize that the aromatic fragments of soluble substances exhibit a lower level of condensation, but a higher substitution level containing more hydroaromatic and naphthene cycles as compared to HA. According to data concerning the distribution of carbon throughout structural groups (see Table 2), the content of alkyl fragments in HMA is higher as compared to that for insoluble components. This

fact is confirmed by the presence of intense, well resolved absorption bands at the wave numbers of 2980 (shoulder), 2920 , 2850 , 1460 , 1380 cm^{-1} in IR spectra. At the same time the absorption bands corresponding to aromatic compounds (1615 , 1256 , 880 , 760 cm^{-1}) exhibit a lower intensity as compared to residual HA (HA without HMA) those are characterized by a higher aromaticity level and by prevailing $\text{C}_{\text{ar}}\text{-O}$ fragments with respect to $\text{C}_{\text{alk}}\text{-O}$ ones. As compared to insoluble components, the functional composition of HMA is characterized by a lowered content of carbonyl, carboxyl, quinoid and phenolic groups, but a prevailing amount of compounds with methoxy groups and carbohydrates.

The analysis of data presented in Table 1 allows us to assume that the fractionation of HA in parallel with the extraction occurring in accordance with the laws of mass transfer results in chemical interaction between HA components and a solvent, accompanied by oxidation-and-hydrolytic transformations. This fact is indicated, firstly, by an increase in the amount of oxygen and a decrease in the content of carbon and hydrogen in the insoluble fraction as compared to initial HA. Secondly, from the calculation of total elemental composition of HA fractions (see Table 1) one can see that the total content of carbon in the fractions is lower, whereas that of hydrogen and oxygen is higher than in the substance not exposed to separation. Thirdly, the balance of carbon distribution throughout structural fragments (see Table 2) calculated by analogy with the elemental composition demonstrates that in the sum of the fractions there is a decrease in aromaticity as well as an increase in the content alkyl structures observed as compared to non-separated HA. At the same time, a less amount of carbonyl, carboxyl, methoxy groups and carbohydrate fragments are contained therein, but there are much more quinoid and phenolic structures present.

Quantitative treatment of ^{13}C NMR spectral data has allowed us to obtain a predictive estimate of HS physiological activity according to Φ_1 parameter (see Table 2) which reflects the relationship between hydrophilic and hydrophobic properties of HS macromolecules [5]. The values of Φ_1 parameter for the samples under investigation vary within a narrow ran-

ge. The greatest potential of physiological is exhibited by FA extracted by methylethylketone, and HA.

CONCLUSION

The HS groups studied extracted from the Sergeyev coal can be characterized mainly by aliphatic nature, though the fraction of aromatic compounds therein is also considerable. The greatest aromaticity is exhibited by HA containing a maximum quantity of substituted and condensed cycles. The feature of the composition of water-soluble acids consists in high contribution of carbonyl and alkoxy fragments. The fractionation of HA results in the formation of demethoxylated insoluble compounds with an increased content of phenolic structures, oxygen and nitrogen. Hymatomelanic acids, on the contrary, are impoverished with heteroelements; their aromaticity level is much lower, whereas the contribution of the alkyl fragments is higher comparing to HA and insoluble components. The presence of intra- and intermolecular hydrogen bonds determines

the ability HS with respect to complex formation. The extraction with ethanol is accompanied by oxidation-and-hydrolytic processes those indicate relative instability of HA.

The data we have obtained concerning HS polyfunctional composition, as well as the estimates of HS physiological activity indicate a high potential of brown coals from the Sergeyev coalfield as a source of humic fertilizers.

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