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Comparative Characteristics of The Humic And Hymatomelanic Acids in Peats of The Middle Taiga.

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ABSTRACT

The article compares spectral characteristics and elemental composition of the humic and hymatomelanic acids extracted from different types and kinds of peats in the Middle Ob region. It has been found that the infrared spectra of the humic and hymatomelanic acids extracted from the peats in the Middle Ob region have common characteristic absorption peaks, and they differ in the peak intensity and width. The electronic spectra of the investigated acids increase monotonically to shorter wavelengths and have no characteristic peaks. In percentage, the studied hymatomelanic acids contain more carbon and hydrogen and less oxygen and nitrogen than humic acids.

Keywords: humic acids, hymatomelanic acids, elemental analysis, Middle Taiga, West Siberia.

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INTRODUCTION

The territory of the Middle Taiga in Western Siberia has a significant number of swamps, which accumulates a large quantity of peat. The peat performs many important biospheric functions mainly due to the humic acids contained therein [1].

The hymatomelanic acids are the poorly studied part of the humic acids. They are extracted from the crude humic acids using ethanol. Hoppe-Seyler was the first who had isolated them in 1889, but many scientists expressed doubts about their real existence [9].

G.I. Glebova substantiated independence of the hymatomelanic acid group. She established a necessary set of identification features for the hymatomelanic acid group with the following quantitative levels of these features. Only when using a complex of methods, the hymatomelanic acids can be clearly identified from the humic acids. Elemental composition of the hymatomelanic acids ranges in mass proportions from 58 to 62% for carbon, from 6 to 7% for hydrogen, from 2 to 5% for nitrogen and from 29 to 31% for oxygen. The atomic ratio H/C for the hymatomelanic acids is significantly higher than that of the humic. The quasi-coefficients of extinction are rather low. Infrared spectra of hymatomelanic acids are similar to spectra of the humic acids, but they have more narrow absorption bands [2].

At present, a number of publications on specific properties of the hymatomelanic acids exists, they relate to their elemental composition, functional groups, optical density, principles of carbon skeleton structure, IR spectra, etc. [4] [5] [7].

It is more expedient to study the hymatomelanic acids in comparison with the humic acids extracted from the same sample. This allows a visual assessment of differences in the physico-chemical properties and structure.

OBJECTS AND METHODS USED TO STUDY

The humic and hymatomelanic acids in the peats of different types and species from the territory of the Middle Ob region were selected as the objects of study. Table 1 presents characteristics of peat samples.

Table 1. Original peats

Sampling area	Code	Type of peat	Degree of peat decomposition, %
Nefteyugansk District	1.1	Sphagnum, high-moor	30
Khanty-Mansiysk District	2.1	Wood, transition-moor	50
	2.2	Scheuchzeria, transition-moor	35
Oktyabrskiy district	3.1	Wood-grass, low-moor	30
	3.2	Eriophorum, transition-moor	25
	3.3	Sphagnum, high-moor	20
Beloyarskiy District	4.1	Eriophorum, high-moor	55
	4.2	Sphagnum, low-moor	10
	4.3	Sedge, transition-moor	40

The humic acids were extracted according to standard procedures of Instorf (Eastern European Institute of Peatland Studies) modified at the Department of General Chemistry of the Tyumen State

Agricultural Academy [3]. The humatmelanic acids were being extracted with ethanol from the resulting precipitate of the humic acids within 12 hours.

EA3000 Elemental Analyzer (EuroVector) determined the mass fractions of carbon, nitrogen and hydrogen. The mass fraction of oxygen was calculated by subtraction of mass fractions of the elements specified by the analyzer, and it is, in fact, the sum of oxygen and sulfur. The 60 Cary spectrophotometer recorded electronic spectra. Infrared spectra were obtained on the Specord IPR spectrophotometer.

RESULTS AND DISCUSSION

IR spectra of the studied humatmelanic acids are similar to each other just like spectra of the analogous humic acids, but the difference between the spectra of the humic and humatmelanic acids is noticeable. Figure 1 shows the superposition of the humic acid spectrum on the spectrum of the humatmelanic acids extracted from a wood-grass peat (sample 3.1).

The spectra clearly demonstrate the maxima characteristic for the humic acids at 1,281 and 1,265; 1,463 and 1,466; 1,637 and 1,607; 1,719 and 1,707 cm^{-1} typical for the humatmelanic and humic acids, respectively. The allowed absorption peaks in the area of 500-1,000 cm^{-1} appear to be caused by mineral components.

Absorption bands with maxima at 1,281 and 1,265 cm^{-1} are due to asymmetric C-O bond stretch of simple ethers and their similar compounds. The peak intensities show a slight predominance of these groups in the humic acids. Symmetric stretching vibrations in the same group cause the bands at 1,078 cm^{-1} , which are usually less intense. The humic acids form no peak, just a bend.

The absorption band at 1,463 and 1,466 cm^{-1} can be attributed to deformation vibrations of C-H bond in CH_2 groups.

The absorption band at 1,637 and 1,607 cm^{-1} , which is caused by the stretching vibrations of conjugated double bonds of carbon atoms, indicates the presence of aromatic rings in molecules of the studied humatmelanic and humic acids. Instead of the humic acids' intense peak, the humatmelanic acids are characterized by a non-intense bend, which can indicate their more aliphatic structure in comparison with the humic acids.

The band with a maximum at 1,716 cm^{-1} belongs to a free carboxyl group - COOH. It is also known that the intensity of this absorption band is in direct proportion to the content of the carboxyl groups in a molecule. It is evident from the spectra that the humic acids have much more carboxyl groups.

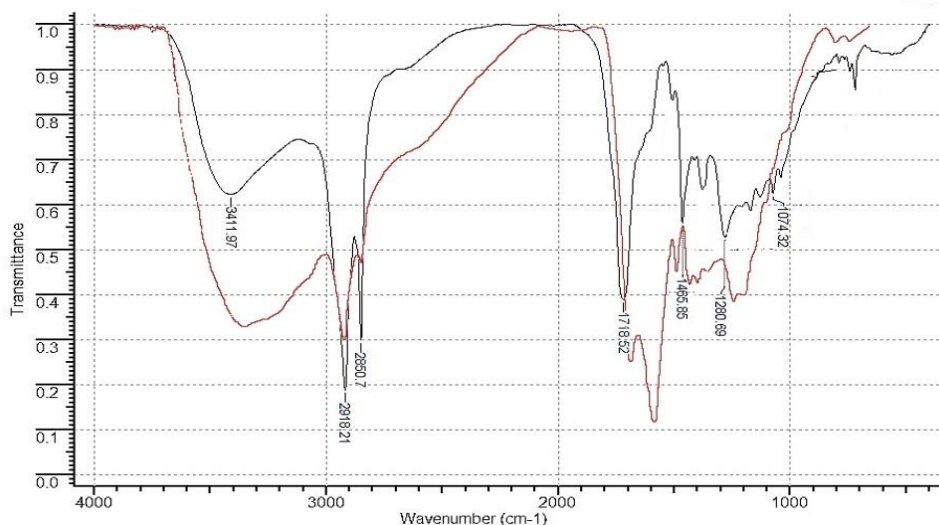


Figure 1. Infrared spectra of humic and humatmelanic acids extracted from a wood-grass peat

The absorption bands with maxima at $2,850\text{ cm}^{-1}$ and $2,922\text{ cm}^{-1}$ are due to the stretching vibrations of C-H bonds in aliphatic CH_3 and CH_2 groups. The humic acids have more intense peaks, that confirms their more aliphatic structure.

A very wide band with a maximum in the area at about $3,412\text{ cm}^{-1}$ for the humic acid and a wider and more intense absorption band in the area at $3,370\text{ cm}^{-1}$ for humic acid are caused by hydrogen bonds. The main participation of a hydrogen bond is not in its molecular interactions, but in its intermolecular interactions occurring in the side structures that are arranged in a plane. This is explained mainly by the presence of hydroxyl and carboxyl groups, which amount is greater in the humic acids.

Based on the resulting infrared spectra, it can be concluded that the structure of the humic and humatmelanic acids differs. They contain all absorption bands characteristic for these compounds, but the peak intensity and width are different. The humatmelanic acid spectra differ from the humic acid one with a larger number of narrow, sharp absorption bands less intense for simple ether, conjugated double, carboxyl, hydroxyl bonds, but more intense for stretching vibrations of C-H bonds in aliphatic CH_3 and CH_2 groups.

Two electronic spectra belonging to the sample extracted from the high-moor eriophorum peat are shown as sample 3.2 (Figure 2).

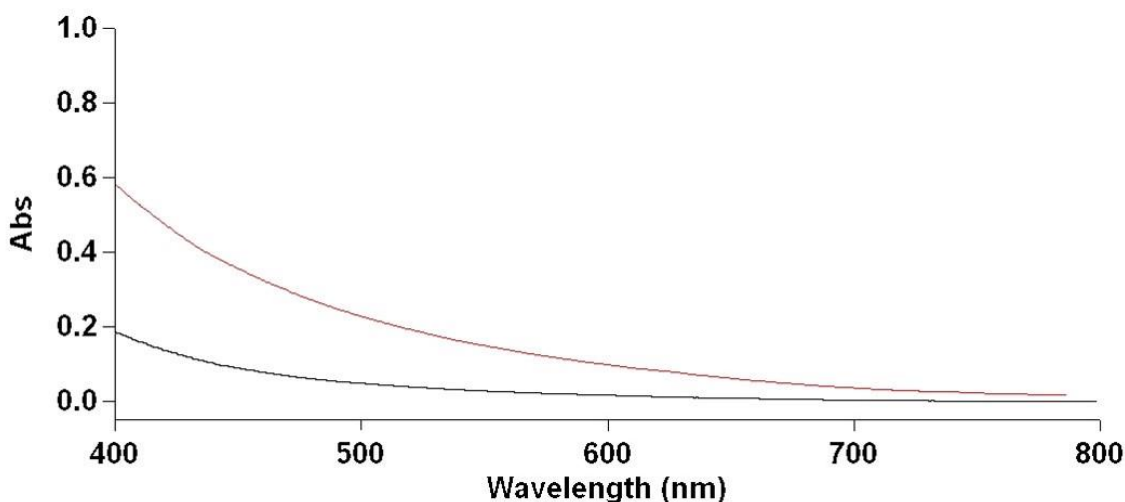


Figure 2. Absorption spectra of the alkaline solutions in the humic and humatmelanic acids extracted from high-moor eriophorum peat

Three samples (humatmelanic acids extracted from high-moor wood, wood-grass, and sphagnum peats), which had not been dissolved completely before recording a spectrum, were excluded from the general considerations. The remaining spectra are similar.

The decline in the humic acid's optical density continues beyond 800 nm, which can be explained by a more conjugated structure in comparison with the humatmelanic acids.

All spectra increase monotonically towards shorter wavelengths and have no characteristic peaks. However, non-specific substances that strongly absorb light at shorter wavelengths do not prevent conducting the study in the area of 450 – 750 nm.

With increasing a wavelength, the ratio D_{465}/D_{650} expresses how steep the optical density falls. It can be assumed that the steepness of the light absorption curve reflects a ratio between aromatic and aliphatic fragments in molecules of the humic acids.

Low extinction coefficients compared with the humic acids show that the humatmelanic acids have less chromophore groups and smaller conjugation of the carbon atoms. At a certain similarity between the

spectra, the light absorption intensity for different acids is not equal, which indicates different ratios of aromatic nuclei and open peripheral chains in different samples (Table 2).

Table 2. Results of electron spectroscopy

Peats	Code	R, %	D ₄₆₅	D ₆₅₀	D ₄₆₅ /D ₆₅₀	E ₄₆₅
Hymatomelanic acids						
Sphagnum, high-moor	1.1	30	0.081	0.024	3.375	0.013
Scheuchzeria, transition-moor	2.2	35	0.127	0.064	1.984	0.017
Eriophorum, transition-moor	3.2	25	0.092	0.027	3.407	0.013
Sphagnum, high-moor	3.3	20	0.066	0.026	2.538	0.015
Eriophorum, high-moor	4.1	55	0.098	0.027	3.630	0.02
Sedge, transition-moor	4.3	40	0.056	0.016	3.500	0.013
Humic acids						
Sphagnum, high-moor	1.1	30	0.300	0.058	5.170	0.058
Scheuchzeria, transition-moor	2.2	35	0.378	0.063	6.000	0.044
Eriophorum, transition-moor	3.2	25	0.336	0.061	5.510	0.061
Sphagnum, high-moor	3.3	20	0.376	0.063	5.970	0.056
Eriophorum, high-moor	4.1	55	0.281	0.05	5.620	0.07
Sedge, transition-moor	4.3	40	0.463	0.078	5.940	0.066

Elemental composition of the hymatomelanic acids in the studied peats of the Middle Ob region. The sample's carbon content (in percent by weight) ranges from 61.05 to 71.09%, the hydrogen content – from 7.58 to 9.50%, the nitrogen content - from 0.47 to 1.60%, and oxygen content - from 18.95 to 30.32%. According to the data obtained by G.I. Glebova [2] for the hymatomelanic acids of soils, the elemental composition (in percent by weight) varies between 58 and 62% of carbon; 6 and 7% of hydrogen; 2 and 5% of nitrogen; 29 and 31% of oxygen (Table 3).

Differences in the elemental composition of the humic and hymatomelanic acids extracted from peats of the Middle Taiga consist in a higher percentage of carbon and hydrogen in the hymatomelanic acids and lower percentage of nitrogen and oxygen.

Table 3. Results of elemental analysis

Types of peats	Code	Elemental composition, %				Atomic ratio		
		C	H	N	O	H:C	O:C	N:C
Hymatomelanic acids								
Sphagnum, high-moor	1.1	67.60	8.70	0.64	23.07	1.53	0.26	0.01
Wood, transition-moor	2.1	65.85	9.15	0.75	24.27	1.65	0.28	0.01
Scheuchzeria, transition-moor	2.2	61.02	7.58	1.09	30.32	1.48	0.37	0.02
Wood-grass, low-moor	3.1	70.74	9.29	0.71	19.28	1.56	0.20	0.01
Eriophorum, transition-moor	3.2	69.76	8.85	0.50	20.90	1.51	0.22	0.01
Sphagnum, high-moor	3.3	71.09	9.50	0.47	18.95	1.59	0.20	0.01
Eriophorum, high-moor	4.1	64.05	7.86	1.60	26.50	1.46	0.31	0.02
Sedge, transition-moor	4.3	66.75	8.85	0.62	23.80	1.58	0.27	0.01

Sphagnum, low-moor	4.2	70.40	8.89	0.61	20.11	1.50	0.21	0.01
Humic acids								
Sphagnum, high-moor	1.1	53.31	4.38	1.62	40.69	0.98	0.57	0.03
Wood, transition-moor	2.1	54.84	5.02	1.64	38.50	1.09	0.53	0.03
Scheuchzeria, transition-moor	2.2	40.02	3.23	1.85	54.90	0.95	1.02	0.03
Wood-grass, low-moor	3.1	58.56	4.96	1.68	34.80	1.01	0.45	0.02
Eriophorum, transition-moor	3.2	57.55	4.78	2.03	35.64	0.99	0.47	0.03
Sphagnum, high-moor	3.3	54.78	4.59	1.94	38.69	0.99	0.53	0.03
Eriophorum, high-moor	4.1	57.31	4.35	1.67	36.67	0.90	0.48	0.02
Sedge, transition-moor	4.3	56.62	4.25	1.98	37.15	0.89	0.49	0.02
Sphagnum, low-moor	4.2	53.46	4.64	2.51	39.40	1.03	0.55	0.04

According to Van Krevelen [6], an important indicator is the atomic ratio H/C, which clearly characterizes the class of hydrocarbons. For the humatomelanic acids of peats, this ratio is usually approximately equal to 1.5, which indicates an increase in the share of aliphatic side chains compared with the humic acids, where this value does not exceed 1. Among the humatomelanic acids, the transition-moor wood peat has the highest ratio H/C - 1.65, and the lowest ratio has the high-moor eriophorum peat - 1.46, which indicates the atomic ratio versus botanical composition relationship. The ratio O/C of the humatomelanic acids is about twice as less as that of the humic ones, it varies from 0.20 to 0.37. The ratio N/C is almost the same for all the studied samples: 0.01 - 0.02 for humatomelanic acids and 0.02 - 0.04 for humic.

Evaluation of atomic ratios allows solving some issues of transformation mechanisms for plant residues and individual groups of humic substances. For this purpose, the diagram of atomic ratios H/C–O/C is convenient to use (Figure 3).

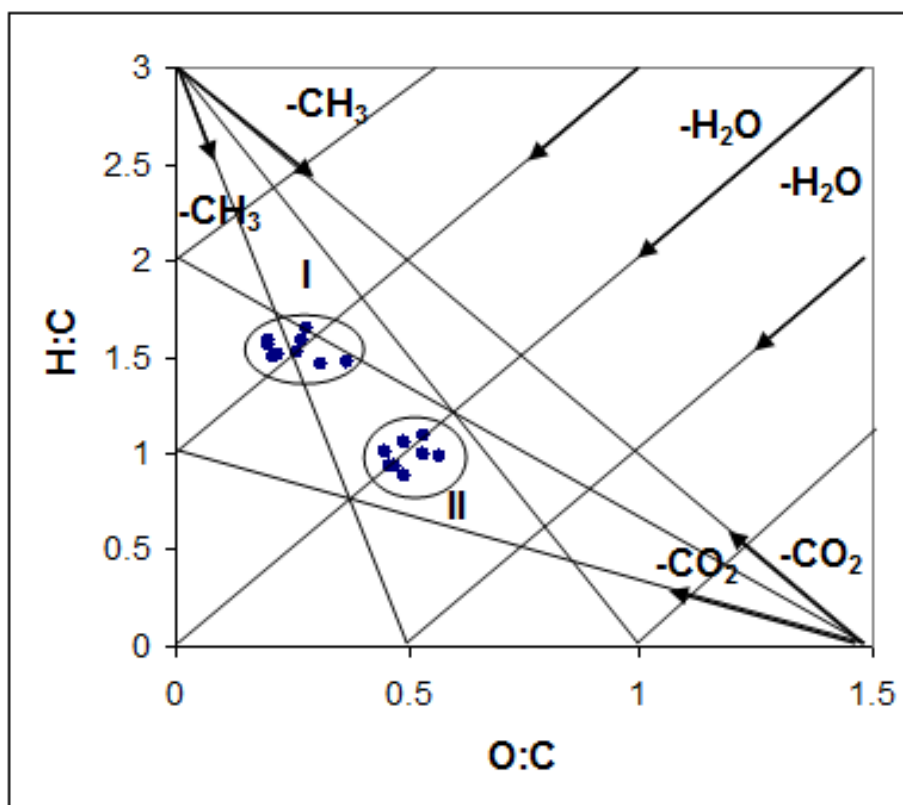


Figure 3. Diagram of atomic ratios

The diagram demonstrates two distinct areas. For area II with the humic acids, the average ratios are $H/C = 0.97$, $O/C = 0.50$, for area I with the hymatomelanic acids, the average ratios are $H/C = 1.54$, $O/C = 0.23$. In the transition from area II to area I, decarboxylation (more precisely, loss of C and O atoms in a ratio of 1: 2) and dehydration (loss of H and O atoms in a ratio of 2: 1) occur. Differences between the above areas are associated with a difference in the amount of oxygen and hydrogen atoms.

CONCLUSIONS

The atomic ratios H/C of the hymatomelanic acids depend, unlike the humic ones, on the botanical composition, and they are typical for the grass, sedge, moss, and wood peats. The atomic ratios H/C of the hymatomelanic acids significantly exceed the atomic ratios of the humic acids, which confirms a greater aliphatic component's contribution to their structure.

The IR spectra show structural differences in the humic and hymatomelanic acids, which consist in fewer amount of the functional groups characteristic for the humic acids and a more developed aliphatic component.

The extinction coefficients of electronic spectra indicate a less conjugated system of carbon atoms in the hymatomelanic acids compared with the humic ones.

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