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The Peat Humic Acids Electronic Paramagnetism Research for Ob-Irtysh Flood Plains.

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ABSTRACT

Peat humic acids (HA) of the Ob-Irtysh flood plains electronic paramagnetism (EPR) researches results are given in this article (Khanty-Mansi JSC Yugra). Their distinctions, which allowed to diagnose mixture molecular structure features depending on botanical composition of initial peat, its extent of decomposition and specifics of formation are revealed. It is revealed that all mixtures possess electronic paramagnetism. Concentration of the paramagnetic centers (PMC) is an associativity measure in macromolecules and can be used for calculation of the conditional molecular masses. PMC mass in dorsa/mg for humic acids of the studied peat varies from $0{,}64 \cdot 10^{-14}$ to $5{,}38 \cdot 10^{-14}$.

Keywords: Humic acids, electronic paramagnetism, peat, botanical structure, vegetable raw materials, Khanty-Mansi JSC Yugra, Ob-Irtysh flood plain.

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INTRODUCTION

HA accumulation in peat deposits happens due to these compounds possessing the greatest thermal stability in comparison with other components which are a part of organic peat matter. HA have great influence on physical and chemical properties of peat in general and in many respects define uniqueness of peat bogs ecological conditions. However the assessment of HA role in natural processes is still significantly limited in view of their variable structure and lack of data on the chemical nature and molecular structure.

Electronic paramagnetism is an important property of HA, characterizing uniqueness of their molecular structure in general [1]. The analysis of EPR ranges enables to receive diverse data on environment with paramagnetic particle.

For comparison purposes mixtures of various peat HA, on integral intensity of EPR signals essential information, is provided by definition of number of the paramagnetic centers in the studied substances, which gives the chance to calculate the conditional average molecular mass [2]. The prime form of EPR signal provides grounds for making assumption about existence in a molecule of only one uncoupled electron [3].

OBJECTIVES AND RESEARCH METHODS

Current work research objects are humic acids emitted from the surface layers of terrestrial, transitional and low-lying peat of Khanty-Mansi Autonomous Area, selected around confluence of Ob and Irtysh.

The total characteristic of the studied peat which is presented by wood, sedge and sphagnum peat is given in Table 1.

Table 1: The common classification of the Khanty-Mansi Autonomous Area, Yugra, studied peat

Types of peat	Categories of peat	Peat-forming biogeocenoses
Valley peat	Wood peat	Eutrophic peat
	Sedge peat	Eutrophic peat
Transition peat	Wood peat	Mesotrophic peat
	Sedge peat	Mesotrophic peat
Terrestrial peat	Sphagnum peat	Oligotrophic peat
	Sedge peat	Oligotrophic peat

Exemplars were selected in autumn time (when water content of peat bogs is reduced) from the surface layers of various landscapes (0-20 cm), and from peat profiles.

For the characteristic of initial peat their botanical structure was defined (tab. 2).

Table 2: Botanical composition of peat studied exemplars

Exemplar code	Structure, contents %	Types and categories of peat
1.1	Sphagnum narrow-leaved-25, lichens-20, sphagnum of magellan-5, sphagnum Baltic-5, cotton grass-15, sedge spherical-15, low shrubs-10, pine-5	Sphagnum, terrestrial
1.2	Sphagnum brown (fucsum)-85, sphagnum magellan-5, cotton grass-5, low shrubs-5, pine (+)	Sphagnum, terrestrial
1.3	Sphagnum brown (fucsum)-85, sphagnum magellan-5, Shreber plevrotsum and other hypnaceous mosses-5, pine-5, low shrubs (+), cotton grass (+)	Sphagnum, terrestrial
1.4	Sphagnum brown-75, cotton grass-15, pine-5, acritical herbs-5, low shrubs (+)	Sphagnum, terrestrial
1.5	Sphagnum narrow-leaved (angustfolium)-70, sphagnum Baltic-10, sphagnum brown-5, cotton grass-5, low shrubs-10	Sphagnum, terrestrial
1.6	Sphagnum narrow-leaved-50, sphagnum brown-25, sphagnum Baltic-15, low shrubs-5, cotton grass (5)	Sphagnum, terrestrial

1.7	Sphagnum fuskum-100, low shrubs (+), sphagnum of magellan (+), cotton grass vaginal (+)	Sphagnum, terrestrial
2.1	Sedge hummocky-90, acritical herbs-5, bushes-5	Sedge, transitional
2.2	Beacked sedge-45, slender sedge-10, bog bean-15, bushes-10, white birch-5, cotton grass-10, bog moss-5	Sedge peat Transition peat
2.3	Sedge acritical (alive and dead roots)-80, cowberry-15, Koch leptidyctium*-5	Sedge, terrestrial
2.4	Sedge caespitose-100	Sedge peat Valley peat
2.5	Sedge hummocky-55, cotton grass-20, sedge uliginose-10, beacked sedge-10 low shrubs-5, bog bean (+)	Sedge peat Transition peat
2.6	Sedge hummocky-55, bog bean-20, white birch-15, birch dwarfish-10, horsetail (+)	Sedge peat Transition peat
2.7	Carex chordorrhiza-40, slender sedge-30, beacked sedge-5, sedge uliginose-5, bog bean three-leaved-10, horsetail-5, Eriophorum polystáchyon-5, Sphagnum L. Acutifolia (+)	Sedge peat Valley peat
3.1	Pine-45, bushes-10, white birch-5, sedge acritical-10, slender sedge-5, beacked sedge-5	Wood, transition
3.2	White birch-45, bog bean-45, horsetail-5, bluejoint-5, cedar (+)	Wood, transition
3.3	White birch-35, bog bean-50, fir-tree-5, horsetail-5, bluejoint-5	Wood, transition
3.4	Low shrubs-45, pine-15, sedge spherical-15, Shreber plevrotsum*-15-), mineral fraction-10	Wood, terrestrial
3.5	White birch and coal-65, bushes-20, sedge spherical-5, cotton grass-5, lichens-5, Pohlia nutans * (+) cephalociella (+)	Wood, transition
3.6	White birch-65, sedge hummocky-15, birch dwarfish-10, pieces of coal-5, Polytrichum commune*-5	Wood peat Transition peat

All sphagnum peats here are terrestrial type and contain reference for this group in the structure, the marsh plants. Generally they contain sphagnum brown, then in decreasing sequence: hypnaceous mosses and lichens, followed by sphagnum narrow-leaved, Baltic, magellan.

Sedge peat consists of sedge caespitose, as well as of beaked sedge and Carex lasiocarpa, hummocky sedge. The exemplar of sedge, low-lying peat is 100% sedge caespitose.

In two first exemplars of wood peat pine prevails, in all others white birch does. At some exemplars there are bushes, different types of sedge and wood coniferous (fir-tree, cedar).

The settlement territory lies in average taiga zone, it is exposed to continental climate with severe winters, blizzards, potent snow cover and drifts. Snow cover during the winter period exceeds 75-80 centimeters. Duration of steady frosts is from 145 to 167 days. Average annual rainfall is up to 450 mm. Average long-term temperature of winter (January) is - 28,5 C °; summer (July) is + 18 C °. During summer period north winds reduce temperature and increase humidity.

EPR measurements were taken in Novosibirsk Institute of Organic Chemistry on radiospectrometer (BRUKER-ESP 300) with the double resonator necessary for precise measurements of the standard exemplar q-factor TEMPO (q = 2,0059) without SHF reorganization, by switching of the direction of SHF stream. Concentration accuracy measurement is ± 8%. Line position across the field and double integrals measurements were carried out according to the WIN-EPR program.

RESULTS AND DISCUSSION

Exemplars of the humic acids were received by method of electronic paramagnetic resonance and studied according to various types of peat of Khanty-Mansi Autonomous Area.

All humic acids give the symmetric, singlet signals of EPR 5 wide a gauss with a g-factor close to a g-factor of the free electron. This signifies the identical nature of their paramagnetic centers (fig. 5, 6, 7).

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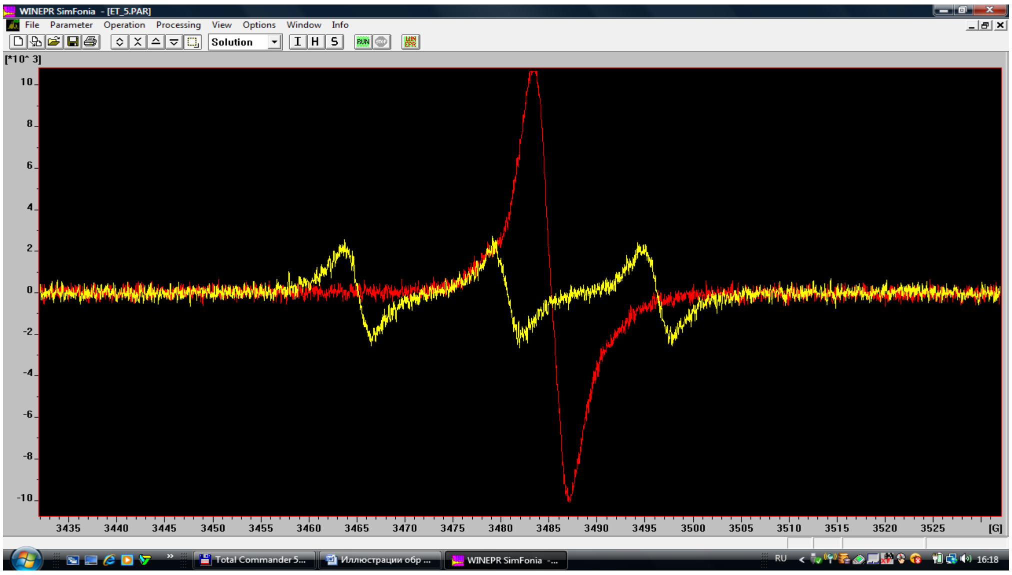

Figure 5: EPR range of low-lying sedge peat humic acid

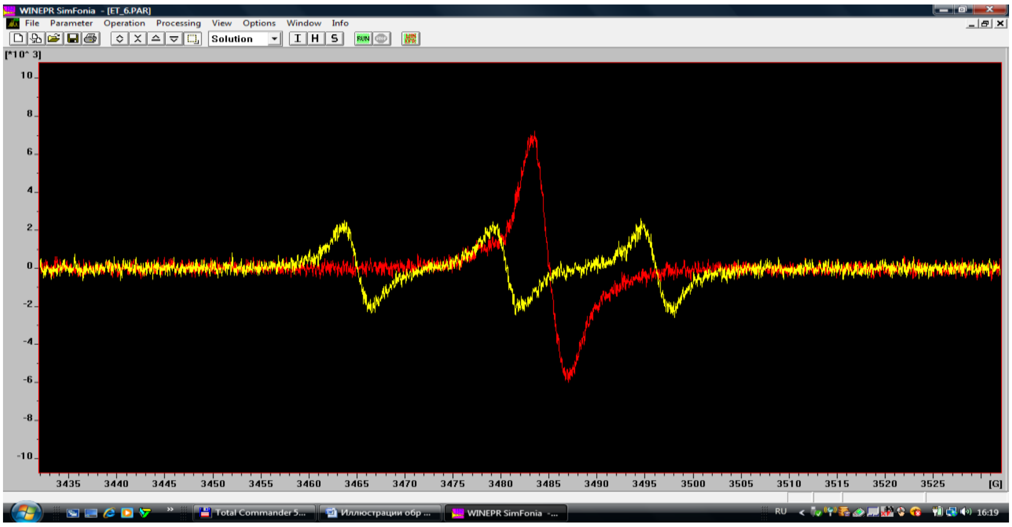

Figure 6: EPR range of transitional wood peat humic acid

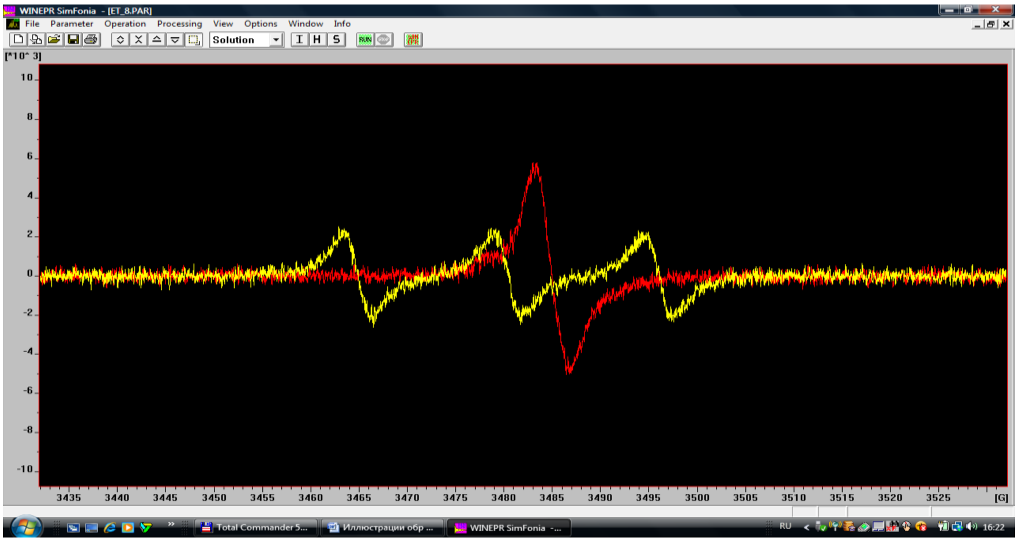

Figure 7: EPR range of terrestrial sphagnum peat humic acid

Proceeding from the received ranges, it is possible to draw a conclusion that various botanical structure and extent of decomposition humic acids produce various intensity signal.

The quantitative definition of the paramagnetic centers in humic acids shows that various exemplars have the unequal content of uncoupled electrons: from 0,56 to 5,38·10-14 dorsa/mg (tab. 3). Change of g-factor of the studied humic acids concerning standard g-factor can serve as a source of information, all values are approximately equal (g-factor standard=2,0036).

Table 3: EPR method research results on humic acids for Khanty-Mansi Autonomous Area

Exemplar code	Categories of peat	R, %	Exemplar mass	Number of paramagnetic centers	Specific concentration, spin/mg	g-factor
1.1	Sphagnum T	5	3.90	$2{,}31\cdot10^{-14}$	$0{,}8\cdot10^{-14}$	2.0033
1.2	Sphagnum T	10	4.03	$4{,}84\cdot10^{-14}$	$1{,}26\cdot10^{-14}$	2.0033
1.3	Sphagnum T	15	3.60	$2{,}30\cdot10^{-14}$	$0{,}64\cdot10^{-14}$	2.0034
1.4	Sphagnum T	30	3.90	$5{,}09\cdot10^{-14}$	$1{,}30\cdot10^{-14}$	2.0032
1.5	Sphagnum T	35	4.20	$4{,}23\cdot10^{-14}$	$1{,}19\cdot10^{-14}$	2.0032
1.6	Sphagnum T	40	2.90	$15{,}6\cdot10^{-14}$	$5{,}38\cdot10^{-14}$	2.0032
1.7	Sphagnum T	55	3.50	$9{,}48\cdot10^{-14}$	$2{,}71\cdot10^{-14}$	2.0032
2.1	Sedge Tr	10	4.70	$5{,}10\cdot10^{-14}$	$1{,}09\cdot10^{-14}$	2.0032
2.2	Sedge Tr	15	3.70	$2{,}86\cdot10^{-14}$	$0{,}77\cdot10^{-14}$	2.0033
2.3	Sedge T	35	3.35	$4{,}26\cdot10^{-14}$	$1{,}28\cdot10^{-14}$	2.0033
2.4	Sedge V	40	4.90	$8{,}49\cdot10^{-14}$	$1{,}73\cdot10^{-14}$	2.0033
2.5	Sedge Tr	45	3.60	$5{,}64\cdot10^{-14}$	$1{,}57\cdot10^{-14}$	2.0033
2.6	Sedge Tr	50	3.10	$16{,}10\cdot10^{-14}$	$5{,}18\cdot10^{-14}$	2.0033
2.7	Sedge V	55	3.20	$1{,}91\cdot10^{-14}$	$0{,}60\cdot10^{-14}$	2.0033
3.1	Wood Tr	20	3.60	$2{,}03\cdot10^{-14}$	$0{,}56\cdot10^{-14}$	2.0034
3.2	Wood Tr	25	3.80	$3{,}07\cdot10^{-14}$	$0{,}81\cdot10^{-14}$	2.0034
3.3	Wood Tr	30	3.10	$2{,}64\cdot10^{-14}$	$0{,}85\cdot10^{-14}$	2.0034
3.4	Wood T	35	5.20	$4{,}94\cdot10^{-14}$	$0{,}95\cdot10^{-14}$	2.0034
3.5	Wood Tr	45	5.50	$9{,}20\cdot10^{-14}$	$1{,}67\cdot10^{-14}$	2.0035
3.6	Wood Tr	50	3.40	$11{,}40\cdot10^{-14}$	$3{,}37\cdot10^{-14}$	2.0032

Note: % R – extent of decomposition, V-terrestrial peat, P - transition peat, N - low-lying peat.

The humic acids received from wood peat with extent of decomposition by 20% (exemplar 3,1), sphagnum peat with extent of decomposition by 5 and 15% (exemplar 1,1 and 1,3), and also low concentration humic acids of sedge peat with extent of decomposition by 15 and 55% (exemplars 2,2 and 2,7), where value does not exceed 0,60-0,77·10-14 dorsa/mg, have low paramagnetic activity (from 0,56 to 0,80·10-14 dorsa/mg). Despite the fact that exemplar 2,7 has high extent of decomposition and falls into low-lying peat type, it contains small amount of PMC; this can be explained by huge variety of peat-forming growth present in its structure.

The majority of exemplars have higher values of concentration, from 2,71 to 5,38·10-14 dorsa/mg, (exemplar 2,1) sphagnum peat with extent of decomposition by 55%, wood peat (exemplars 3,6) with extent of decomposition equal to 50%, sphagnum peat (exemplar 1,6), extent of decomposition – 40%.

Having defined number of the paramagnetic centers, it is possible to calculate the conditional molecular mass [4]. It is necessary to consider that the prime form of EPR signal gives grounds to draw conclusion that in a molecule only one uncoupled electron is present.

The molecular mass which is calculated according to the maintenance of paramagnetic centers, has particular advantage before other methods, since researches use humic acids in solid state. In other methods, for defining molecular masses, an exemplar is placed in solution, where molecules have various ionic strength. It can be the reason of the under size molecular mass in comparison with the sizes characterizing their solidity. The molecular mass of the studied exemplars is calculated by the following formula:

$$M=N_0/N_e,$$

Where M – molecular mass, N_0 – Avogadro number (6,02 · 1023), N_e - number of the paramagnetic centers in 1 mg of substance.
Values of molecular masses are presented in Table 4.

Table 4: Molecular masses of peat humic acids in Khanty-Mansi Autonomous Area

Exemplar code	Categories of peat	R, %	Conditional molecular mass
1.1	Sphagnum T	5	$24{,}08\cdot10^{-6}$
1.2	Sphagnum T	10	$3{,}06\cdot10^{-6}$
1.3	Sphagnum T	15	$3{,}62\cdot10^{-6}$
1.4	Sphagnum T	30	$4{,}63\cdot10^{-6}$
1.5	Sphagnum T	35	$5{,}79\cdot10^{-6}$
1.6	Sphagnum T	40	$1{,}12\cdot10^{-6}$
1.7	Sphagnum T	55	$2{,}22\cdot10^{-6}$
2.1	Sedge Tr	10	$13{,}68\cdot10^{-6}$
2.2	Sedge Tr	15	$6{,}62\cdot10^{-6}$
2.3	Sedge Tr	35	$4{,}93\cdot10^{-6}$
2.4	Sedge V	40	$3{,}48\cdot10^{-6}$
2.5	Sedge Tr	45	$3{,}83\cdot10^{-6}$
2.6	Sedge Tr	50	$1{,}16\cdot10^{-6}$
2.7	Sedge V	55	$1{,}97\cdot10^{-6}$
3.1	Wood Tr	20	$7{,}34\cdot10^{-6}$
3.2	Wood Tr	25	$7{,}44\cdot10^{-6}$
3.3	Wood Tr	30	$7{,}08\cdot10^{-6}$
3.4	Wood T	35	$6{,}34\cdot10^{-6}$
3.5	Wood Tr	45	$3{,}60\cdot10^{-6}$
3.6	Wood Tr	50	$1{,}79\cdot10^{-6}$

According to provided data the molecular mass of humic acids changes from 1,12·10-6 (exemplar No. 1.6, sphagnum peat with extent of decomposition by 40%) to 24,08·10-6 (exemplar No. 1.1, sphagnum peat with extent of decomposition by 5%). Humic acids of poorly decayed initial peat have the greatest molecular mass.

Carriers of specific properties of humic acids are the fused aromatic rings which have sufficient interface carbon-carbon bonds, with the delocalized electrons providing the free movement within all molecules. Peripheral irregular building blocks are variable components which can or cannot be a part of macromolecules.

Low paramagnetism, and respectively low intensity of humic acids electronic ranges of absorption of one peat in comparison with others, proves the least maintenance of the conjugate S=S connections, the reference for aromatic structures, which basically define number of the paramagnetic centers [5]. This circumstance confirms rather insignificant contribution of π-connected systems in molecular structure.

It should be noted that on concentration of spins (the delocalized electrons) HA of various peats are distributed in particular sequence.

The greatest level of electronic paramagnetism is noted in HA of peats, which are formed under conditions of larger oxygen providing, larger biological activity. These acids are formed on less humidified sites of bogs.

For descriptive reasons dependencies of values of molecular masses on extent of decomposition were constructed in correlative dependencies (fig. 4, 5).

In botanical groups of HA exemplars well expressed correlation is traced: with increase in extent of peat decomposition molecular mass value decreases. This concerns humic acids of sedge and wood peat. As for humic acids of sphagnum peat, here we can speak only about the tendency bound to decrease of molecular mass depending on increase in extent of decomposition.Decrease in correlation is apparently caused by influence of haloid acids during extraction, which affect the periphery of macromolecule oligotrophic sphagnum peat stronger.

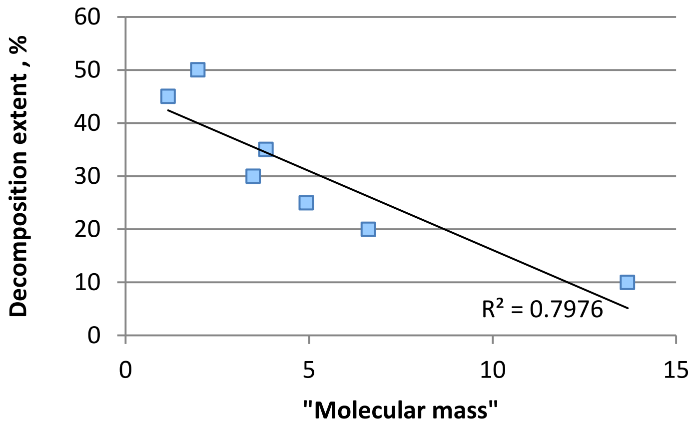

Figure 4: Dependence of humic acids "molecular mass" of sedge peat on extent of decomposition

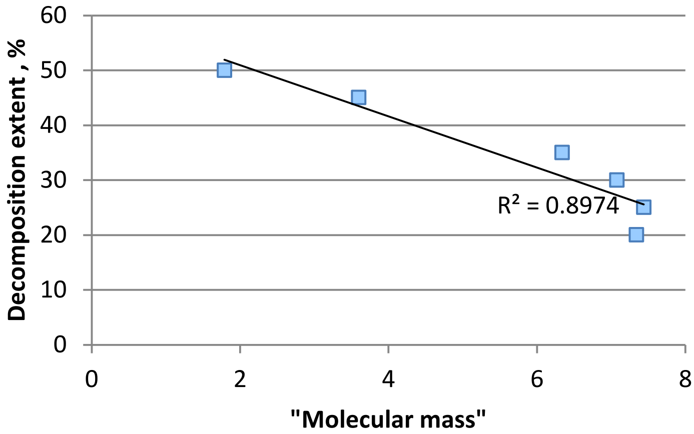

Figure 5: Dependence of humic acids "molecular mass" of wood peat on extent of decomposition

Correlative dependence of "molecular mass" of humic acids and extent of various botanical structure peat exemplars decomposition in a decreasing sequence is the following: humic acids of wood R^2=0,90 peat, humic acids of sedge R^2=0,80 peat, humic acids sphagnum R^2=0,33 peat.

SUMMARY

1. Electronic paramagnetism is observed in all exemplars of humic acids. All mixtures have a g-factor close to a g-factor of the free electron. It shows the identical nature of their paramagnetic centers. The PMC maintenance changes from $0,64 \cdot 10^{-14} – 5,38 \cdot 10^{-14}$ dorsa/mg.
2. The molecular mass defined on their basis decreases at increase in number of paramagnetic centers and extent of decomposition of initial peat. Changes in sphagnum is from $24,08 \cdot 10^{-6}$ to $1,12 \cdot 10^{-6}$, sedge is from $13,68 \cdot 10^{-6}$ to $1.16 \cdot 10^{-6}$, wood is from $7,44 \cdot 10^{-6}$ to $1,79 \cdot 10^{-6}$.
3. Composition features, structure and properties of humic acids, which were created from various types of peat of Khanty-Mansi Autonomous Area, are shown in the ratio aliphatic and aromatic parts, are defined in ranges of EPR and depend on botanical composition of peat and its extent of decomposition.

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CONCLUSION

Proceeding from the obtained data, it is possible to draw a conclusion that the conditional molecular mass of humic acids depends on extent of decomposition of initial peat and its botanical structure.

This circumstance signifies that the humic acids passing incipient states of humification have high values of molecular masses, owing to existence of the irregular peripheral chains. This goes for soil-forming process in general. In nature there are steadier structures, owing to humic acids gradually losing peripheral chains, and their molecular mass decreasing.

Degree or depth of organic peat matter humification is the important diagnostic principle, which often serves for dividing peats on species. The EPR method, as well as the X-ray diffraction analysis [6] increases objectivity and reliability of humification extent definition.

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