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The Thermal Stability Comparative Analysis of Humic Acids in the Sphagnous Peat of the Western Siberia Taiga Zone Raised Bogs.

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ABSTRACT

In the article thermal researches results for the humic acids (HA) in sphagnous peat which is the most suitable objects for hymification process study characterized by simple botanical composition with high sphagnous mosses residuals content are provided. The impact assessment of the initial peat botanical composition on thermodynamic stability of compound groups derived from it is given. It is shown that results of the thermogravimetric composition analysis reflect features of botanical composition of the initial peat. Correlation of composition mass lost in the low-temperature area (from 0 to 400 °C) which is followed by two exothermal effects of the macromolecule periphery expansion to weight loss in the high-temperature area (from 400 to 800 °C) having one pronounced exothermal effect of core expansion is revealed. Mean smallest value of these relations (Z) for composition of scheuchzerite peat also makes 0,59, then in the increasing sequence: compositions of sphagnous phuscum peat (0,66), complex (0,67), scheuchzerite-sphagnous (0,69) and sphagnous matted peat (0,70) follow. The less this relation is, the higher thermal stability of a macromolecule composition is. Maximum temperatures of the researched peat composition destruction in high-temperature area which mean values vary from 497,3 to 521,2 °C are set and show correlative dependence with Z index. It is defined that composition structure and properties changes under the influence of heating in the samples taken from peat of small decomposition extent are more expressed.

Keywords: Humic acids, the thermogravimetric analysis, sphagnous peat, Mukhrino, Khanty-Mansi Autonomous Area - Yugra, Western Siberia.





INTRODUCTION

Humification of the died-off vegetable organisms and microbial weight is global natural process which owing to selection thermodynamic steady connections leads to "preservation" of organic matter in the biosphere, protecting it from a total mineralization to a certain extent [5]. Thermodynamic stability is adequate reflection of the humin substances molecular structure features depending on starting organic material and conditions in which process of humification proceeds [1].

Thermal characteristics of humic acids contain the valuable information characterizing conditions and humification mechanism in various types of soils [1, 13, 15, 19, 20]. They reflect the most important properties of composition, and along with other physical and chemical methods of the analysis are very informative and perspective for studying the humification process and composition molecular structure [5, 1, 8].

Thermal analysis methods are successfully applied when studying humic acids of different soil types organic matter [1, 4, 6, 12, 13, 23, 25] and peat [3, 7, 11, 14, 15, 16, 17, 18, 20, 24] etc. The number of the early articles devoted to thermogravimetric composition analysis is rather big therefore it is impossible to make the exhaustive literary review, but over the last ten years such works have not been enough.

The researches directed to studying peat composition of the middle-taiga zone in Western Siberia were carried out earlier as well [9, 10, 21, 22]. But the works concerning studying the thermodynamic stability of the raised sphagnous peat composition of Khanty-Mansi Autonomous Area where the main reserves of Russian Federation peat are concentrated were practically not carried out. These researches conducted on the example of raised peat types with the high content of sphagnous mosses oddments which are the best model for humification process studying are especially important for knowledge of the composition nature.

Besides, thermal analysis methods applied to humic acids research earlier led to irreplaceable loss of a large exemplar number. Modern devices of synchronous thermal analysis allow to significantly increase informational content of this method and to reduce humic acids consumption approximately by 100 times without distorting results of the analysis [11].

The current research purpose was studying the thermodynamic stability of humic acids in sphagnous peat, representative of the taiga zone raised bogs in Western Siberia.

During work the following tasks were set and solved:

- to carry out studying the physical and chemical properties of peat humic acids with use of the
- thermogravimetric analysis method.
- to reveal interrelation between the maximal temperature of a thermo-effect in composition and the
- relation of weight loss in the low-temperature area to weight loss in high-temperature area.

OBJECTIVES AND RESEARCH TECHNIQUES

Exemplars were selected around the field of educational and experimental station "Mukhrino" of Ugra State University located in the central part of Western Siberia in 30 km to the southwest from the city of Khanty-Mansiysk on a left-bank terrace of Irtysh on the typical marsh massif (a bog of "Mukhrino"). Coordinates of peat land: 60.89535n 68.639033E.

The common peat depth in a sampling point makes 380 cm. Up to the depth of 220 cm the peat deposit is put by layers of strongly flooded sphagnous matted peat from oddments of uliginose sphagnous mosses (sphagnum papillous – *Sphagnum papillosum* Lindb., Janszen – S. *jensenii* Lindb., Lindberg – S. *Lindbergii* Schimp. ex.Lindb., Baltic – S. *balticum* (Russ.) Russ. ex. C. Jens.) with scheuchzeria dash (5-15%) and cotton grass (5%), alternating with pro-layers of scheuchzerite-sphagnous and scheuchzerite peat in which the maintenance of scheuchzeria oddments increases respectively up to 20-35% and 75%. In this part of deposit formed on the bank of the growing lake under conditions of a lakeside quaking bog there are buried layers of water at a depth of 60-70, 100-110, 170-190 of 200-210 cm.



Below (at a depth of 220-330 cm) the top horizon of uliginose peat is replaced by sphagnous layer phuscum peat in combination with sphagnous complex peat deposited in less flooded conditions pine suffruticous-sphagnous compositions with dominance of a sphagnous brown – Sphagnumfuscum (Schimp.) Klinggr. on hummocks and ridges and in more wet space between hummocks and swampy hollows between them. Sphagnous phuscum peat on 65-95% consists of sphagnous moss oddments with impurity of low shrubs (5-10%). As a part of sphagnous complex peat besides the uliginose sphagnous oddments of mosses and scheuchzeria are presented.

The lower horizon of raised peat (330-370 cm) in a peat column is again presented by layer of scheuchzerite-sphagnous peat. The thin layer of hypnaceous peat (370-380 cm) separates it from a meter layer of lake deposits from the the water macrophyte oddments lying in the basis of a peat deposit.

For studying of composition exemplars thermal characteristics from a surface on all depth of raised peat (0-370 cm) with high content the sphagnous mosses were selected. Sampling was made by means of the *Eijkelkamp* brand (Peatsampler, production the Netherlands) peat drill with a 10 cm step. The botanical composition of the studied peat is given in table 1.

Depth, cm	Botanical composition, (%)	R, %	Peat type		
0-10	Sphagnum papillouse (75), Jensen Sphagnum (10), Scheuchzeria (10), Lindberg sphagnum (5)	0	Sphagnum matted		
10-20	Lindberg sphagnum (70), Scheuchzeria (20), Great sphagnum (5), cotton grass (5)	0	Scheuchzerite-Sphagnum		
20-30	Sphagnum papillouse (60), Scheuchzeria (30), Jensen Sphagnum (5) cotton grass (5)	5	Scheuchzerite-Sphagnum		
30-40	Sphagnum papillouse (55), Lindberg sphagnum (20), Scheuchzeria (15), Jensen Sphagnum (5), cotton grass (5)	5	Sphagnum matted		
40-50	Sphagnum papillouse (45), Lindberg sphagnum (25), Scheuchzeria (20), cotton grass (10)	5	Scheuchzerite-Sphagnum		
50-60	Sphagnum papillouse (40), Lindberg sphagnum (15), Jensen Sphagnum (15), Scheuchzeria (10), cotton grass (10), hypnum moss (5), mud sedge (5)	15	Sphagnum matted		
60-70	Water				
70-80	Sphagnum papillouse (45), Lindberg sphagnum (30), Scheuchzeria (15), Jensen Sphagnum (5), mud sedge (5)	15	Sphagnum matted		
80-90	Lindberg sphagnum (35), Sphagnum papillouse (25), Scheuchzeria (25), cotton grass (10), Jensen Sphagnum (5)	20	Scheuchzerite-Sphagnum		
90-100	Lindberg sphagnum (30), Sphagnum papillouse (30), Jensen Sphagnum (25), Scheuchzeria (15)	20	Sphagnum matted		
100-110	Water				
110-120	Jensen Sphagnum (30), Sphagnum papillouse (25), Lindberg sphagnum (20), Scheuchzeria (20), Great sphagnum (5)	25	Scheuchzerite-Sphagnum		
120-130	Jensen Sphagnum (40), Scheuchzeria (30), Sphagnum papillouse (20), sphagnum balticum (5), Great sphagnum (5)	20	Scheuchzerite-Sphagnum		
130-140	Jensen Sphagnum (30), Sphagnum papillouse (25), Scheuchzeria (25), Lindberg sphagnum (15), Great sphagnum (5)	25	Scheuchzerite-Sphagnum		
140-150	Sphagnum papillouse (40), Jensen Sphagnum (20), Lindberg sphagnum (10), sphagnum balticum (10), Great sphagnum (10), Scheuchzeria (10)	20	Sphagnummatted		
150-160	Jensen Sphagnum (30), Sphagnum papillouse (25), sphagnum balticum (15), Scheuchzeria (15), Lindberg sphagnum (10), Great sphagnum (5)	15	Sphagnum matted		
160-170	Sphagnum papillouse (35), Scheuchzeria (35), Jensen Sphagnum (20), Lindberg sphagnum (5), Great sphagnum	25	Scheuchzerite-Sphagnum		

Table 1. Botanical structure and decomposition extent studied in peat column

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	(5)				
170-190	Water				
190-200	Scheuchzeria (75), Sphagnum papillouse (10), Lindberg	40	Scheuchzerite		
	sphagnum (5), Great sphagnum (5), Jensen Sphagnum (5)				
200-210	Water	r	1		
210-220	Scheuchzeria (75), Sphagnum papillouse (15), Jensen Sphagnum (10)	25	Scheuchzerite		
220-230	Brown sphagnum (45), Sphagnum papillouse (20), sphagnum balticum (15), Scheuchzeria (15), Jensen Sphagnum (5)	15	Sphagnum complex		
230-240	Brown sphagnum (90), Scheuchzeria (5), subshrub (5)	10	Sphagnum phuscum peat		
240-250	Brown sphagnum (85), subshrub (10), Scheuchzeria (5)	10	Sphagnum phuscum peat		
250-260	Sphagnum papillouse (25), Brown sphagnum (20), Scheuchzeria (20), sphagnum balticum (10), Jensen Sphagnum (10), Great sphagnum (5), subshrub (5), mud sedge (5)	15	Sphagnum complex		
260-270	Brown sphagnum (45), Scheuchzeria (15), cotton grass (15), subshrub (15), Sphagnum papillouse (5), sphagnum balticum (5)	15	Sphagnum complex		
270-280	Brown sphagnum (90), subshrub (10) Sphagnum phuscum peat (15)	10	Sphagnum phuscum peat		
280-290	Sphagnum papillouse (40), Brown sphagnum (25), subshrub (15), sphagnum magellanic(10), sphagnum balticum (5), Scheuchzeria (5)	15	Sphagnum complex		
290-300	Brown sphagnum (65), Scheuchzeria (20), subshrub (10), sphagnum magellanic(5)				
300-310	Sphagnum papillouse (40), Brown sphagnum (25), Scheuchzeria (25), subshrub (10)	15	Scheuchzerite-Sphagnum		
310-320	Brown sphagnum (70), subshrub (15), Sphagnum papillouse (10), Scheuchzeria (5)	10	Sphagnum phuscum peat		
320-330	Brown sphagnum (90), Scheuchzeria (5), subshrub (5)	5	Sphagnum phuscum peat		
330-340	sphagnum balticum (35), Scheuchzeria (30), Sphagnum papillouse (15), Jensen Sphagnum (10), sphagnum magellanic(5), Great sphagnum (5)	15	Scheuchzerite-Sphagnum		
340-350	Scheuchzeria (40), sphagnum balticum (25), Sphagnum papillouse (15), Great sphagnum (10), sphagnum magellanic(5), hypnum moss (5)	20	Scheuchzerite-Sphagnum		
350-360	Scheuchzeria (35), sphagnum balticum (30), Sphagnum papillouse (25), Jensen Sphagnum (10)	30	Scheuchzerite-Sphagnum		
360-370	Scheuchzeria (40), sphagnum balticum (25), Sphagnum papillouse (15), Great sphagnum (10), hypnum moss (10)	25	Scheuchzerite-Sphagnum		

Selection of composition was carried out by the reference technique of *Instorf* modified at department of the Common Chemistry of the Tyumen State Agricultural Academy [5], only at the last stage of extraction we did not carry out deashing of preparations by halogen hydracids which promote removal of macromolecule fragments and partially destroy results.

The thermal analysis of humic acids exemplars was carried out at the Institute of Organic Chemistry of the Siberian Branch of the Russian Academy of Science (Novosibirsk) on the synchronous STA 409 PC Luxx thermoanalyzer (Netzsch firm) in the inert atmosphere in a platinum crucible. Mass losses of humic acids exemplars when heating are designated in this device on a high precision that is caused by sensitivity of the used thermoweights - 1,25mkg.

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RESULTS AND DISCUSSION

Use of the modern synchronous thermal analysis allowed with a high precision and at the small volume of exemplar to obtain data on process of thermal decomposition of humic acids in sphagnous peat of raised bogs. Typical thermograms of the studied peat composition are presented in figure 1.



Figure 1. Differential Scanning Curves (DSC) of humic acids in sphagnous raised peats: ■ – Scheuchzerite, ■ – Sphagnum phuscum peat, ■ – Sphagnum matted, ■ – Scheuchzerite-Sphagnum, ■ – Sphagnum complex

Thermal degradation causes a number of exotherms demonstrating gradual destruction of a molecule of composition. In its structure two parts, sharply various on thermal stability, clearly are allocated: nuclear aromatic (steadier) and side aliphatic chains of which smaller thermal stability is considerably common.

In Figure 1 it is visible that at the low-temperature area there are two thermo-effects. The first exotherm in the area of 150 °C is caused by removal of the adsorption water and partial decomposition of the molecule periphery at all exemplars, it is expressed poorly as in this area it is suppressed by heat-absorbing reactions of the chemical bonds rupture.

The beginning of the adsorption water removal is observed already at 50-60 °C. At the same temperature disintegration of side chains – decarboxylation and splitting of aliphatic chains skeleton is already possible.

The second thermo-effect of composition disintegration is observed around 150 to 400 °C and on intensity is expressed in an array: scheuchzerite peat, sphagnous complex, sphagnous phuscum peat, scheuchzerite-sphagnous sphagnous matted peat (Fig. 1). It is characterized by destruction of the structural components which are a part of peripheral molecules composition part. Process of organic compounds thermal decomposition is always followed by reactions of dehydration and decarboxylation. Practically at all studied peat types this thermo-effect is reached in very narrow range from 333,0 ° to 337,0 °C.

More brightly, but not in strictly coinciding inverse sequence, distinction in intensity of the exothermic reactions of the studied peat composition is shown in the range of temperatures from 500 to 600 °C which are bound to destruction of steadier aliphatic chains, separate cycles, benzenoid structures and destruction of nuclear part.



Most weakly the thermo-effect of composition in this area is shown in phuscum peat. Intensity of a thermo-effect increases among: sphagnous matted, scheuchzerite-sphagnous, sphagnous complex and also reaches the maximal values for scheuchzerite peat (Fig. 1).

Temperature range at which the maximal values of thermo-effect composition for different types of raised peat in this area are observed significantly more widely and reaches 50 °C (from 477 ° to 528 °C). Before others the thermo-effect, the bound to destruction of nuclear part of molecules composition, is shown in scheuchzerite-sphagnous and sphagnous matted peat. At higher temperatures increase of the exothermic reactions intensity in composition of phuscum peat, sphagnous complex and scheuchzerite peat is observed. Results of the thermal analysis are presented in table 2.

Peat types			HA mass loss in %					Max t °C	
	Donth cm	D %	Undor	150			Ash-content	Q,	of the
	Deptil, cili	N,70	1500	1000	400-700°	Z	of HA, %	kJ /r	thermo-
			130	400*					effect
1	2	3	4	5	6	7	8	9	10
Scheuchzerite-Sphagnum	5	2,44	31,44	54,88	0,62	11,24	23,97	521,2	
10-20	20-30	5	1,93	39,69	48,73	0,85	9,65	23,59	477,0
	40-50	5	3,69	33,08	55,14	0,67	8,09	23,92	512,4
	80-90	20	2,56	38,28	50,80	0,80	8,36	23,05	480,7
	110-120	25	1,75	31.85	56,47	0,59	7,43	23,15	519,0
	120-130	25	1,99	34,93	54,12	0,68	9,93	23,13	507,2
	130-140	25	2,19	37,92	50,85	0,78	8,96	23,26	458,6
	160-170	25	2,55	33,94	55,37	0,66	9,99	23,63	508,7
	330-340	15	3,12	30,28	61,61	0,54	9,39	22,54	529,2
	340-350	30	3,88	32,27	59,15	0,61	4,70	20,16	502,6
	25	1,31	38,08	55,53	0,70	5,08	22,47	485,5	
350-360	360-370	20	2,03	37,05	52,54	0,74	4,99	23,51	465,7
Average values and		<u>18.8</u>	<u>2.45</u>	<u>34.90</u>	<u>54.60</u>	0.69	<u>8.15</u>	<u>23.03</u>	<u>497.32</u>
confidence limit		5.7	0.48	2.00	2.27	0.05	1.37	0.64	14.53
Sphagnum matted	5	2,41	35,76	53,74	0,71	8,09	23,51	495,9	
30-40	50-60	15	2,77	31,80	56,48	0,61	8,95	23,00	510,9
	70-80	15	2,38	36,17	51,65	0,75	9,80	23,21	499,2
	90-100	20	2.02	36,44	57,35	0,67	8,38	23,38	506,5
	140-150	20	2,47	36,71	53,30	0,73	9,04	23,80	498,0
	150-160	15	2,02	36,36	51,63	0,74	7,52	24,18	495,7
Average values and		<u>15.0</u>	<u>2.35</u>	35.54	<u>54.03</u>	0.70	<u>8.63</u>	23.51	501.03
confidence limit		5.48	0.29	1.86	2.41	0.05	0.80	0.42	6.24
Scheuchzerite	190-200	40	3,19	30,48	58,32	0,57	8,01	22,08	521,5
	210-220	25	2,92	30,55	55,78	0,60	10,99	23,55	520,9
Average values and		<u>32.5</u>	<u>3.06</u>	<u>30.52</u>	<u>57.05</u>	0.59	<u>9.50</u>	<u>22.82</u>	<u>521.20</u>
confidence limit		32.25	0.58	0.15	5.46	0.06	6.41	3.16	1.29
Sphagnum complex	220-230	15	3,36	32,56	54,58	0,66	9,50	22,63	511,1
	250-260	15	1,86	35,79	56,19	0,67	6,65	22,29	501,7
	15	2,63	33,53	54,50	0,66	9,34	23,17	512,7	
290-300	300-310	15	2,79	36,68	58,10	0,68	7,00	19,02	494,7
Average values and		<u>15.0</u>	<u>2.66</u>	<u>34.64</u>	<u>55.84</u>	<u>0.67</u>	<u>8.12</u>	<u>21.78</u>	<u>505.05</u>
confidence limit		0.00	0.86	2.67	2.36	0.01	2.09	2.60	11.73
Sphagnum phuscum peat	10	2,21	37,91	56,41	0,71	3,47	23,13	495,7	
230-240	240-250	10	1,86	28,15	60,15	0,50	9,84	23,46	527,1
	260-270	15	2,46	35,08	56,54	0,66	5,92	23,05	517,4
	270-280	10	4,32	34,20	54,79	0,70	6,69	21,16	512,5
	280-290	15	2,73	35,19	55,08	0,68	7,00	19,02	503,5
	310-320	10	2,65	37,46	50,50	0,79	9,39	22,54	464,2
	320-330	5	2,57	31,81	58,62	0,58	2,43	24,03	514,9
Average values and		10.7	2.69	34.26	56.01	0.66	6.39	22.34	505.04
confidence limit		3.07	0.70	3.01	2.75	0.08	2.46	1.53	18.39

Table 2. Loss of weight and thermal effects at thermal decomposition of humic acids.

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Note: numerator – mean value, denominator – accuracy of an interval assessment (P =0.95), Z – the relation of weight loss in the low-temperature area to weight loss in high-temperature area.

The percentage of ash in composition changes from 2,43 to 11,24%. The relation of weight loss in the low-temperature area to weight loss in high-temperature area (the relation "periphery" / "core") varies (Z) for the studied exemplars over a wide range from 0,59 to 0,70. At the same time mean values increase in sequence: scheuchzerite peat - 0,59, phuscum peat - 0,66, sphagnous complex peat - 0,67, scheuchzerite-sphagnum peat -0,69, sphagnous matted peat - 0,70. The least values Z noted for composition of scheuchzerite peat show it is higher in comparison with other exemplars of thermodynamic stability, "maturity" of composition macromolecules; it is characterized by the largest temperatures of thermo-effects.







Despite convention of thermal reactions division of composition destruction to the low-temperature and high-temperature areas, use of an index Z allows to reveal structural features of humic acids for different peat types [13]. Correlative dependence between an index Z and the maximal temperature of the thermo-effect which is given in figure 2 is defined for descriptive reasons. Considering that peat represents changeable natural object which was formed for many years under various climatic conditions, the received dependence is rather high 0,72. In the Figure it is visible that at decrease of an index Z the maximal temperature of the thermo-effect increases.

For the comparative analysis correlative dependencies between an index Z and temperature of the thermo-effect of composition for separate peat types (Fig. 3) are constructed. The greatest correlation (R=0,99) between an index Z and the maximal temperature of the thermo-effect is observed in composition of sphagnous complex peat (Fig. 3, C). Then in a decreasing sequence sphagnous matted (R=0,82), scheuchzerite-sphagnous (R=0,73) peat types and sphagnous phuscum peat (R=0,71) (Fig. 3, A, C, D) follow. Correlative dependence of scheuchzerite peat is separately not investigated as it is presented by only two exemplars.

Decomposition extent of the initial peat taken for research varied from 5% for scheuchzeritesphagnous and the sphagnous matted peat in an upper of a peat deposit an sphagnous phuscum peat (at a depth of 220-330 cm) to 40% for scheuchzerite peat (190-200 cm). Dependence between decomposition extent of initial peat and the maximal temperature of the thermo-effect, aswellas index of Z in composition is not revealed.



The new received results about thermal stability of raised peat composition unlike earlier performed works of such plan define features of starting organic material of the peat resources in the Khanty-Mansi AA Yugra which are formed in specific environmental conditions and therefore have no analogs.





Under pic: Max t ^oC of the thermo-effect

Figure 3. – Correlative dependence between an index Z and temperature of a thermo-effect for separate peat types: A – scheuchzerite-sphagnous, B – sphagnous matted, C – sphagnous complex, D – phuscum peat.

One of the main tasks when studying composition, is establishing correlation between structure of humic acids and conditions of their formation. It is necessary for diagnostics and classification of peat, for the forecast of humic acids composition changes in the course of peat-forming as structure and properties of humic acids are intimately bound to geographical position and factor features of the peat-forming.

Their constitutional formula which allows to explain the most important properties of composition gives the fullest characteristic of humic acids. In order to understand the features of the chemical composition nature of various peat types we resort to the preparations analysis of various origin and their thermal characteristics. For this purpose all arsenal of the modern instrumental technique is used.

Therefore also interest in research of "thin" structure of humin substances with application of the modern analysis methods increases more and more. In spite of the fact that applied value of humic acids thermal stability researches is yet not fully used by soil scientists and agrochemists, prospects of such works for most of experts do not raise doubts.

CONCLUSIONS

1. For the first time in a taiga zone of Western Siberia thermal stability of sphagnous peat humic acids characterized by quantitatively different size of molecular-chain scission in the ranges from 220 to 400 °s from 400 to 800 °C is investigated.



- 2. The comparative results characteristic of raised peat types humic acids thermal analysis with various contents of sphagnous mosses is shown in various values of maximal temperatures for thermo-effects which change from 464,2 to 529 °C, and correlate with the relation of weight loss in the low-temperature area to weight loss in the high-temperature area changing from 0,50 to 0,85.
- 3. The most suitable model for studying the process of humification is sphagnous peat study, uniform in botanical structure with decomposition extent of 5-25% as in the course of further peat decomposition, compositions taken from them, are leveled on structure character.

SUMMARY

Generalizing results of the carried-out thermal analysis, one may say, that the comparative composition analysis is possible only at the least decomposition extent of initial peat and the more or less homogeneous botanical structure. HA may differ depending on botanical structure, but only to a certain extent, and after high decomposition extent of peat (more than 40%) when they are generally humificated completely, the difference in structure of composition is practically not found [9]. Therefore we investigated composition of peat with the least extents of decomposition generally of 5-25%, (two exemplars of 30 and 40%) and with a dominance of the sphagnous mosses oddments in botanical structure.

Process of humification takes place in particular conditions which influence peat formation. In the sphagnous peat of raised bogs of a taiga zone of Western Siberia the reduction properties, due to excess humidification and high acidity are expressed. These properties find reflection in the ratio of aromatic and aliphatic parts which are reflected in a contour of the differential scanning curve compositions.

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