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Thermodynamical Stability and Element Composition Peat Humic Acids Khanty-Mansiysk District.

MP Sartakov[1]*, YM Deryabina[2], and NV Chukhareva[3].

[1]Ugra State University, Khanty-Mansiysk, ul. Chekhova, 16
[2]Novosibirsk Institute of Organic Chemistry named after N.N. Vorozhtsov SB RAS Academician Lavrentyev Avenue, 9
[3]National Research Tomsk Polytechnic University, Tomsk, pr. Lenina, 30.

ABSTRACT

This article provides new data that characterize structural features of humic acid of peats in Khanty-Mansiysk district. The article presents the results of thermic and weigh analysis and elemental composition of humic acids extracted from peats of various types and species which have provided important information about the structure of these substances. Humic acid of scheuchzeria and sphagnum peat have a less share of stable structural fragments of macromolecules, and then in ascending order they are followed by wood, grass and sedge peat.
Keywords: humic acid, peat, thermal stability of humic acids, elemental composition of humic acids, Khanty-Mansiysk autonomous district.

***Corresponding author**

INTRODUCTION

Humification of dead plant organisms and microbial mass is a global natural process that due to the selection of a thermodynamically stable compounds leads to the "conservation" of organic matter in the biosphere, protecting it to some extent from total mineralization [1].

There is no doubt that thermodynamic stability is an adequate reflection of peculiarities of molecular structure of humic substances, depending on the initial substrate, conditions and stages of formation of humic acid. The composition and characteristics of molecular structures of humic acids provide information about the specifics of humification process reflecting characteristics both the original organic material, and the conditions in which the process takes place.

Therefore, there has been increasing interest in the study of "thin" structure of humic substances using modern instrumental mechanisms. Despite the fact that the practical importance of these studies in the not yet fully used by peat scientists, the prospect of such work is not doubted by the majority of experts.

OBJECTS AND METHODS OF RESEARCH

As the objects of the study we used the preparations of humic acids isolated from the surface layers of peat of different types and species at the confluence of the Ob and the Irtysh (Table. 1). Extraction was performed as previously described [1].

Table 1: Botanical composition

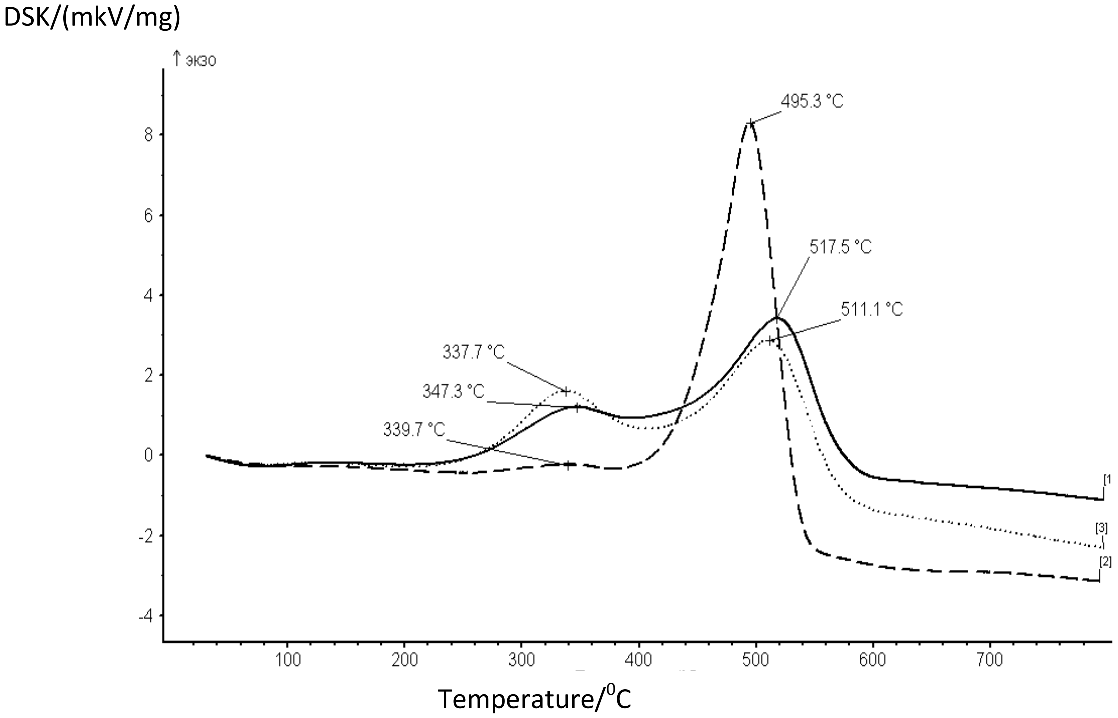
Type and kind of peat	Composition	R
scheuchzeria (upper)	subshrubs 5%, mud sedge 10%, scheuchzeria 80%, bog bean 5%,	20
Sphagnum fuscum peat (upper)	subshrubs 5%, Sphagnum fuscum 85%, Sphagnum Magellan 5%.	30
Grassy (transitional)	White birch 5%, pine 5%, beaked sedge 20%, not determined sedges 10%, bog bean 45%, horsetail 5%, woodreed 5%, Meesia triquetra * 5%.	30
Grassy (transitional)	White birch 5%, subshrubs 10%, slender sedge 5%, beaked sedge 30%, not determined sedges 10%, bog bean 40%.	35
Wood-sedge (lowland)	White birch 25%, dwarf birch 5%, embers 5%, vilyuysky sedge 10%, Omsk sedge 25%, turfy sedge 15%, bog bean 5%, bulged sphagnum 5%, Varnstrof sedge 5%, mineral contamination - dust-like fractions and individual grains of sand.	55
Wood (transitional)	White birch 5%, pine 45%, shrubs 10%, slender sedge 5%, beaked sedge 5%, Omsk sedge 5%, not determined sedges 10%, bog bean 5%, sphagnum of akutifolium section 5%, sphagnum of sphagnum section 5%.	40
sedge (transitional)	shrubs 5%, mound sedges 90%, not determined grasses 5%.	40
Sedge and cotton grass (transitional)	White birch 5%, not determined sedges 35%, cotton grass 50%, bog bean 10%.	45

Note: R - the degree of decomposition. * Wort (green) moss.

Thermal analysis was performed on the synchronous thermal analyzer STA 409 PC Luxx (company Netzsch) at the Institute of Organic Chemistry named after N.N. Vorozhtsov, SB RAS, Novosibirsk. The method allows simultaneous recording of weight loss, determination of the characteristic temperatures and thermal effects. Degradation was carried out both in air atmosphere and in inert atmosphere, in a platinum crucible, heating rate of 10^0C per minute. Hinge of the test sample was 5-10 mg. Sensitivity of weights was 0.1 mg.

RESULTS AND DISCUSSION

On the basis of representations of the two-term structure of macromolecules of humic acids and previously proposed their model (Komissarov, Loginov) [1] we carried out thermogravimetric study of humic acids. As a result, thermoanalytical studies in peat humic acids we found some clearly defined temperature ranges of weight loss at 60-120, 120-240, 240-400 and 400-700 °C. DSC diagrams give an idea of thermal effects occurring at high oxidative destruction of the samples. It is easy to see that all the samples have twostage curve, ie, decomposition of the samples occurs in two stages - before 400^{0}C and from 400 to 600^{0}S. However, the form of these curves is markedly different (Figure 1). For samples of humic acids of sphagnum and sedge peats the low-temperature thermal effect (up to 400^0) and high temperature (up to 600^0) are approximately equal. And for samples of wood high-temperature effect is much superior as compared with low temperature. Thus, referring to the DSC curve of humic acids one can accurately diagnose the presence of woody vegetation in peat deposits.



Note: • • • HA from sedge peat - - - HA from wood peat
- HA from sphagnum peat

Figure 1: - DSC diagrams of humic acids of peats

For all samples on thermograms endothermic effect at 60-120 ° C with maximum intensity of thermoeffect 60-75 ° C is observed, which is caused by removal of the adsorbed water and cleavage of skeleton of molecule of humic acids in peripheral portion. This is evidenced by the value of the loss of mass. The first small exotherm effect at low temperatures of 120-240 ° C with maximum intensity at 145-180 ° C corresponds to molecular periphery degradation of peat humic acids. It is most clearly pronounced in upper peats humic acids and less pronounced in transitional and fen peats. [2]

The second distinct exotherm effect at 240-400 ° C with a maximum intensity of 330-370 ° C is caused by further destruction of humic acids. The predominant reactions in this temperature range are dehydrogenation reaction, decarboxylation and parallel sequential reactions associated with the start of central nuclear structures splitting [2].

High temperature effects occurring at temperatures above 400 ° C, with maximum intensity at 510-540 ° C are associated with destruction of the most stable structures with oxidation of released carbon [3,4]. Thermal degradation confirmes that GK of upper scheuchzeria and sphagnum peats have more aliphatic chains than humic acids of wood, grass and sedge transitional and lowland peats. In the same sequence increase in the proportion of stable groups occurs, as evidenced by a reduction of (Z) ratio. Humic acids of scheuchzeria and sphagnum peats it equals 0,68-0,88, wood - 0,55-0,58, grassy - 0,50-0,53 and sedge peats 0,45-0,46. (Table. 2).

The reduction in coefficient Z occurs in humic acids with lower molecular weight due to intensive destruction of bridge groups with a relative accumulation of stable groups.

Table 2: Thermal and weight characterization of humic acid of peats in Ob-Irtysh interfluve

Peat type	Mass loss in low-temperature region, % 60-400^{0}C	Mass loss in high-temperature region 400-700^{0}C	Total mass loss, %	Z (I:II)
Scheuchzeria (upper)	39,5363	58,1214	97,6	0,68
Sphagnum peat (upper)	32,7352	66,0602	96,1	0,88
Grassy (transitional)	33,8467	63,8638	97,7	0,53
Grassy (transitional)	31,6230	63,2497	94,9	0,50
Wood and sedge (lowland)	32,5935	55,7284	88,3	0,58
Wood (transitional)	33,9472	62,2071	96,2	0,55
sedge (transitional)	28,8692	62, 2245	91,1	0,46
Sedge and cotton grass (transitional)	27,3106	61,3106	89,2	0,45

Z characterizes the ratio of weight loss in the low temperature region of thermolysis to the weight loss in the high temperature interval.

It should be noted that having different molecular weight general principle structure of humic acids is retained. From the viewpoint of heat resistance separate fractions of HA of various peats from Khanty-Mansiysk district are represented by the same fragments (Fig. 1).

The results of the elemental analysis allow to characterize the individual peculiarities of humic substances of different peats in Ob-Irtysh floodplain and give some information about the principles of their structure. For these purposes, it is more convenient to use not the percentage of the composition of humic acids set in the analysis, but the atomic ratios of elements (Table. 3).

The atomic ratios H / C, O / C, N / C, as is known, indicate the number of atoms of hydrogen, oxygen and nitrogen, falling in the molecule (particle) of humic substances on one carbon atom. In relation to each of the mentioned pairs we judged the relative branching of the side chains, nitrogen-containing compounds role in the formation of humic substances.

On the basis of the principles by the way of interpolation of the limit structures for conditional evaluation of aromatic and aliphatic components using a modified formula Van Crevel aliphatic carbon ($C_{al.}$) of humic acids was calculated. It was assumed that the H / C of the aromatic portion equals 0.33 K (factor for oxygen functions accounting) - 0.67 [5].

$$C_{al.} = (H/C)gk + 2(O/C)К – (H:C)_{arom.}/ (H/C)_{al.} + (H/C)_{arom},$$

$C_{al.}$ - carbon content of aliphatic fragments in humic acids; H / C and O / C - were taken from the results of elemental analysis. This figure is not intended to describe the general structure of the substance, but it gives some information about the ratio of linear and cyclic polymerized carbon. For a more accurate calculation of $C_{al.}$ we should take into account the number and the nature of oxygen functions as a substantial portion of hydrogen is replaced by oxygen atoms [6].

In our studies, the largest share of Cal corresponds to GK of scheuchzeria and sphagnum peat (0.67).

Table 3: The ratio of H, O, N to C, the proportion of carbon of aliphatic fragments of peats HA in Ob-Irtysh floodplain.

Peat	H/C	O/H	N/H	$C_{ал.}$
Scheuchzeria (upper)	0,99	0,51	0,02	0,67
Sphagnum peat (upper)	1,02	0,46	0,03	0,67
Grassy (transitional)	0,90	0,48	0,03	0,64
Grassy (transitional)	0,94	0,46	0,03	0,65
Wood and sedge (lowland)	0,90	0,47	0,03	0,65
Wood (transitional)	1,09	0,53	0,03	0,66
sedge (transitional)	1,01	0,46	0,03	0,66
Sedge and cotton grass (transitional)	0,92	0,46	0,02	0,65

CONCLUSIONS

- All thermograms of humic acids are characterized by the presence of typical for all drugs endogenous and exothermoeffects that confirms the presence of the same structural fragments. The thermal stability of the samples decreases in the direction: sedge, grassy, wood and sphagnum peat.
- The elemental composition of humic acids of peats varies. It was found that the proportion of aliphatic structures in macromolecules varies between 0,64-0,67.

CONCLUSION

Use of modern simultaneous thermal analysis allows with high accuracy and low flow of the sample to obtain important information about the process of thermal decomposition of the humic acids of different origins. There is evidence of significant differences in the outline of DSC curves and values Z, which says that if there are sufficient samples these indicators can be used to diagnose humic acids of various types and kinds of peats.

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REFERENCES

[1] Komissarov I.D., Loginov L.F. The block diagram and the simulation of macromolecules of humic acids // Scientific. Proceedings of the Tyumen Agricultural Institute, 1971. T. 14. S. 125-131.
[2] Tihova V.D. Sartakov M.P. Thermal characterization of humic acids of peats in the middle Ob // Bulletin of the Krasnoyarsk State Agrarian University. -2009. -№. 11. C. 26-29.
[3] Shapchenkova O.A. Aniskina A.A. Loskutov S.R. Thermal analysis of frozen soil organic matter (Central Siberian Plateau). Soil Science. 2011. №4. Pp 439-446.
[4] Shapchenkova O.A., Aniskina A.A., Loskutov S.R. Thermal analysis of organic matter in cryogenic soils (Central Siberian plateau)
[5] D.S. Orlov, L.A. Grishina Workshop on Chemistry humus. Moscow. Moscow State University. 1981. -272 p.
[6] Sartakov MP The elemental composition of humic acids of peats in middle Ob. Agrarian Herald of Urals. 2008. №2. S. 84-85