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# Impact of Heat Treatment on Humic Acid Elemental Content and Thermal Stability

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**Abstract**

The article examines the impact of thermal peat modification on the elemental content and properties of humic acids. It has been revealed that preliminary heat treatment of different peat types characterized by various decomposition degrees causes the changes in elemental content; precisely it leads to the increase in macromolecule benzoid degree and subsequent enhancement of its thermal stability.

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*Keywords:* peat, heat treatment, thermal stability, group composition, elemental content;

## 1. Introduction

Humic acid is known as a key constituent of soils (peat) which defines their characteristic features. Additionally, humic acid, being a valuable source material for a great variety of products, has potential use in various industrial applications (medicine, agriculture, cosmetics industry, etc.). The specific properties, amount, and quality of humic acid directly define its application in this or that industry.

The current research addresses a rather complicated issue. It is explained by the fact that when extracting humic acid from different types of peat, organic and inorganic components of humic acid matrix are altered to different extents[1,2]. As a result, the obtained humic acids significantly differ both in composition and properties. Therefore, to

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solve this task, it is required to carry out a great number of investigations intended to develop the methods for not only regulating humic acid yield but also monitoring the alteration of their composition and properties. Therefore, the current research, being focused on solving the above-mentioned task, is of great practical and theoretical importance.

The previous joint research[3,4] has revealed that thermal peat treatment at 250 °C in its decomposing gases is the method to increase the yields of humic acids from peat. However, the obtained data are not sufficient for figuring out the impact of preliminary heat treatment on the composition and properties of humic acids extracted from different peat samples characterized by various decomposition degrees. It is required to carry out additional complex research, precisely, to investigate elemental composition of humic acids and outline the structural changes of humic acid macromolecule at first approximation based on the obtained calculated characteristics.

Therefore, the main objective of the present research is to investigate the impact of heat treatment on the elemental composition and properties of humic acids extracted from different peat samples, as well as to analyze the alteration of thermal stability characteristics.

## 2. Materials and Methods

For the research, humic acids extracted according to technique[5] from 0.25 mm fraction of air-dried and heat-treated terrestrial, transition, and fen peat with low and medium decomposition degree (R=5…45 %) have been chosen. The mentioned peat samples were taken from Vasugan wetland located in Tomsk region (the Russian Federation). The codes were attributed to each peat sample: humic acid from terrestrial peat (HA h), humic acid from transition peat (HA m), humic acid from fen peat (HA l).

The elemental content (C, H, N, S+O) of peat organic matter were investigated at Novosibirsk Institute of Organic Chemistry of the Siberian Branch of Russian Academy of Science by automatic elemental analyzer EURO EA3000. The elemental content was measured by burning the samples, weight 1.5 mg, in a vertical reactor (oxidation tube) at 1050 °C in inert helium atmosphere, with oxygen (10ml) being added while burning. The products obtained as a result of pyrolysis reaction were subsequently oxidized by oxidic-catalytic composition at the lower part of the reactor and then passed through the reduction zone filled with copper which had been preliminary reduced by hydrogen at 500 °C. The mixture of nitrogen oxide and sulfur was converted to N2 and SO2, respectively.

The obtained N2, CO2, H2O, SO2 were separated using Porapak Q column and identified by thermal conductivity detector - katharometer according to technique[6]. The obtained mean values were calculated for dry and ashless humic acid samples (Table 1).

Table 1. Impact of peat heat treatment on humic acid elemental content

| Peat | T,° C | Humic Acid | Mean elemental content of humic acids extracted from of air-dried and heat-treated peat, % daf | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | C | ΔC, % rel. | H | ΔH, % rel. | N | ΔN, % rel. | O* | ΔO, % rel. |
| Humic acids from terrestrial peat with low decomposition degree | | | | | | | | | | |
| Fuskum | - | HA $h_1$ | 58.09 | +10.7 | 5.89 | -28.7 | 3.04 | +7.6 | 35.32 | -12.8 |
| (R = 5 %) | 250 | HA $h_{1-250}$ | 64.30 | | 4.20 | | 3.27 | | 30.81 | |
| Sphagnum | - | HA $h_2$ | 57.08 | +10.3 | 6.03 | -16.8 | 2.21 | +5.4 | 34.68 | -14.4 |
| (R = 5 %) | 250 | HA $h_{2-250}$ | 62.96 | | 5.02 | | 2.33 | | 29.68 | |
| Humic acids from terrestrial peat with medium decomposition degree | | | | | | | | | | |
| Cottongrass-sphagnum | - | HA $h_3$ | 59.98 | +1.2 | 5.23 | -5.5 | 2.64 | +0.4 | 32.16 | -1.4 |
| (R = 25 %) | 250 | HA $h_{3-250}$ | 60.70 | | 4.94 | | 2.65 | | 31.71 | |
| Cottongrass-sphagnum | - | HA $h_4$ | 58.90 | +3.0 | 5.31 | -7.9 | 2.14 | +0.9 | 33.65 | -4.0 |
| (R = 35 %) | 250 | HA $h_{4-250}$ | 60.65 | | 4.89 | | 2.16 | | 32.30 | |
| Humic acids from transition peat with medium decomposition degree | | | | | | | | | | |
| Cottongrass-sphagnum | - | HA $m_1$ | 58.79 | +4.5 | 5.28 | -16.7 | 3.37 | +3.9 | 32.56 | -5.9 |
| (R = 25 %) | 250 | HA $m_{1-250}$ | 61.44 | | 4.40 | | 3.50 | | 30.66 | |
| Sedge-sphagnum | - | HA $m_2$ | 60.06 | +2.4 | 4.87 | -13.1 | 2.96 | +8.1 | 32.11 | -3.2 |
| (R = 30 %) | 250 | HA $m_{2-250}$ | 61.49 | | 4.23 | | 3.20 | | 31.08 | |
| Humic acids from fen peat with medium decomposition degree | | | | | | | | | | |

| | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| Sedge-hypnum | - | HA $l_1$ | 59.78 | +2.7 | 4.79 | -20.5 | 4.39 | +7.7 | 31.04 | -3.1 |
| (R = 25%) | 250 | HA $l_{1-250}$ | 61.39 | | 3.81 | | 4.73 | | 30.07 | |
| Woody-sedge peat | - | HA $l_2$ | 59.87 | +4.0 | 5.09 | -17.5 | 3.62 | +17.7 | 31.43 | -6.8 |
| (R = 30 %) | 250 | HA $l_{2-250}$ | 62.24 | | 4.20 | | 4.26 | | 29.30 | |

The presented data show the changes in humic acid elemental content as a result of heat treatment under given conditions, i.e. carbon and nitrogen increase with decreasing hydrogen and oxygen. The relative changes in elemental content (ΔC, ΔH, ΔN, ΔO) of terrestrial peat humic acids prove the significance of the initial decomposition degree: the higher peat R, the lower the values ΔC, ΔH, ΔN, ΔO. It is explained by more intensive decomposition of organic matter that takes place at the stage of peat formation, which in its turn leads to slight impact of heat treatment on the elemental content of humic acids extracted from peat with medium decomposition degree.

Based on the elemental analysis carried out according to[7] using atomic ratio H:C и O:C, benzoid degree α (%) of each humic acid has been calculated. Precisely, for air-dried peat humic acids benzoid degree α ranges from 30.04 to 36.37 %, while for heat-treated peat humic acids benzoid degree α has higher values from 35.49 to 42.29 % (Table 2). The obtained data can clarify the changes in the proportion of inner (nuclear) and peripheral parts of humic acid macromolecule, with the latter increasing.

Table 2. Impact of peat heat treatment on humic acid benzoid degree and thermal stability

| Sample | H:C | O:C | α, % | G, % daf | ΔG, % rel. |
|---|---|---|---|---|---|
| HA $h_1$/ HA $h_{1-250}$ | 1.21/1.09 | 0.43/0.33 | 31.26/35.49 | 62.61/49.10 | -21.57 |
| HA $h_2$/ HA $h_{2-250}$ | 1.26/0.95 | 0.46/0.35 | 30.04/37.67 | 63.21/50.75 | -19.71 |
| HA $h_3$/ HA $h_{3-250}$ | 1.04/0.97 | 0.40/0.39 | 34.62/36.20 | 59.91/51.83 | -13.49 |
| HA $h_4$/ HA $h_{4-250}$ | 1.07/0.96 | 0.43/0.40 | 33.39/36.18 | 58.70/51.33 | -12.56 |
| HA $m_1$/ HA $m_{1-250}$ | 1.07/0.85 | 0.42/0.37 | 33.76/39.20 | 56.22/50.92 | -9.23 |
| HA $m_2$/ HA $m_{2-250}$ | 0.96/0.75 | 0.40/0.39 | 36.03/41.29 | 60.93/53.91 | -11.52 |
| HA $l_1$/ HA $l_{1-250}$ | 0.69/0.74 | 0.39/0.37 | 36.37/42.29 | 59.31/55.10 | -7.10 |
| HA $l_2$/ HA $m_{2-250}$ | 1.01/0.86 | 0.39/0.35 | 35.31/40.03 | 59.00/54.78 | -7.15 |

In order to confirm the above-mentioned assumption, derivatographic analysis of humic acids in inert nitrogen atmosphere at a heating rate of 5 deg/min has been carried out, and thermal stability (weight loss indicator G, % daf) of all investigated samples has been calculated at temperature 600 °C (Table 2).

According to G values, it has been revealed that thermal peat modifications result in decreasing weight loss indicators of humic acid. In other words, such humic acids contain more thermal stable elements which could constitute the inner (nuclear) part of molecule but do not refer to its peripheral part.

The relative change in humic acid weight loss (ΔG) as a result of peat heat treatment shows that the most profound changes in thermal stability are characteristic feature of terrestrial peat humic acids with low decomposition degrees: ΔG = 19.71 and 21.57 % rel. When decomposition degree increases, ΔG indicator decreases (Table 2), which corresponds to regularities revealed by elemental content analysis (Table 1).

## 3. Conclusion

- Preliminary heat treatment of peat results in carbon content increase, oxygen and hydrogen content decrease in humic acids, which in its turn increases benzoid degree of humic acid macromolecules.
- Heat-treated peat humic acids are characterized by better thermal stability.
- More profound relative changes in elemental content and weight loss indicators are characteristic feature of humic acids extracted from heat-treated peat with low decomposition degree.

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