

Comparative characteristics of thermal stability of humic acids of sapropels of the middle ob region and south of OB-Irtysh Basin of Western Siberia

Características comparativas de la estabilidad térmica de los ácidos húmicos de los sapropelos de la región OB de medio y del sur de la cuenca de OB-Irtysh de Siberia Occidental

Características comparativas da estabilidade térmica dos ácidos húmicos dos sapropels da região OB do meio e sul da bacia de OB-Irtysh da Sibéria Ocidental

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Abstract

The study of humic acids has more than a century history with a natural and logical evolution of focuses on their development processes, composition and properties. Despite the considerable material accumulated to date, the nature of this group of organic compounds still has not been sufficiently studied. We have decided that the distinctive features of hydrochemical and hydrobiological factors in the formation of sapropels of the studied lakes will be reflected in the thermal stability of humic acids extracted from them. Thermal analysis of humic acids extracted from the upper layers of bottom sediments of lakes of Kondinsk district of Khanty-Mansi Autonomous okrug and Barabinsk district of the Novosibirsk region, made using modern synchronous thermal analysis, has been resulted in the article. According to the obtained data, it is observed that with increasing of maximum temperature of the thermal effect, the value of Z decreases (the ratio of the mass loss in the low temperature space to the mass loss in the high temperature space), which indicates the increase in thermal stability, formation of humic acids. The indicator of humic acids of sapropels of the Kondinsk lakes varies from 0,56 to 0,67, and these intervals are much wider from 0.45 to 0.75 in the Barabinsk lakes. According to

Resumen

El estudio de los ácidos húmicos tiene más de un siglo de historia con una evolución natural y lógica de enfoques en sus procesos de desarrollo, composición y propiedades. A pesar del considerable material acumulado hasta la fecha, la naturaleza de este grupo de compuestos orgánicos aún no ha sido suficientemente estudiada. Hemos decidido que las características distintivas de los factores hidroquímicos e hidrobiológicos en la formación de sapropelos de los lagos estudiados se reflejarán en la estabilidad térmica de los ácidos húmicos extraídos de ellos. El resultado del análisis térmico de los ácidos húmicos extraídos de las capas superiores de los sedimentos del fondo de los lagos del distrito de Kondinsk de Okrug Autónomo de Khanty-Mansi y el distrito de Barabinsk de la región de Novosibirsk, realizado con el moderno análisis térmico sincrónico, ha sido publicado. Según los datos obtenidos, se observa que al aumentar la temperatura máxima del efecto térmico, el valor de Z disminuye (la relación entre la pérdida de masa en el espacio de baja temperatura y la pérdida de masa en el espacio de alta temperatura), lo que indica El aumento de la estabilidad térmica, formación de ácidos húmicos. El indicador de ácidos húmicos de

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thermogravimetric analysis the only statement of changes in chemical structure is possible, and the direction of the process can be assumed taking into account the data of the structural chemistry in combination with other spectral and chemical analysis methods.

Keywords: sapropel, humic acid, thermal analysis, Middle Ob region, the Ob-Irtysh basin, Western Siberia, typology of lakes, thermal decomposition, humification, aquatic vegetation.

sapropelas de los lagos de Kondinsk varía de 0,56 a 0,67, y estos intervalos son mucho más amplios de 0,45 a 0,75 en los lagos de Barabinsk. Según el análisis termogravimétrico, la única declaración de cambios en la estructura química es posible, y la dirección del proceso se puede asumir teniendo en cuenta los datos de la química estructural en combinación con otros métodos de análisis espectral y químico.

Palabras claves: Sapropel, ácido húmico, análisis térmico, región del medio Ob, la cuenca Ob-Irtysh, Siberia occidental, tipología de lagos, descomposición térmica, humificación, vegetación acuática.

Resumo

O estudo dos ácidos húmicos tem mais de um século de história com uma evolução natural e lógica de focos em seus processos de desenvolvimento, composição e propriedades. Apesar do considerável material acumulado até hoje, a natureza desse grupo de compostos orgânicos ainda não foi suficientemente estudada. Decidimos que as características distintivas dos fatores hidroquímicos e hidrobiológicos na formação de sapropelas dos lagos estudados serão refletidas na estabilidade térmica dos ácidos húmicos extraídos dos mesmos. Análises térmicas de ácidos húmicos extraídos das camadas superiores de sedimentos de fundo dos lagos do distrito de Kondinsk, distrito de Okrug e autônomo de Khanty-Mansi, na região de Novosibirsk, usando análise térmica síncrona moderna, resultaram no artigo. De acordo com os dados obtidos, observa-se que com o aumento da temperatura máxima do efeito térmico, o valor de Z diminui (a razão da perda de massa no espaço de baixa temperatura para a perda de massa no espaço de alta temperatura), o que indica o aumento da estabilidade térmica, formação de ácidos húmicos. O indicador de ácidos húmicos de sapropels dos lagos de Kondinsk varia de 0,56 a 0,67, e estes intervalos são muito mais largos de 0,45 a 0,75 nos lagos de Barabinsk. De acordo com a análise termogravimétrica, a única declaração de alterações na estrutura química é possível, e a direção do processo pode ser assumida levando em conta os dados da química estrutural em combinação com outros métodos de análise espectral e química.

Palavras-chave: Sapropel, ácido húmico, análise térmica, região de Middle Ob, bacia Ob-Irtysh, oeste da Sibéria, tipologia de lagos, decomposição térmica, humificação, vegetação aquática.

Introduction

The humification of fossil plants, animals, organisms and their metabolites is a global natural process at a planetary scale. The humic substances are included in the composition of organic matter in soils, peat, fossil coal, some shale and sapropels. They are the result of complex biochemical transformations of organic matter and a factor of its "conservation", protecting to some extent from the total mineralization.

They contain information about the specifics of humification process, reflecting both the characteristics of the original organic material and conditions in which the process occurs, in

their composition and peculiarities of the molecular structures (Chukov et al, 2017).

Interesting work on the study of thermal analysis and thermal modification of peat humic acids is presented in articles by Chukhareva N.V. (Chukhareva et al, 2016; Chukhareva et al, 2015; Chukhareva et al, 2003; Sartakov et al, 2017). In scientific practice, humic acids of sapropels were studied to a lesser extent than peat.

Therefore, interest in the study of the "fine" structure of humic substances using modern instrumental techniques is more and more increasing. Despite the fact that the applied meaning of these studies have not been fully used by soil scientists and the agronomists, most of

experts have no doubt in the prospect of such works.

The purpose and objectives: The aim of this work is to study the thermal stability of humic acids extracted from sapropels of the lakes of the Middle Ob region and southern Ob-Irtysh basin, Western Siberia. Objectives of the research are to identify the distinctive features of humic acids, due to the hydrochemical and hydrobiological factors in the formation of sapropels, using modern synchronous thermal analysis.

Objectives and Research Method

Samples of sapropels for producing humic substances were selected from the upper layers of bottom sediments of lakes Konda Khanty-Mansi Autonomous okrug and Barabinsk lakes of the Novosibirsk region.

Lakes of the southern Ob-Irtysh basin differ in diversity of chemical composition of the lake water due to heavy accumulation of salts, especially of sodium, which provide greater water hardness. Maxillopods Cladocera (cladocerans) dominate by biomass in zooplankton. These processes are less pronounced in the Middle Ob region, there are significantly less chlorides, sulfates, bicarbonates of calcium and magnesium and water is soft, Maxillopods Cladocera (cladocerans) dominate by biomass in zooplankton. Aquatic vegetation

includes the same hard and soft plants, but they compose much more wetland vegetation.

Thermal analysis was conducted with a thermogravimetric analyzer TGA/SDTA 851e (METTLER TOLEDO STAR, Germany), which allows high accuracy and small amount of sample to obtain important information about the process of thermal decomposition of humic acids of various genesis.

Experimental part: samples of the sapropels delivered to the laboratory, were brought to air-dried basis, pulverized in a disc mill and sifted through a sieve with apertures of 1 mm. Roots and other not decomposing plant residues were previously mechanically removed.

Extraction of humic acids was carried out according to previously described methods (Komissarov and Streltsova, 1971). The ash content of preparations does not exceed 2,52%. Combustion of samples was carried out under free access of air to the stove space.

Results and Discussion

Differential scanning curves (DSC) of diagrams of humic acids of sapropels, as can be seen in Figure 1, give understanding of the thermal effects occurring under high-temperature oxidative decomposition of data samples.

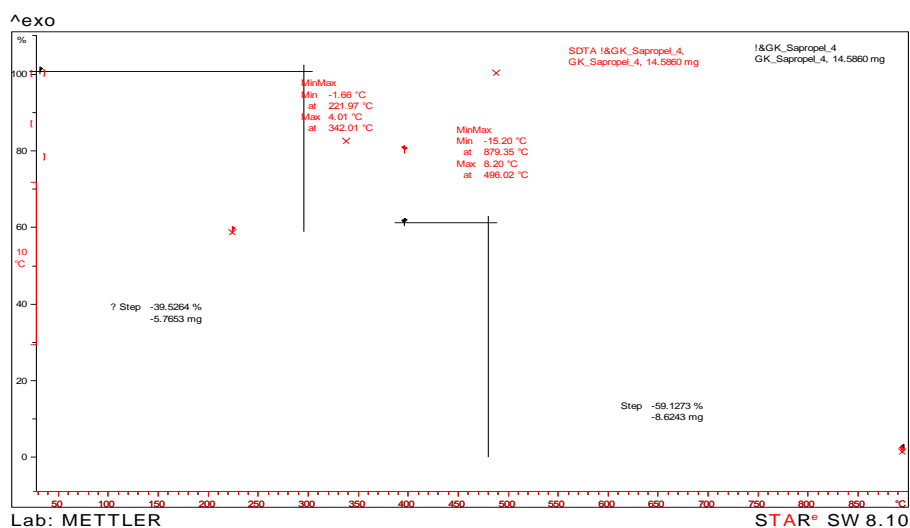


Figure 1 – DSK-diagram of humic acid sapropel

It is easy to note that thermal degradation causes a number of exothermic and endothermic effects, indicative of the gradual destruction of the molecules. Two parts dramatically different by thermal stability are clearly distinguished in its composition: nuclear aromatic (more stable) and

side aliphatic chains, which are characterized by a much lower thermostability. High intensity of exothermic reactions between 500 and 600 °C is due to the destruction of the nuclear part, endothermic and exothermic effects in the area of low temperatures (60 – 400 °C) are

associated with changes and gradual destruction of the peripheral part.

Division of thermal reactions of destruction of humic acids in low and high temperature areas, characterized by the index Z (Bolotov et al, 2010; Tikhova and Sartakov, 2009; Chernikov,

1984), allows to identify the structural features of humic acids of different origin (tab. 1). Indicator (Z) is currently successfully used for characteristics both of humic acids of different genetic types of soils and humic acids of modern and fossil microneites, including peloids, shales, peats and coals.

Table 1 – Data of TGA, batch of humic acids of sapropels

Lakes	Mass loss in a low temperature area (50 - 4000C)	Mass loss in a high temperature area (400-7000C)	Z	Ash content, %
Khanty-Mansi AO (Kondiknsk lakes)				
Medvezhye	35,14	62,83	0,56	2,20
Srednesatyginiski Tuman	39,53	59,13	0,67	1,50
Pyakuto	38,81	60,03	0,65	1,21
Schuchye	35,28	62,74	0,56	2,28
Kogalymlor	36,10	62,81	0,57	1,12
Novosibirsk oblast (Barabinsk lakes)				
Zarechnoe	42,31	56,06	0,75	1,56
Bol.Kayly	35,35	63,09	0,56	1,73
Peschanoe	31,60	65,93	0,45	2,52
Rossiyskoe	35,60	62,10	0,56	2,37

Note: Z is the ratio of the mass loss in the low temperature area to the mass loss in the high temperature area.

As can be seen from the table, the indicator of the humic acids of sapropels of the Kondinsk lakes varies from 0,56 to 0,67, and these intervals are much wider from 0.45 to 0.75 of humic acids of sapropels of the Barababinsk lakes. Reducing of the coefficient of Z occurs in humic acids with lower molecular weight due to

intensive destruction of the bridged groups during the relative accumulation of stable groups. The stable groups of low-molecular fractions become much less stable.

Also, we obtained the maximum temperature of thermoeffect in the high temperature area on the thermograms, which amounted to 569, 6 0C, of humic acids of the lake Peschanoye, and in the low temperature area equal to 346,4 0C of humic acids of the lake Kogalymlor (table. 2).

Table 2 - Maximum temperature thermoeffect of humic acids of sapropels.

Lakes	Max t 0C. Thermal effect in a low temperature area	Max t 0C. Thermal effect in a high temperature area
Khanty-Mansi AO (Kondiknsk lakes)		
Medvezhye	342,9	542,5
Srednesatyginiski Tuman	342,0	496,0
Pyakuto	340,3	517,2
Schuchye	343,2	509,7
Kogalymlor	346,4	535,4

Novosibirsk oblast (Barabinsk lakes)

Zarechnoe	321,2	473,6
Bol.Kayly	326,5	490,3
Peschanoe	330,4	569,6
Rossiyskoe	336,3	562,3

A very clear trend has been traced (Fig.2), it indicates that when you increase the maximum temperature of the thermal effect the Z value

decreases, which indicates the increase in thermal stability, formation of humic acids.

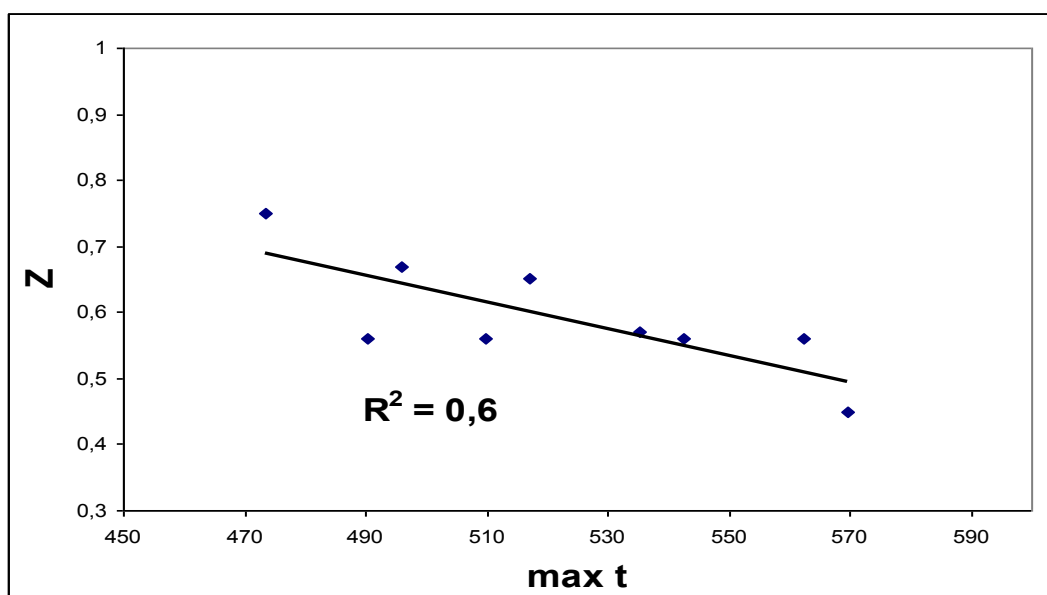


Figure 2 – the Dependence of index Z from the maximum temperature of thermal effect.

According to the obtained data humic acids extracted from sapropel of lake Peschanoe are characterized by the highest level of "maturity" and humic acids extracted from sapropel of lake Zarechnaya Novosibirsk region are characterized by the smallest level of "maturity".

It should be noted that general principle of structure of humic acids remains when different molecular weight. The fractions of humic acids are similar fragments for different sapropels of the Middle Ob and southern Ob-Irtysh basin from the viewpoint of the thermal stability.

Using data of thermogravimetric analysis of humic acids it would be possible to provide a process of thermal degradation and experimentally substantiate each of its stages if the idea of structural structure of humic acids was more complete.

According to the diagram the only possible statement of changes in chemical structure, and

the direction of the process can be assumed, considering these structural chemistries in combination with other spectral and chemical analysis methods.

Deductions

1. Data on thermal stability of humic acids of sapropels of the Middle Ob and southern Ob-Irtysh basin, Western Siberia, formed in lakes of various types have been obtained for the first time.
2. Thermal stability of humic acids of the studied objects varies, but, in general, it is characterized by the presence of typical preparations of endo and exo thermoeffect, which confirms the presence of identical structural fragments.

Conclusion

According to the obtained data a very clear trend has been observed that indicates that with increasing of maximum temperature of the thermal effect the value of Z decreases (the ratio of the mass loss in the low temperature area to the mass loss in the high temperature area), which indicates the increase in thermal stability, formation of humic acids. The indicator of humic acids of sapropels of the Kondinsk lakes varies from 0,56 to 0,67, and these intervals are much wider from 0.45 to 0.75 of the Barabinsk lakes. According to thermogravimetric analysis only statement of changes in chemical structure is possible, and the direction of the process can be assumed, considering data of structural chemistry in combination with other spectral and chemical analysis methods. A more detailed study of the process of thermal degradation is possible only with a more complete understanding of the molecular structure of humic acids.

Conflict of Interest

The author confirms that the submitted data does not contain conflict of interest.

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