



SPECTRAL CHARACTERISTICS OF HUMIC AND HYMATOMELANIC ACIDS IN LAKE PEATS OF THE RIGHT BANK OF THE OB RIVER (WESTERN SIBIRIA)

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Abstract

The objective of this work is to study the spectral characteristics of humic and hymatomelanic acids of bottom sediments of eight small lakes located on the right bank of the Ob River (Western Siberia) in the Surgut District of the Khanty-Mansiysk Autonomous Okrug - Yugra. We obtained electronic spectra in ultraviolet and visible parts of the spectrum and infrared spectra. For the electronic spectra of humic and hymatomelanic acids, we calculated extinction coefficients at wavelengths of 465 and 650 nm and determined chromaticity coefficients. The infrared spectra of humic and hymatomelanic acids were compared.

Key words: Humic Acids, Hymatomelanic Acids, UV Spectroscopy, IR Spectroscopy, Sapropel, Western Siberia.

Introduction

Humic substances are a macrocomponent of organic matter of aquatic and soil ecosystems, peloids and solid fossil fuels. Humic substances are classified on the basis of their different solvability in alkalies and acids. Humic substances consist of humin and humic acids. The subdivision of humic acids into groups is rather relative and it is based on the difference in solvability in aqueous dilute solutions of acids, alkalies and other solvents. To characterize organic substances of complex biochemical objects, it is common to single out the following groups: fulvic acids, humic acids (HA) and hymatomelanic acids (HMA). HMA are extracted from wet HA by ethanol (Orlov, 1985).

Sapropels are modern or subfossil, fine-structured, colloidal deposits of continental water reservoirs. Sapropel composition includes the remains of microscopic aquatic organisms, a considerable amount of organic matter (including humic substances), a certain amount of inorganic components of biogenic origin, as well as mineral impurities of a salutary nature (Korde, 1960).

Sapropel deposits draw the attention of researchers due to the possibilities of their practical use. Sapropel is

used in medicine as applications, diluted baths for mud therapy, in agriculture as fertilizer, in animal husbandry as a mineral supplement (Shtin, 2005). Mechanochemically carboxymethylation of humic acids increases their solubility in water, which is very important for obtaining plant growth stimulants (Efanov *et al.*, 2019; Efanov and Sartakov, 2020). The study of HA and HMA of sapropels is important for the development of new products for medicine and agriculture. Analogous works analyzing HA and HMA in peats of this region are similar in their results with those analyzing humic acids in sapropels (Rybachuk *et al.*, 2016).

Materials and Methods

Sapropel was sampled from eight small lakes located on the right bank of the Ob River in the Surgut District of the Khanty-Mansiysk Autonomous Okrug - Yugra. Geomorphologically, the lakes are located on the second supra-floodplain terrace.

The sampling of sapropels was carried out according to the "Guidelines for methods of hydrobiological analysis of surface waters and bottom sediments" (Abakumov *et al.*, 1983). The samples were classified according to the ash and organic content.

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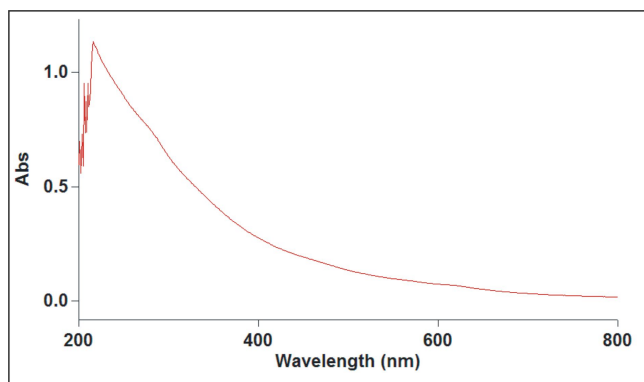


Fig. 1: Electronic absorption spectrum of HA of S-1 sample.

The bottom sediments of Lake S-1 are siltstone sands of clastogenic type, silicate class and sandy kind. They are characterized by a higher content of elements constituting the terrigenous part (Al, K, Na) compared with other samples studied.

The bottom sediments of lakes Vach Lor, S-189 are sapropelic clay silts of clastogenic type, organic-silicate class and organic-sandy kind. They are characterized by an average content of ash (45.51% and 42.16% respectively) and an average content of elements constituting the terrigenous part (Al, K, Na) compared with other samples studied.

The bottom sediments of lakes S-5, S-6, S-3, S-89, S-294 are typical sapropels, they belong to biogenic type and organic class. The ash content is the lowest; it decreases in the row S-5, S-6, S-3, S-89, S-294. The content of elements constituting the terrigenous part (Al, K, Na) and Fe is the lowest; it decreases in the row S-5, S-6, S-3, S-89, S-294.

No traces of anthropogenic effects have been identified in any of the samples studied.

The extraction of HA and HMA was done according to the Instorf method modified at the faculty of General Chemistry of Tyumen State Agricultural Academy (Komissarov and Loginov, 1971), but without demineralization by hydrochloric acid, which causes partial

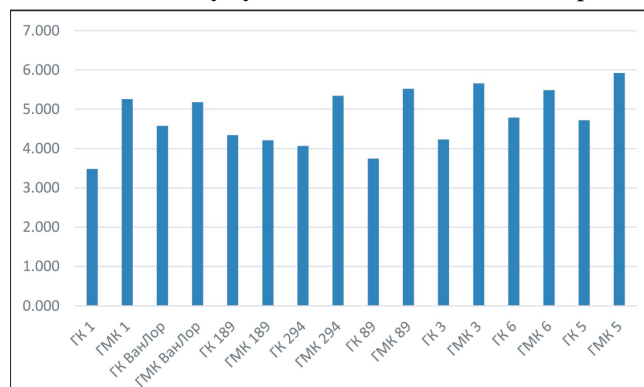


Fig. 2: HA and HMA chromaticity coefficients chart.

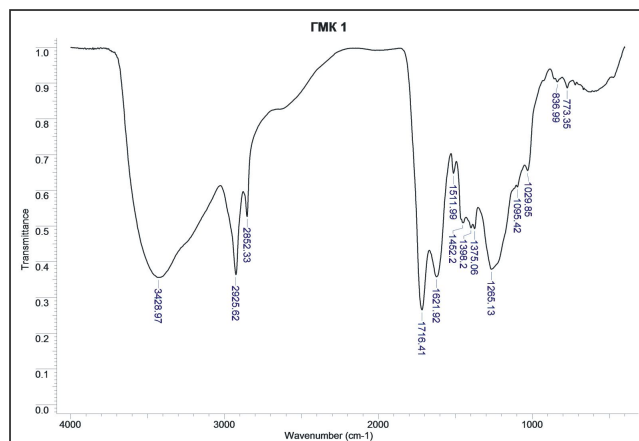


Fig. 3: HMA IR spectrum of Sample 1.

removal of aliphatic periphery and leads to averaging the results.

UV spectra and IR spectra of the samples were recorded at Novosibirsk Institute of Organic Chemistry SB RAS (analysts V.D. Tikhova, Yu.M. Deryabina). According to (Orlov and Grishinina, 1981) we calculated extinction coefficients:

$$E_{465} = \frac{D_{465}(100 + a)}{pl \cdot 100}$$

where

E_{465} - extinction coefficient at the wavelength of 465 nm;

D_{465} - absorbency at the wavelength of 465 nm

p - weighed quality of HA (mg) taken to make 100 ml of solution

l - working length of the sample cell

a - ash content of HA (% of ashless substance)

Results and Discussion

Fig. 1 shows the curve of the absorption spectrum in UV and visible parts for HA extracted from bottom sediments of Lake S-1.

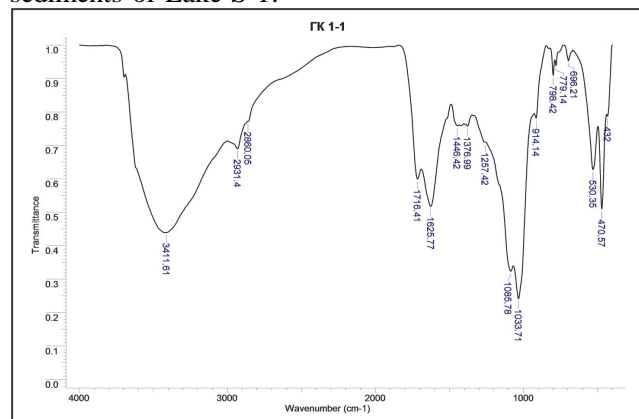


Fig. 4: HA IR spectrum of Sample 1.

The character of HA and HMA absorption spectra is of the same type and it corresponds to typical spectra of all humic substances. All spectra demonstrate intensive absorption in their ultraviolet part. The absorption in this spectrum part is connected with the fact that the aromatic ring is a conjugated condensed system of π -electron shells of benzole rings. The data obtained in this spectrum part are not considered reliable because spectral curve characteristics and absorption intensity in UV spectrum much depend on various factors, even in case of studying HA extracted from one and the same sample.

Visible spectrum absorption values of humin substances are especially widely used. The curves of studied HA and HMA are typical for humin substances: flat curves without distinct bands. This type of absorption curves, without peaks in longer wavelength spectrum, is connected with their overlapping as a result of a complex structure of HA molecules.

For all HA and HMA samples we determined absorbency values at the wavelengths of 465 nm (D465) and 650 nm (D650). These wavelength were chosen on the basis of the classical principles of HA spectra interpretation. We also calculated extinction coefficients (E_{465} , E_{650}) showing extinction of light caused by absorption and dispersion. The results are presented in table 1.

In all HA and HMA samples we observe higher values of extinction coefficients (E_{465} , E_{650}) for HA as compared with those for HMA. It should be noted that HA and HMA of Vach Lor sample have very similar extinction coefficients. To conditionally evaluate the

Table 1: Electronic spectroscopy results.

Bottom sediment type	Sample	D ₄₆₅	D ₆₅₀	E ₄₆₅	E ₆₅₀	E ₄₆₅ /E ₆₅₀
Siltstone sands	HA 1	0,174	0,050	0,050	0,014	3,480
	HMA 1	0,184	0,035	0,043	0,008	5,257
Sappropelic clay silts	HA Vach Lor	0,151	0,033	0,040	0,009	4,576
	HMA Vach Lor	0,202	0,039	0,038	0,007	5,179
	HA 189	0,178	0,041	0,040	0,009	4,341
	HMA 189	0,160	0,038	0,035	0,008	4,211
Sapropels	HA 294	0,317	0,078	0,067	0,016	4,064
	HMA 294	0,219	0,041	0,048	0,009	5,341
	HA 89	0,303	0,081	0,060	0,016	3,741
	HMA 89	0,171	0,031	0,038	0,007	5,516
	HA 3	0,220	0,052	0,049	0,012	4,231
	HMA 3	0,198	0,035	0,045	0,008	5,657
	HA 6	0,220	0,046	0,046	0,010	4,783
	HMA 6	0,192	0,035	0,041	0,007	5,486
	HA 5	0,236	0,050	0,050	0,011	4,720
HMA 5	0,225	0,038	0,044	0,007	5,921	

structure of HA and HMA, chromaticity coefficients E_{465}/E_{650} were calculated. The ratio shows the steepness of the falling absorbency if the wavelength is increased and it implies that carbon atoms are conjugated with hetero atoms in molecules of humic acids. They are characterized by lower values for HA and higher values for HMA, with the exception of Sample 189, for which these values are almost the same (Fig. 2).

IR spectra of all HA are similar to one another, as well as those of HMA. The difference is observed when comparing HA spectra with HMA spectra. Fig. 3 and 4 show HA and HMA spectra of Sample 1.

The above spectra clearly show peaks, which are typical for humic acids. The resolved absorption peaks in the zone of 500-1000 cm^{-1} are likely to indicate mineral components.

The absorption bands with peaks at 1257 (HA) and 1265 (HMA) cm^{-1} are conditioned by asymmetric stretching of C-O bond in simple ethers and similar structures. The peak intensity shows that these groups prevail in HMA.

The presence of aromatic rings in the molecules of studied HA and HMA is indicated by the absorption band at the wavelengths of 1625 and 1621 cm^{-1} conditioned by stretching of conjugated double bonds of carbon atoms. This peak for HMA is more intensive.

The band with the peak at wavelength 1716 cm^{-1} belongs to free carboxyl group $-\text{COOH}$. This band intensity is known to be directly related to the content of carboxyl groups in a molecule. Spectra show that HMA contain many more carboxyl groups.

The absorption bands with peaks at wavelengths of 2852, 2860 cm^{-1} and 2931, 2952 cm^{-1} are conditioned by stretching vibrations of C-H bonds in aliphatic CH_3 and CH_2 groups. HMA peaks are more intensive, which indicates a more branched aliphatic periphery of HMA.

A very wide band with a peak at wavelengths of about 3411 and 3428 cm^{-1} is conditioned by hydrogen bonds. A hydrogen bond is realized not in molecular, but in intermolecular interactions occurring in side structures located in the same plane. This band is more intensive for HMA, which indicates higher content of hydroxyl and carboxyl groups.

Registering comparable and most probable structural fragments of humic acids is possible only on the basis of computer analysis of their IR spectra (Tikhova *et al.*, 2019).

Conclusion

The extinction coefficients of the studied HA are higher than those of HMA of one and the same sample; the chromaticity coefficients of the studied HA are lower than those of HMA of one and the same sample. The exceptions are HA and HMA extracted from sapropelic clay silts, for which these coefficients are similar. The results of the study indicate a higher aromatic content of HA as compared with that of HMA. The samples extracted from sapropelic clay silts are similar in this characteristic. The IR spectra indicate higher content of aliphatic and aromatic fragments, as well as oxygen-containing functional groups in HMA of the studied bottom sediments.

Acknowledgments

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References

- Abakumov, V.A., N.P. Bubnova, N.I. Holikova, T.P. Goridchenko, R.A. Liepa, N.L. Svirskaya and V.M. Katanskaya (1983). Guidance of methods for the hydrobiological analysis of surface waters and bottom sediments. *Saint Petersburg: Gidrometeoizdat (in Russian)*.
- Efanov, M.V., I.V. Anan'ina, V.V. Kon'shin and M.P. Sartakov (2019). Mechanochemical method for peat carboxymethylation. *Russian Journal of Applied Chemistry*, **92(8)**: 1158-1160.
- Efanov, M.V. and M.P. Sartakov (2020). Carboxymethylation of Peat Humic Acids by a Mechanochemical Method. *Solid Fuel Chemistry*, **1**: 21-25.
- Komissarov, I.D. and L.F. Loginov (1971). Humin products. *Treatises of Tyumen Agricultural Institute*, **14**: 266.
- Korde, N.V. (1960). *Biostratification and typology of Russian sapropels*. - M.: Publishing House of the Academy of Sciences of the USSR, 219.
- Orlov, D.S. (1985). *Soil Chemistry*. - M. 380.
- Orlov, D.S. and L.A. Grishinina (1981). *Humus chemistry tutorial*. M.: Publishing House of Moscow State University, 272.
- Rybachuk, O.V., I.D. Komissarov, E.M. Osnitsky and M.P. Sartakov (2016). Comparative Characteristics of The Humic And Hymatomelanic Acids in Peats of The Middle Taiga. *Research Journal of Pharmaceutical, Biological and Chemical Sciences*, **7(6)**: 3097-3103.
- Shtin, S.M. (2005). *Lake sapropels and their integrated development*. - M.: Publishing House of Moscow State University, 373.
- Tikhova, V.D., Y.M. Deryabina, R.S. Vasilevich and E.D. Lodygin (2019). Structural features of tundra and taiga soil humic acids according to IR EXPERT analytical system data. *Journal of Soils and Sediments*, **19(6)**: 2697-2707.