Received: 15 August 2021 | Revised: 21 September 2021 | Accepted: 11 October 2021
DOI: 10.22034/ecc.2021.300013.1220

Eurasian Chemical Communications
SAMI

FULL PAPER

Thermal characteristics of humic and hymatomelanic acids of lake sapropels of the ob river right and left banks

Mikhail Petrovich Sartakov[a,*] |Natalia Valeryevna Shpynova[a] |Evgeny Mikhailovich Osnitsky[a] |Olga Alexandrovna Gurova[a] |Diana Ivanovna Tsvettsykh[a] |Igor Disanovich Komissarov[b]

[a]*Institute of Oil and Gas, Yugorsk State University, Khanty-Mansiysk, Russia*

[b]*Department of Chemistry, State Agrarian University of the Northern Trans-Urals, Tyumen, Russia*

***Corresponding Author:**
Mikhail Petrovich Sartakov
Email: mpsmps@bk.ru
Tel.: +7 (34671) 21186

The research aimed to study the thermal characteristics of Humic and Hymatomelanic acids in the bottom sediments of ten small lakes of the right bank of the Ob river and ten small lakes of the left bank of the Ob River. The studies were conducted using STA 409 PC Luxx synchronous thermal analyzer (Netzsch) with an inert atmosphere in a platinum crucible. The ash content of Humic and Hymatomelanic acids was determined. The ash content of the studied Humic acids was found to depend on the mineralization of the original bottom sediments. Humic acids, silt sands, and sapropel-clayed silts have the highest ash content. Hymatomelanic acids have a low ash content regardless of the mineralization of the original bottom sediments. The ratios of the mass loss in the low-temperature region to the mass loss in the high-temperature area (the "periphery"/"core" ratio) (Z) were calculated. The studies showed similarities and differences between the Humic and Hymatomelanic acids.

KEYWORDS

Humic acids; hymatomelanic acids; thermal analysis; sapropels; Western Siberia.

Introduction

Humification of dead plant organisms and microbial mass is a global natural process that, due to the selection of thermodynamically stable compounds, leads to the conservation of organic matter in the biosphere, protecting it to a certain extent from total mineralization [1]. Thermal characteristics reflect the peculiarities of the molecular structure of humic substances (HS), based on the initial organic material and the conditions of the humification process in a past study [2].

The thermal characteristics of humic acids contain valuable information characterizing the conditions and mechanism of humification in peats, soils, and sapropels [3]. They reflect the critical properties of humic acids (HA), and Hymatomelanic acids (HMC) [4].

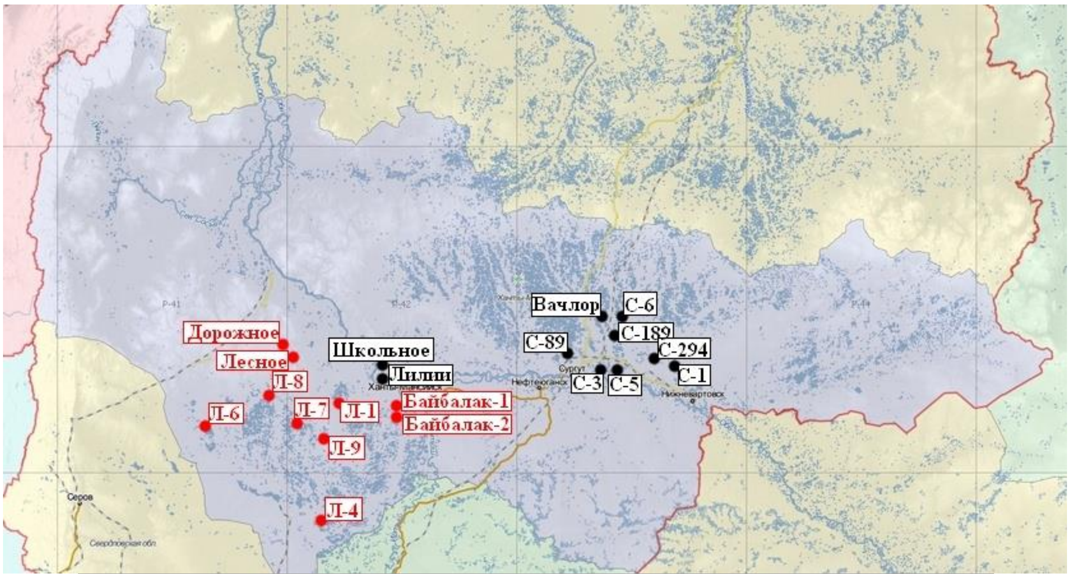
Subjective and quantitative qualities of compound components and acid-base utilitarian gatherings of humic acids (HA) in five pools of the Ob of Khanty-Mansi Autonomous Okrug-Yugra's left bank were depicted [10].

No generally acknowledged standard techniques for sapropel extraction or the examination and portrayal of the sapropel removal have been observed. For pharmacological applications, a typical methodology for the extraction interaction of active substances from sapropel and the examination techniques of the concentrates should be set up [11].

The balance surface strain and viscoelasticity modulus test conditions on the convergence of hymatomelanic corrosive salt arrangements are portrayed enough as far as the model of genuine two-dimensional answers polymolecular adsorption polyelectrolytes [12].

Objects and methods

Sapropel was sampled from the surface layers (0-20 cm) of bottom sediments of 20 small lakes: Ten on the left bank and the other ten on the right bank of the Ob River (Figure 1).



Дорожное	Dorozhnoe
Лесное	Lesnoe
Школьное	Shkolnoe
Лилии	Lilii
Байбалак-1	Baibalak-1
Байбалак-2	Baibalak-2
Вачлор	Vachlor
Л-1 (4, 6, 7, 8, 9)	L-1 (4, 6, 7, 8, 9)
С-1 (3, 5, 6, 89, 189, 294)	S-1 (3, 5, 6, 89, 189, 294)

FIGURE 1 Small lakes of the left and right banks of the Ob River

The lakes of the middle Ob are located on the second above-flood plain terrace. The surface area of the left bank lakes ranges from 2.2 to 154.7 hectares, reaching 4.8 meters. The surface area of the lakes of the right bank of the Ob river ranges from 3.9 to 120.3 hectares; the depth reaches 6.1 meters. Spring floods and precipitation supply most lakes. The lakes are located among cedar, pine, birch forests, and vast swamps. Mixed overgrowing type of reservoirs is a combination of rafts and vast thickets. The bottom of the lake is covered with a carpet of macrophytes.

Bottom sediments can be grouped according to their content of organic matter [5]. Based on this classification, bottom sediments of lakes on the right bank of the Ob, S-1, Liliii, are silty sands, Shkolnoye lakes are weakly sapropelic aleurolitic silts, S-189, and Vach Lor are sapropelic-argillaceous silts, S-294, S-89, S-3, S-6, S-5 - Sapropels. Bottom sediments of the lakes on the left bank of the Ob river, L-7, Baibalak 2, are silty sands, L-6, Dorozhnoe, Baibalak 1, Lesnoe - weakly sapropel silt silts, L-4, L-1 - clayed sapropel silts, L-8 - sapropel-clayed silts, and L-9 - Sapropels [6].

According to another classification, Sapropels can be divided into type, class, and kind according to the content of ash, calcium, and iron oxides, and biological and mineralogical composition [5]. The content of selenium and other trace elements is consistent with their content in the region's peat [6]. Sapropels of the lakes of the right bank of the Ob River, S-5, S-6, S-3, S-89, S-294, are of a biogenic type and organic class. The sapropels of the lakes of the right bank of the Ob River, Vach Lor, S-189, Shkolnoe, Liliii, S-1, are clastogenic. Samples from Vach Lor, S-189 are of organ-silicate class and organic-sandy, while samples from Shkolnoe, Liliii, and S-1 are of silicate class and sandy. Sapropels of the lakes of the left bank of the Ob River, L-9, L-8, are of the biogenic type and organic class. Sapropels of the lakes of the left bank of the Ob River, L-1, L-4, Baibalak 1, L-6, Lesnoe, Dorozhnoe, L-7, Baibalak 2, are of clastogenic type. A sample from L-1 is of organo-silicate class and organic-sandy, and samples from L-4, Baibalak 1, L-6, Lesnoe, Doroznoe, L-7, Baibalak 2 are of silicate class and sandy [7].

Sapropel was dried at 40 degrees Celsius, delipidized with benzene, and decalcified with sulfuric acid. HA was extracted with a 0.1 M sodium hydroxide solution for 12 hours. HA was precipitated with a 0.25 M sulfuric acid solution. HMA was extracted with ethanol from HA within 12 hours [8].

Thermal analysis of HA and HMA samples was carried out at the Novosibirsk Institute of Organic Chemistry, Siberian Branch, Russian Academy of Sciences (by V.D. Tikhova, Iu.M. Deriabin) on an STA 409 PC Luxx synchronous thermal analyzer (Netzsch) with an inert atmosphere in a platinum crucible. The device ensures accurate measurement of weight loss of samples of humic acids during heating due to the 1.25 µg sensitivity of the used thermal balances.

Results and discussion

The modern synchronous thermal analysis made it possible with high accuracy and a small sample volume to obtain data on the thermal decomposition of humic acids in lacustrine sediments. Most of the obtained thermograms have a form typical of humic acids (Figure 2).

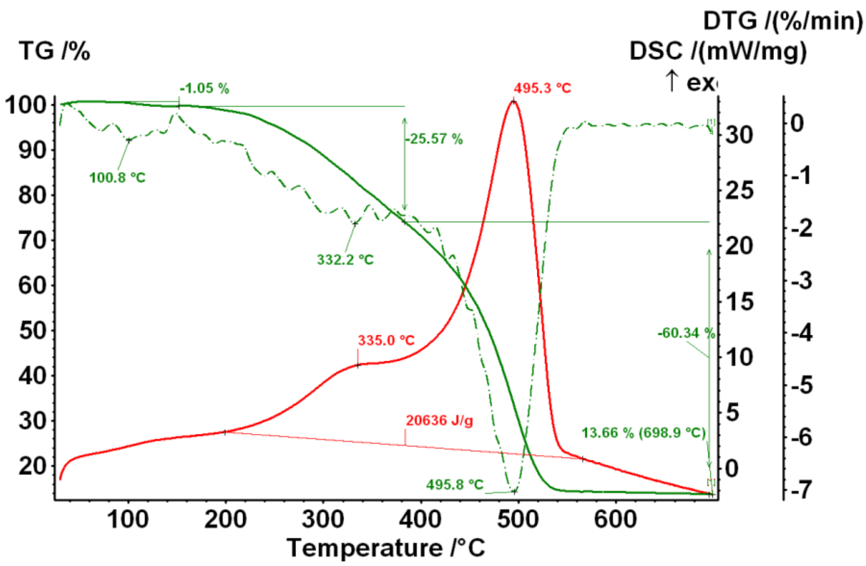


FIGURE 2 Differential scanning curve (DSC) of humic acids of the C-294 sample

Thermal destruction causes several exothermic effects, indicating the gradual destruction of the humic acid molecule. It contains two distinguished parts with sharply different thermal stability: The nuclear aromatic (more stable) and aliphatic side chains, characterized by a significantly lower thermal stability.

Figure 3 shows two thermal effects in the low-temperature region. The first exothermic effect in the region up to 150°C, caused by the removal of adsorption water and partial decomposition of the molecule's periphery, is weak or absent in all samples due to its suppression by endothermic bond opening reactions in this region.

The most intense thermal effect in humic acids occurs at 400-600°C, which is due to the destruction of more stable aliphatic chains, individual cycles, benzoic structures, and the destruction of the nuclear part. This thermal effect in the studied HA of sapropels of lakes of the right bank of the Ob River is achieved in the range from 414.9 to 495.3°C. In HMA from the lakes of the right bank of the Ob river – at 440.1 to 527.6°C. In HA from the lakes of the left bank of the Ob River, this thermal effect is achieved at 417.2 to 468.4°C. In HMA from the lakes of the left bank of the Ob river – at 417.8 to 504.1°C.

In contrast to HA, the studied HMA has two thermal effects at 400-600°C (Figure 3), which indicates the differences in the construction of the stable part of HA and HMA. The intensity of these peaks is different. Thermal destruction of the studied HMA in the high-temperature range proceeds in two reaction.

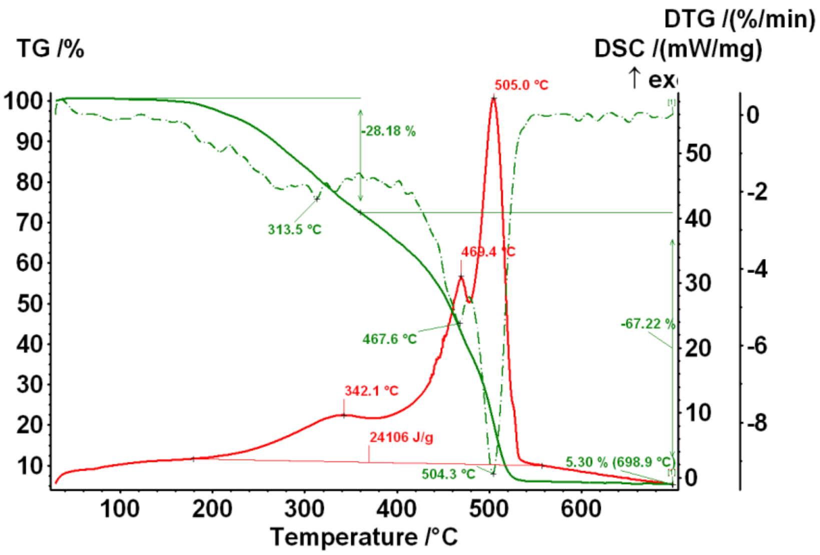


FIGURE 3 Differential scanning curve (DSC) of Hymatomelanic acids of the C-294 sample

Among the sapropel HA from the lakes of the right bank of the Ob River, the lowest and the highest maximum thermal effects are observed in the samples extracted from the bottom sediments of lake S-189 and lake S-294, respectively. Among the sapropel HMA from the lakes of the right bank of the Ob river, the lowest and the highest maximum thermal effects are observed in the samples extracted from the bottom sediments of lake Shkolnoe and lake S-6 respectively. Among the sapropel HA from the lakes of the left bank of the Ob river, the lowest value of the maximum thermal effect is observed in the sample extracted from the bottom sediments of Lake Baibalak-1, the highest in the bottom sediments of lake L-8. Among the sapropel HMA from the lakes of the left bank of the Ob river, the lowest and the highest maximum thermal effect is observed in the sample extracted from the bottom sediments of lake L-6 and lake L-1, respectively. The results of thermal analysis for HA and HMA from the lakes of the right and left banks of the Ob River are presented in Tables 1 and 2, respectively.

TABLE 1 Results of thermal analysis of HA and HMA of bottom sediments of the lakes of the right bank of the Ob River

Type of bottom sediment	Sample	Weight loss, %			Z	Q, kJ/kg	max t, °C of thermal effect	Ash content, %
		Up to 150 °C	150-400 °C	400-700 °C				
Siltstone sands	S-1 HA	0.00	20.26	36.29	0.56	13.691	423.9	43.45
	S-1 HMA	0.00	35.26	60.77	0.58	26.290	525.6	3.97
	Lilii HA	0.00	29.80	47.84	0.62	18.168	479.1	22.36
	Lilii HMA	0.00	42.97	49.26	0.87	21.995	489.9	7.77
Low sapropel siltstone sludge	Shkolnoe HA	0.00	27.13	40.70	0.67	16.036	452.9	32.17
	Shkolnoe HMA	0.00	44.56	47.05	0.95	21.347	440.1	8.39
Sapropel clayed sludge	Vachlor HA	0.00	26.04	40.31	0.65	16.530	441.5	33.65
	Vachlor HMA	0.45	33.29	62.11	0.54	24.701	474.1	4.15
	S-189 HA	1.10	22.87	44.33	0.52	16.019	414,9	31.70
Sapropels	S-189 HMA	0.00	46.21	48.20	0.96	26.271	509.8	5.59
	S-294 HA	1.05	25.57	60.34	0.42	20.636	495.3	13.04
	S-294 HMA	0.00	28.18	67.22	0.42	24.106	505.0	4.60
	S-89 HA	0.96	27.70	64.71	0.43	23.917	492.0	6.63
	S-89 HMA	0.00	32.16	63.53	0.51	27.053	508.1	4.31
	S-3 HA	1.36	25.98	51.46	0.50	17.505	456.6	21.20
	S-3 HMA	0.00	29.55	67.48	0.44	26.224	483.4	2.97
	S-6 HA	1.03	30.68	60.35	0.51	22.146	473.4	7.94
	S-6 HMA	0.00	30.09	64.27	0.47	26.265	527.6	5.64
	S-5 HA	1.35	34.20	58.17	0.59	21.626	475.4	6.28
	S-5 HMA	0.00	30.01	65.86	0.46	24.559	502.6	4.13

TABLE 2 Results of thermal analysis of HA and HMA of bottom sediments of the lakes of the left bank of the Ob river

Type of bottom sediment	Sample	Weight loss, %			Z	Q, kJ/kg	max t, °C of thermal effect	HA ash content, %
		Up to 150 °C	150-400 °C	400-700 °C				
Siltstone sands	L-7 HA	0.00	21.51	36.44	0.59	13.198	465.9	42.05
	L-7 HMA	0.00	43.80	50.14	0.87	21.539	497.0	6.06
	Baibalak-2 HA	0.00	27.74	40.78	0.68	15.296	451.3	31.48
	Baibalak-2 HMA	0.00	43.82	46.44	0.94	20.957	436.5	9.74
Low sapropel	L-6 HA	0.00	22.67	54.76	0.41	20.860	467.6	22.57
	L-6 HMA	0.00	39.67	43.00	0.92	19.879	417.8	17.33

siltstone sludge	Dorozhnoe HA	0.00	28.57	53.04	0.54	19.877	466.4	18.39
	Dorozhnoe HMA	0.00	41.95	50.28	0.83	21.563	453.6	7.77
	Baibalak-1 HA	0.00	22.90	42.46	0.54	16.763	417.2	34.64
	Baibalak-1 HMA	0.00	35.52	60.66	0.59	23.450	474.7	3.82
	Lesnoe HA	0.00	21.91	45.08	0.49	15.717	442.2	33,01
	Lesnoe HMA	0.00	42.49	52.14	0.81	21.373	444.5	5.37
Clay sapropel sludge	L-4 HA	0.00	20.74	53.55	0.39	17.676	454.7	25.71
	L-4 HMA	0.00	44.91	43.90	1.02	19.011	418.1	11.19
	L-1 HA	0.00	23.83	57.72	0.41	21.194	448.6	18.45
	L-1 HMA	0.00	45.33	47.52	0.95	23.183	504.1	7.15
Sapropel clayed sludge	L-8 HA	0.00	27.32	59.14	0.46	23.684	468.4	13.54
	L-8 HMA	0.00	41.70	51.52	0.81	22.487	497.8	6.78
Sapropels	L-9 HA	0.00	28.17	57.33	0.49	19.561	439.1	14.50
	L-9 HMA	0.00	46.17	45.67	1.01	20.917	448.6	8.16

The low-to-high temperature mass loss ratio (the “periphery” / “core” ratio - Z coefficient) for HA and HMA samples of bottom sediments of lakes of the right bank of the Ob river varies from 0.42 to 0.67 and from 0.42 to 0.96, respectively. We excluded three samples of HMA, i.e., Lili with a value of 0.95, Shkolnoe with a value of 0.95, and S-189 with a value of 0.96 (Figure 4). Z coefficient for HA and HMC samples of bottom sediments of lakes of the left bank of the Ob river varies from 0.39 to 0.68 and from 0.59 to 1.02, respectively. Z coefficients of the HMA of the bottom sediments of the lakes of the left bank of the Ob River exceed Z coefficients for the corresponding HA (Figure 5).

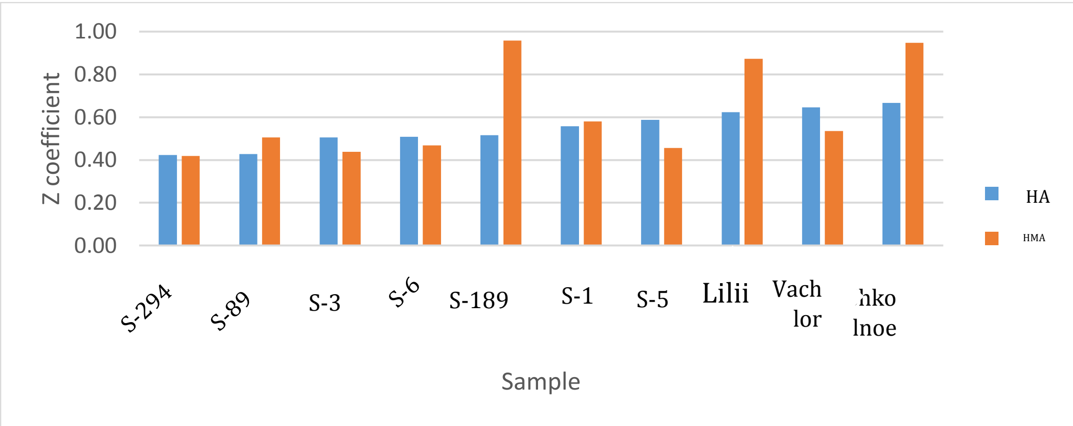


FIGURE 4 Diagram of Z coefficient of HA and HMA of bottom sediments of lakes of the right bank of the Ob River

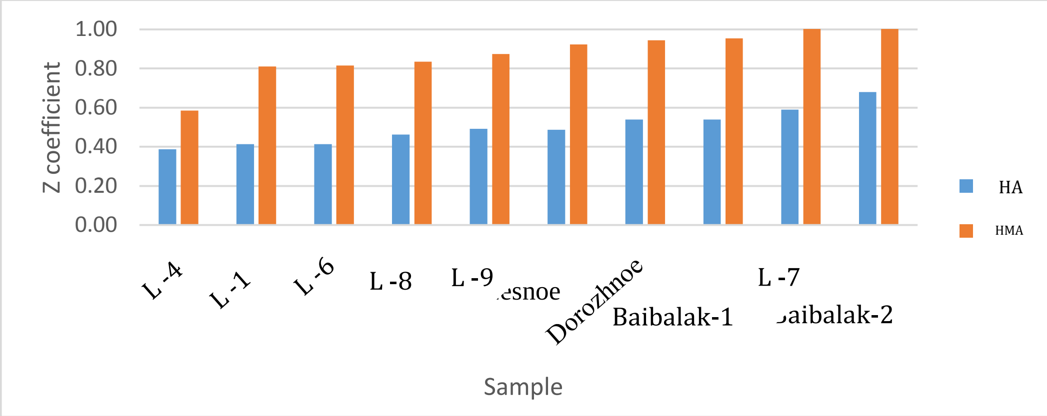


FIGURE 5 Diagram of Z coefficient of HA and HMA of bottom sediments of lakes of the left bank of the Ob river

Most of the samples of HA from the bottom sediments of the lakes of the right bank of the Ob River have Z coefficients close to the corresponding HMA values. Their weight loss in the high-temperature region is two times greater than that in the low-temperature area. Thus, the weight of the aromatic part is approximately twice as large as the weight of the aliphatic "periphery". These HA and HMA are similar in the structure of macromolecules. The exceptions are the samples of lakes S-189, Liliii, and Shkolnoe. For these samples, Z coefficients of the HMA significantly exceed Z coefficients of the corresponding HA. HA of these three samples has Z coefficients close to the values of other HA. For HMA, the weight loss in the high-temperature region is close to the low-temperature one, which indicates a close quantitative ratio of the aromatic part and the aliphatic “periphery”. These HMA have a different structure of macromolecules from other HMA of bottom sediments of lakes of the right bank of the Ob River.

For HA and HMA samples of bottom sediments of the lakes of the Ob River's left bank, a comparison of the corresponding Z coefficients gives a result different from the samples from the lakes of the right bank of the Ob River. HAs of bottom sediments of the lakes of the left bank have Z coefficients close to the values of other HAs. However, all HMA samples of bottom sediments of the lakes of the left bank are characterized by significantly higher values of Z coefficients than for the corresponding HAs. The most negligible differences in the structure of HA and HMA macromolecules are observed in the L-4 sample. For the rest of HMA, the weight loss in the high-temperature region is close to the low-temperature one, which indicates a close quantitative ratio of the aromatic part and the aliphatic “periphery”. In terms of the arrangement of macromolecules, the HMA samples of bottom sediments of the lakes of the left bank of the Ob River, excluding L-4, are similar to HMA samples from lakes S-189, Lili, and Shkolnoe. The studies of thermal analysis are in line with our previous studies on spectral characteristics [9].

The ash content in the studied HAs depends on the mineralization of the original bottom sediments. HAs of silt sands and sapropel-clayey silts have the highest ash content. HAs contain more Ash than HMA. As shown in Figure (6), the specific calorific value of HA and HMA depends on the ash content in the sample. R^2 is the Probability of correlation.

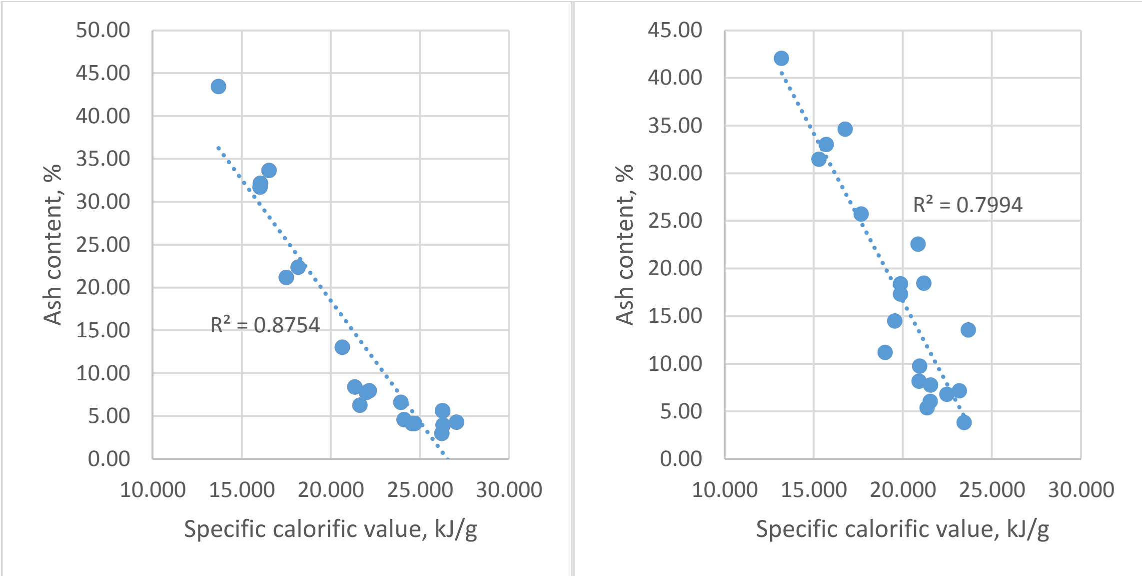


FIGURE 6 HA and HMA specific calorific value to ash content curve (on the left - samples of lakes of the right bank, on the right - samples of lakes of the left bank of the Ob river)

Conclusion

1. Humic and Hymatomelanic acids of sapropel lakes of the right and left banks of the Ob river have thermograms characteristic of humic acids, with a weight loss in the low-temperature and high-temperature regions.
2. The low-to-high temperature weight loss ratios (Z coefficients) are close for all samples of humic acids and lie in the range from 0.39 to 0.68. Z coefficients of HMA of bottom sediments of the lakes of the right bank of the Ob river, excluding samples from S-189, Lilii, Shkolnoe, and HMA of bottom sediments of lake L-4 of the left bank of the Ob River, are within the HA limits. The HMA Z coefficients of bottom sediments of the lakes of the left bank of the Ob river, excluding L-4, and HMA of bottom sediments from lakes S-189, Lili, and Shkolnoye of the right bank of the Ob river are significantly higher than those of HA and other HMA, which indicates a higher content of the aliphatic component in their macromolecules.
3. Humic acids have one peak in the high-temperature region on the thermograms; their thermal destruction in this region proceeds in one reaction. Hymatomelanic acids have two peaks; their thermal destruction proceeds in two reactions.
4. The ash content of the studied humic acids depends on the mineralization of the original bottom sediments. Humic acids extracted from silt sands have the highest ash content. Humic acids extracted from sapropelic-clayed silts have a high ash content. Hymatomelanic acids have a low ash content. The mineralization of the original bottom sediments does not affect the ash content of Hymatomelanic acids.

Acknowledgments

This research was financially supported by the Russian Foundation for Basic Research and the Government of the Khanty-Mansi Autonomous Okrug - Yugra (project no. 18-44-860010).

Orcid:

Mikhail Petrovich Sartakov:
https://orcid.org/0000-0002-3331-081X
Natalia Valeryevna Shpynova:
https://orcid.org/0000-0002-7992-0189
Evgeny Mikhailovich Osnitsky:
https://orcid.org/0000-0003-1571-2118

Olga Alexandrovna Gurova:
https://orcid.org/0000-0001-8502-1553
Diana Ivanovna Tsvettsykh:
https://orcid.org/0000-0003-4855-1138
Igor Disanovich Komissarov:
https://orcid.org/0000-0001-9641-7940

References

[1] S.L. Khil'ko, M.I. Rogatko, R.A. Makarova, R.G. Semenova, *Colloid J.*, **2019**, *81*, 779-89. [crossref], [Google Scholar], [Publisher]

[2] L.V. Perelomov, B. Sarkar, O.I. Sizova, K.B. Chilachava, A.Y. Shvikin, I.V. Perelomova, Y.M. Atroshchenko, *Ecotoxicol. Environ. Saf.*, **2018**, *151*, 178-183. [crossref], [Google Scholar], [Publisher]

[3] Z.K. Kairbekov, I.M. Jeldybayeva, K.O. Kishibaev, D.Z. Abilmazhinova, Z.A. Baimolda, *Chemical Journal of Kazakhstan*, **2019**, *3*, 200-206. [Pdf], [Google Scholar], [Publisher]

[4] J. Ziemska, M. Mazańska, T. Szynal, J. Solecka, Rocz. Panstw. Zakl. Hig., **2020**, *71*, 363-70. [crossref], [Google Scholar], [Publisher]

[5] Y.V. Zhernov, A.I. Konstantinov, A. Zherebker, E. Nikolaev, A. Orlov, M.I. Savinykh, G.V. Kornilaeva, E.V. Karamov, I.V. *Environ. Res.*, **2021**, *193*, 110312. [crossref], [Google Scholar], [Publisher]

[6] A. Zherebker, E. Shirshin, O. Kharybin, Y. Kostyukevich, A. Kononikhin, A.I. Konstantinov, D. Volkov, V.A. Roznyatovsky, Y.K. Grishin, I.V. Perminova, E. Nikolaev, *J. J. Agric. Food Chem.*, **2018**, *66*, 12179-12187. [crossref], [Google Scholar], [Publisher]

[7] A.V. Zashikhin, M.L. Sviridova, *J. Min. Sci.*, **2019**, *55*, 652-657. [crossref], [Google Scholar], [Publisher]

[8] M.G. Chernysheva, G.A. Badun, N.A. Kulikova, I.V. Perminova, *Chemosphere*, **2020**, *238*, 124646. [crossref], [Google Scholar], [Publisher]

[9] M. Sirotiak, A. Pastierová, L. Blinová, *Research Papers Faculty of Materials Science and Technology Slovak University of Technology*, **2021**, *29*, 131-142. [crossref], [Google Scholar], [Publisher]

[10] E.M. Osnitsky, O.A. Gurova, D.V. Boroduy, N.V. Litvinenko, I.V. Grekhova, *J. Comput. Theor. Nanosci.*, **2019**, *16*, 4601-4604. [crossref], [Google Scholar], [Publisher]

[11] A. Klavina, A. Auce, I. Pavlovska, I. Vanadzins, Freshwater Sapropel: Biologically Active Components and Methods of Extraction, *Proceedings of CBU in Natural Sciences and ICT*, **2020**, *1*, 37-46. [crossref], [Google Scholar], [Publisher]

[12] D. Łomińska-Płatek, A.M. Anielak, The comparison of fulvic acids extracted from the primary and secondary effluent, *InE3S Web of Conferences*, **2018**, *44*, 00099. [crossref], [Google Scholar], [Publisher]

How to cite this article: Mikhail Petrovich Sartakov*, Natalia Valeryevna Shpynova, Evgeny Mikhailovich Osnitsky, Olga Alexandrovna Gurova, Diana Ivanovna Tsvettsykh, Igor Disanovich Komissarov. Thermal characteristics of humic and hymatomelanic acids of lake sapropels of the ob river right and left banks. *Eurasian Chemical Communications*, 2021, 3(12), 900-908. **Link:** http://www.echemcom.com/article_139523.html