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INVESTIGATION OF THE PROPERTY OF HUMIC ACIDS BY THERMAL ANALYSIS METHOD

BADANIE WŁAŚCIWOŚCI KWASÓW HUMINOWYCH METODĄ ANALIZY TERMICZNEJ

Abstract: The aim of the work was an assessment of the possibilities of using the thermal analysis method in the identification of humic acids. Thermal analysis (TG/DTA) were subjected humic acids extracted from the Belchatów lignite deposit, using the following extraction solutions: 01 M KOH, 0.1 M NaOH and 0.1 M $Na_4P_2O_7$. For comparison, analysis of humic acids purchased from Aldrich company was performed. Thermo-analytical methods determine in examined samples energy change and corresponding changes in mass. It allows to identify the composition of the samples related to the physico-chemical changes that occur during warming. These changes are being recorded on thermograms in the form of endo- and exothermic peaks.

Keywords: humic acids, alkaline extraction, thermal analysis

Introduction

Reserves of the lignite in Poland are counted in amount to 36.9 billion Mg. Main deposits of the lignite are in a Konin Basin, Turow Basin, Belchatow Basin and Sieniawia Lubuska Basin. The lignite is organic, sedimentary combustible rock (caustobiolith) which was formed as a result of the coalifications of plant material, mainly in the period of the Tertiary, exactly of Miocene. The process of the coalification of the plant material takes place in two stages: biochemical (peat, decomposition) and geochemical (diagenesis, metamorphosis). The lignite arises from peat diagenesis in the increased temperature and pressure, and next as a result of the metamorphism is transformed into a hard coal. Table 1 shows an exemplary analytical composition of lignite. Generally the lignite is composed of water, mineral matter and organic substance. In composition of organic matter are included following groups of components: humic acids, fulvic acids, hymatomelanic acids, humins, bitumen, lignin, cellulose. On account of physicochemical properties it is divided on: low coalification

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lignite (soft), including xsylite and earthy type and high coalification (hard) lignite – matte and shining type [1–3].

Table 1

Analytical composition of the lignite

Moisture	10–70 % mas.
Organic substance	25–89 %
Mineral substance	1–25 % mas.

The lower degree of the coalification of the lignite and its calorific value adversely affect on its quality as a fuel (heat of combustion) and its suitability for energy purposes. In the agriculture due to the high content of the humic substance successfully it can be used as a material for production of preparation improving soil quality and also as a component of mineral – organic fertilizers. Humic acids contained in the lignite are included also in the soil organic matter and are characterized by valuable properties of nutrients complexing thus it is appropriate to use them in agriculture, horticulture, arboriculture or gardening [4–7].

Applying mineral fertilizers we provide the necessary for plants development biogenic elements, so-called macroelements – N, P, K, Ca, Mg, S and microelements – Fe, Mn, Zn, Cu, B, Mo and Ni. If in the soil is not enought organic matter, especially macroelements will not be collected by plants and thus it could lead to water eutrophication. This phenomenon depends on the sorption and complexing properties of organic substance. In order to increase use of valuable fertilizer nutrients, while improving the protection of the environment, in the contemporary agriculture more frequently mineral-organic fertilizers instead of mineral fertilizers are used. This action is compatible with the principles of Sustainable Development, one of the acts, which fertilizer industry must obey in the European Union and with various programs and environmental management systems [8–16].

According to the principles of the Sustainable Development the objectives and effects of fertilization in the agriculture should be connected and balanced . From one side it is necessary to provide the food for the still rising number of the world population, on the other side it is sensible to use for this purpose widely understood environment. It should be taken into account, inter alia, utilization of fertilizer raw materials, the damage associated with the production and use of fertilizers as well as utilization of agricultural acreage [17–20].

Low coalification lignite, containing about 60–80 % of humic acids has a greatest importance in the agriculture. To isolate humic acids from the lignite it is subjected to the extraction. Quantity and quality of extracted humic acids depend on the origin of lignite (the kind of flora from which is originated and conditions – temperatures and pressures) and kind of the used extractant. During obtaining humic acids from the lignite occurs series of chemical and physiochemical processes, inter alia, oxidation, nitration, decomposition leading to release gas products (H_2O, CO_2) and depolymerization of macromolecules of the lignite organic substances [6–21].

Humic acids are polymer, amorphous, organic acids, built mainly of carbon, hydrogen and oxygen and small amount of sulphur and nitrogen. The construction basis of humic acids constitute aromatic ring (C_3-C_6) connected bridges, containing functional groups. For specific properties of humic acids which decide about their utilization in the agriculture, maunly include: exchange ability, hydrophilic, acid character and the ability to reversible chemical reactions. It is believed that above properties, humic acids owe their structure, exactly reactive functional groups, mainly – COOH and – OH [6, 9, 11, 13, 22]. Figure 1 shows a molecular structure of humic acids [23].

Table 2 shows the percentage content of major elements included in the humic acids and their potential connections [24].

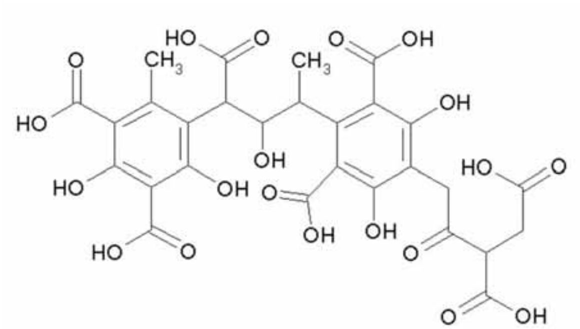

Fig. 1. Molecular structure of humic acids [23]

Table 2

The percentage of major elements included in the humic acids along with the connections they make [24]

Element	Content [% mas.]	Connection
Coal	56–70	– aliphatic chains, – ring-shaped connections – elements of functional groups (-OH, -COOH, >C=O and –OCH_3)
Hydrogen	3.3–6.2	
Oxygen	24–33	– heteroatom in the ring – in the form of bridges – elements of functional groups (-OH, -COOH, >C=O and –OCH_3)
Nitrogen	3	– heteroatom – amide groups
Sulphur	2	– heteroatom – group –SO_3H

Thermal analysis is an analytical technique which allows to determine the thermal effects (DTA) and mass losses (TG) of examined substances. DTG curve is the first derivative of TG curve and reflects the rate of sample mass change with change of temperature. This curve allows a more precise determination of examined value as a temperature function for the points characterizing the changes on the TG curve. These changes occur as a result of physical or chemical transformations and are dependent on the temperature. Method of thermal analysis in combination with mass spectrometry enables the identification of the substance composition. Differential thermal analysis (DTA) uses the energy changes state of the sample influenced by increasing temperature, and the results are visible on the thermogram as endo- and exothermic peaks. Humic substances, after introduction into the soil, undergo many transformations, from which oxidation is most significant. These processes can be analyzed by using the derivatograph [25–30].

Materials and methods

The aim of the study was to evaluate the possibilities of application of thermal analysis to the study of humic acids extracted from Polish lignite deposit. In the research humic acids obtained from Belchatow lignite deposits were used. They were extracted by 0.1M aqueous solution of NaOH, 0.1M aqueous solution of KOH and 0.1M aqueous solution of $Na_4P_2O_7$, where ratio of lignite to aqueous solution was 1:10. Granulation of the lignite was 0.5 mm. Thermal analysis was performed by using derivatograph Netzsch STA 449 F3. Samples were being warmed from temperature 35 ^{o}C to 800 ^{o}C in the small container from Al_2O_3, in the dynamic way, where the temperature increase was 5 ^{o}C/min. Measurements were carried out in air atmosphere, whose flow rate was 30 cm^3/min. Samples were analyzed with mass of about 50 to 90 mg. In order to compare the humic acid extracted from Belchatow lignite deposit, thermal analysis under the same conditions commercial humic acids from Aldrich company were subjected.

Results and discussion

Figure 2 shows the TG and DTA curves for Aldrich humic acids. Similarly, Fig. 3–5 show the TG and DTA curves of humic acids extracted from Belchatow lignite by using 0.1 M NaOH, 0.1 M KOH and 0.1 M $Na_4P_2O_7$.

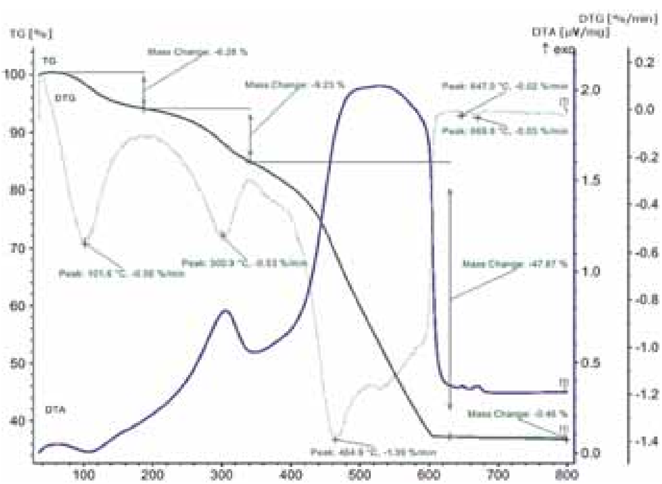

Fig. 2. TG/DTA curves of Aldrich humic acids

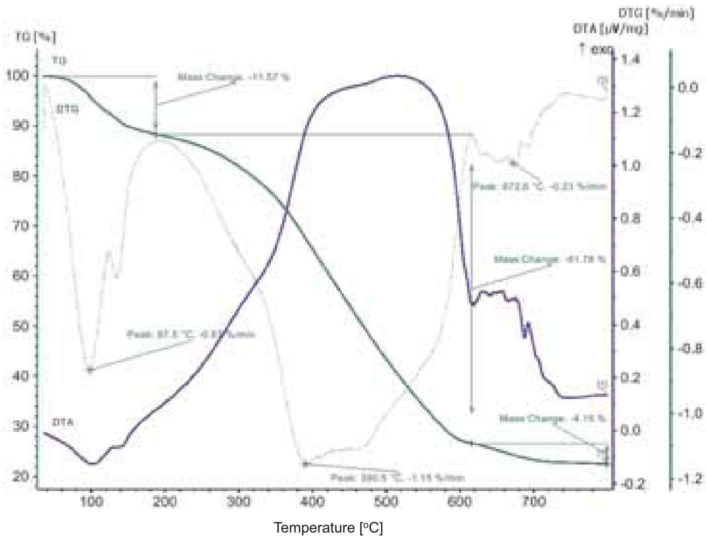

Fig. 3. TG/DTA curves of humic acids extracted from lignite Belchatow with 0.1 M NaOH

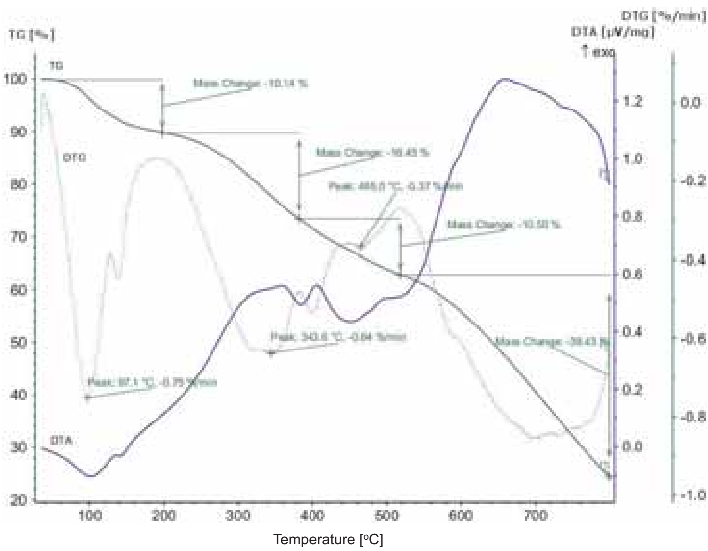

Fig. 4. TG/DTA curves of humic acids extracted from lignite Belchatow with 0.1 M KOH

Thermal analysis of examined samples allows to observe characteristic temperatures of their decomposition, correlated with physical and chemical changes whom are undergone during the measurement. TG and DTG curves enable to estimate mass changes of examined substance during a linear temperature increase. The DTA curve registers the temperature difference between the tested sample and the sample thermally

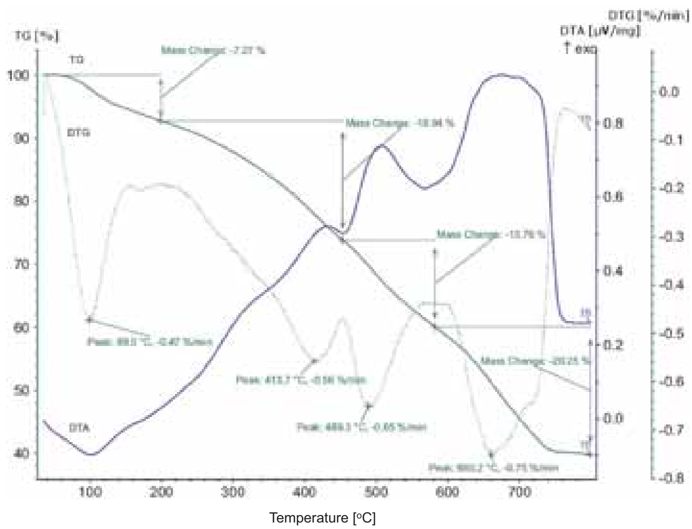

Fig. 5. TG/DTA curves of humic acids extracted from lignite Belchatow with 0.1 M $Na_4P_2O_7$

neutral and in combination with thermogravimetry allows to connect the individual thermal effect with the corresponding transformations, reactions. Table 3 presents the collected results of analysis.

Table 3

The results of thermal analysis (effects of endo- and exothermic) Aldrich humic acids and humic acids extracted from lignite from Belchatow deposit

Sample	Maximum temperature of the disintegration [°C]	Temperature range [°C]	Weight loss [% mas.]	Residue after the process [% mas.]
KH from Aldrich company	101.6	40–180	6.28	36.36
	300.9	180–340	9.23	
	464.9	340–625	47.67	
	669.8	625–800	0.46	
KH Bel. – KOH	97.1	40–200	10.14	24.48
	343.6	200–380	16.45	
	465.0	380–520	10.50	
	620–780	520–800	38.43	
KH Bel. – NaOH	97.5	40–180	11.57	22.50
	390.5	180–605	61.78	
	672.6	605–800	4.15	
KH Bel. – $Na_4P_2O_7$	99.0	40–200	7.27	39.81
	413.7	200–450	18.94	
	489.3	450–580	13.76	
	660.2	580–800	20.25	

The first, endothermic peak occurs both in a sample of humic acids commercial (Aldrich) and those obtained from lignite. This peak occurs near 100 ^{o}C and is associated with moisture loss (dehydration). A small shifts of the peaks due to the fact that water is characterized by varying a different degrees of binding. Above this temperature, followed by degradation of organic matter, which is accompanied by exothermic effect. Transformations between 200–400 ^{o}C are most likely the result of combustion of polysaccharides, degradation of functional groups and phenolic compounds. This conversion is clearly visible on the graph of commercial humic acid (Aldrich). However on the graphs of tested humic acids, obtained in laboratory conditions from lignite using alkaline extraction method significant change are not observed. The loss of mass in this temperature range varies from 9.23 % for commercial humic acids to 61.78 % for humic acids extracted with NaOH. Humic acids extracted with KOH and $Na_4P_2O_7$ have a similar value of the mass loss for temperature range (about 20 %).

The next exothermic peaks is visible in the range of temperature 400–600 ^{o}C and it is associated with the burning of aromatic structures (alkyl aromatic compounds), of polyphenols, decomposition of C-C bonds. In case of Aldrich humic acids, this temperature corresponds the largest weight loss – 47.67 %. That means that the acids contain most of all thermally stable compounds. Humic acids extracted with KOH and $Na_4P_2O_7$ have again a similar value of the mass loss for this range of temperatures – about 10 %. In case of humic acids extracted with NaOH there is a lack of clear boundaries between these ranges of temperatures. On the shown thermogram there is only one large exothermic peak in the temperature range between 180–605 ^{o}C, accompanied by 61.78 % weight loss. This effect is not observed in the case of humic acids purchased from Aldrich company.

The last exothermic effect occurs at the temperatures above 600 ^{o}C and it is probably associated with high-temperature policondensation reactions, depolymerization, pyrolysis. This effect is mainly observed for humic acids extracted in laboratory conditions. The thermogram in Fig. 4 shows that the process at 800 ^{o}C has not yet ended, moreover, precisely in this temperature range 550–650 ^{o}C there is the greatest loss of weight.

Summary

Thermal analysis methods allow to obtain quantitative and qualitative data of the investigated substances. DTA method is useful in the investigation of structural changes occurring during heating of the sample. TG and the first derivative of TG-DTG allow to quantitatively characterize the mass loss of substances. The analysis of obtained derivatograms show that the composition of humic acids obtained in the laboratory condition by alkaline extraction method is variable and depends on the used extractant – extracted humic acids have variable chemical composition and structure.

In conclusion, the use of thermal analysis to the physicochemical characteristics of humic acids is useful and can provide a basis for further research on the possibilities of its application.

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BADANIE WŁAŚCIWOŚCI KWASÓW HUMINOWYCH METODĄ ANALIZY TERMICZNEJ

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Abstrakt: Celem pracy była ocena możliwości wykorzystania metody analizy termicznej w identyfikacji kwasów huminowych. Analizie termicznej (TG/DTA) poddano kwasy huminowe ekstrahowane z bełchatowskiego złoża węgla brunatnego, przy użyciu 0,1 M KOH, 0,1 M NaOH i 0,1 M $Na_4P_2O_7$. Dla porównania wykonano analizę odczynnikowych kwasów huminowych firmy Aldrich. Metody termoanalityczne określają zamiany energetyczne i odpowiadające im zmiany masowe. Pozwala to na identyfikację składu badanych próbek związanych z przemianami fizykochemicznymi zachodzącymi podczas ogrzewania. Zmiany te rejestrowane są na termogramach w postaci pików endo- i egzotermicznych.

Słowa kluczowe: kwasy huminowe, ekstrakcja alkaliczna, analiza termiczna