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# THE STUDY OF INFLUENCE OF METAL IONS ON THERMAL DECOMPOSITION OF HUMIC ACIDS

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## Abstract

Investigations of the influence of the following metal ions: Ca, Mg, Ba, Cr, Mn, Co, Ni, Fe(II), Fe(III), Cu, Zn, Cd, Pb, Hg, Al and Ag on thermal decomposition of humic acids were carried out. Metal-humic compounds were obtained by ion exchange method and by complexing of metal cations on humic acids. For the investigations of thermal decomposition TG and DTA were used. Presence of metal ions in structure of humic acids mostly increases intensity of their thermal decomposition particularly the Hg and Cu ions. They shift this process to lower temperatures 100–300°C. Mass loss of organic matter in this temperature range in humic-mercury compounds are higher by more than 35%, and in humic-copper compounds are higher by more than 20% compared with the mass loss of humic acids itself. Ni and Co ions also increase the intensity of thermal decomposition of humic acids, but Ca, Ba and Mg ions inhibit that process.

**Keywords:** brown coal, humic acids, metal ions, thermal analysis

## Introduction

Brown coals with metal ions are used as catalysts in coal conversion processes, such as gasification, liquefaction or pyrolysis [1]. Many works were focused on investigation of catalytic influence of different metal ions on coal gasification process, and, first of all of calcium, sodium and potassium ions [2–4]. Metal ions introduced to coal wih ion exchange method were characterized by high catalytic activity due to their high dispersion level. The catalytic activity of metals in gasification process of coals with steam increased in the series Mg<Fe<Ca<K<Na.

Presence of such metals as: Ba, Mg and Ca in the coal structure had no influence on the quantity of evolved gas amount during thermal decomposition of brown coal but influenced on contents of individual gas components, i.e. $CO_2$, CO and $H_2O$. Mg ion caused increase of $CO_2$ fraction in the gas, but Ba ion increased CO fraction. Cations of the above mentioned metals did not affect yield of char [5–7].

According to Otake and Walker [8] presence of cations of such metals as: Na, K, Mg, Ca and Ba caused also considerable changes in the composition of gas derived

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from lignite pyrolisis, increasing $CO_2$ and $H_2$ contents in it. Those cations catalyzed lignite gasification process with steam and carbon dioxide.

According to other authors [9] cations of metals such as: Na, Ba and Ni introduced to brown coal with ion exchange and impregnation method affected its pyrolysis in a different way. Nickel enhanced decomposition of oxygen groups, and calcium inhibited that process. Quantity and quality of products of coal thermal decomposition were also affected by secondary reactions catalyzed by metals.

According to Tyler and Schafer [10] removal of metal cations by coal demineralization by means of acids caused considerable increase in yield of coal pyrolysis products, i.e. tar and gases. But the addition of Ca ion to the demineralized coal decreased both tar and volatile products yields in coal pyrolysis. The same phenomenon occurred in investigations carried out by Wornat and Nelson [11]. The addition of Ca ion to the coal caused decrease in tar yield and decrease in the amount of aromatic compounds in the tar as well as of oxygen groups: hydroxyl, carbonyl and etheric groups.

Our work aimed at investigating the influence of selected metal ions on thermal decomposition process of humic acids from brown coal.

## Experimental

Humic acids separated from demineralized earthy brown coal from Bełchatów mine were used.

The humic acids – a basic group component of earthy brown coal were obtained with coal extraction method by means of 3% NaOH solution at temperature of about 90°C with mass ratio of coal to NaOH solution 1:20. The alkaline extract was separated from residual coal by centrifugation and treated with concentrated hydrochloric acid to precipitate the humic acids. The precipitate was washed with distilled water to remove chloride ions, dried and disintegrated. The humic acids obtained in such a manner were subjected to demineralization process with 10% hydrochloric acid at boiling point. The chemical characteristics of demineralized humic acids are as follows: $A^d$ – 0.2%, $C^{daf}$ – 65.2%, $H^{daf}$ – 4.4%, $N^{daf}$ – 0.8%, $S^{daf}$ – 0.3%, $O^{daf}$ – 29.3%.

Two methods of introduction of metal ions to humic acids were used.The first one consisted in ion exchange reaction between metal ions and carboxyl groups of humic acids. The other method consisted in complexing of metal ions by humic acids in alkaline medium.

The ion exchange reaction on humic acids was carried out in a way consisting in repeated shaking of their suspensions with 0.2 M solution of investigated metal salt until pH of solution is balanced with the pH value of the initial solution. After washing of humic acids from salt excess, they were dried at temperature of about 80°C. In that way ionic metal-humic compounds were obtained, which were marked with IH–Me symbol. In those compounds metal ions are bonded with carboxyl groups of humic acids by means of ionic bonds [12].

According to references humic acids show ability to form complex with metal ions in alkaline medium [13], in which both carboxyl groups and OH phenolic groups of humic acids react with metal ions. Therefore, humic acids separated from brown coal were dissolved in 5% NaOH solution. Saturated solutions of salts of individual metals were added to solution of sodium humates. The following salts were used: magnesium(II), calcium(II), zinc(II), lead(II), cobalt(II), nickel(II), manganese(II), copper(II) and cadmium(II) acetates; silver(I) and iron(III) nitrates; aluminium(III), iron(II), barium(II) and mercury(II) chlorides as well as chromium(III) sulfate. In those conditions metal-humic chelates in the form of gel precipitated from solution of sodium humates, which were then filtered, washed with distilled water from salt excess and dried at temperature of about 80°C. The metal-humic chelates obtained were marked with CH–Me symbol.

Contents of individual metal ions determined with atomic absorption spectrometry (AAS) in the metal-humic IH–Me and CH–Me compounds are shown in Table 1. It is visible from the Table that contents of metals in CH–Me compounds are about two times higher than in IH–Me compounds.

## Thermal analysis of metal-humic chelates and compounds

The thermal analysis, i.e. thermogravimetric and differential thermal analysis of compounds investigated were carried out on TG 7 and DTA 7 apparatus of Perkin Elmer Co. with flowing argon. Heating rate of samples in TG apparatus was 40°C $\mathrm{min}^{-1}$, and in DTA apparatus was 10°C $\mathrm{min}^{-1}$. Metal-humic compounds were dried up at temperature 105°C for DTA analysis.

### *TG curves of humic acids and metal-humic CH–Me chelates*

The total mass loss of humic acids in the temperature range 100–1000°C is 44.6%. Basic thermal decomposition of organic matter of humic acids takes place in the temperature range 100–500°C. Loss of their mass in that temperature range is high and is equal to 30.6%, while in the temperature range 500–1000°C is by more than half lower (14.0%).

The total mass loss were calculated from TG curves of metal-humic CH–Me chelates in the temperature range 100–1000°C oscillate in wide limits 24.9–52.8%, and exceptionally in CH–Hg chelate they even get 77.3%. The lowest mass losses (28.2 and 24.9%) are characterized by CH–Pb and CH–Ag chelates.

In the temperature range 100–500°C mass losses of the most of chelates investigated are included in the range 26.3–37.1%. Much lower mass losses in the above mentioned temperature range are shown by CH–Ag, CH–Pb, CH–Ba and CH–Ca (15.8–20.4%). But CH–Hg chelate is characterized by the highest mass loss (68.3%).

In the low temperature range 100–200°C TG curves of many chelates show much more mass loss comparing with humic acids, for which mass loss in that temperature range is 3.7%. This concerns, first of all, the following chelates: CH–Al (7.6%), CH–Ni (6.1%), CH–Mn (6.4%), CH–Cr (5.4%) and CH–Co (5.1%). Those mass losses are connected with hydration water evaporation, or with thermal decomposition of metal hydroxides, which could precipitate when metal-humic chelates were obtained in alkaline medium. Presence of great amount of hydration water in the above mentioned chelates are confirmed also by infra-red spectra, which are not included in this research work (another work is being prepared).

**Table 1** The influence of ion metals and temperature on the thermal decomposition of humic acids (calculated on organic matter)

| No | Sample | Metal contents/% | $\Delta m$/% | | | |
|---|---|---|---|---|---|---|
| | | | Temperature range/°C | | | |
| | | | 100–300 | 300–500 | 500–1000 | 100–1000 |
| 1 | CH–Hg | 28.9 | +35.4 | +1.0 | –1.4 | +23.4 |
| | IH–Hg | 14.6 | +32.3 | –6.7 | –2.7 | +22.6 |
| 2 | CH–Cd | 40.2 | +3.7 | +9.7 | +9.0 | +22.4 |
| | IH–Cd | 17.7 | +2.0 | –0.7 | +4.8 | +6.1 |
| 3 | CH–Zn | 18.2 | +5.6 | –4.3 | +15.0 | +16.3 |
| | IH–Zn | 11.0 | –0.3 | –0.5 | +2.4 | +1.6 |
| 4 | CH–Ni | 22.0 | +5.8 | +10.7 | +1.9 | +18.4 |
| | IH–Ni | 9.5 | +4.7 | +1.9 | +1.0 | +7.6 |
| 5 | CH–Co | 22.5 | +2.8 | +13.0 | +8.2 | +24.0 |
| | IH–Co | 11.0 | +1.7 | +2.9 | +3.0 | +7.6 |
| 6 | CH–Cr | 12.0 | +2.3 | +0.8 | +8.4 | +11.5 |
| | IH–Cr | 1.9 | +0.2 | –0.2 | +3.8 | +3.8 |
| 7 | CH–Pb | 51.2 | +8.4 | +2.8 | 0.0 | +11.1 |
| | IH–Pb | 39.0 | +5.7 | +0.6 | +1.7 | +8.0 |
| 8 | CH–Ba | 30.8 | –1.1 | –2.9 | +15.2 | +11.2 |
| | IH–Ba | 19.0 | +0.9 | –1.4 | +0.5 | 0.0 |
| 9 | CH–Ca | 15.8 | –1.2 | –8.6 | +21.5 | +11.7 |
| | IH–Ca | 7.3 | 0.0 | –1.8 | +5.2 | +3.4 |
| 10 | CH–Fe$^{2+}$ | 19.4 | +4.8 | –2.5 | +8.5 | +10.8 |
| | IH–Fe$^{2+}$ | 6.7 | +4.2 | –0.8 | +5.0 | +8.4 |
| 11 | CH–Fe$^{3+}$ | 15.2 | +4.8 | –0.6 | +8.5 | +12.7 |
| | IH–Fe$^{3+}$ | 6.8 | +5.2 | –2.6 | +5.4 | +8.0 |
| 12 | CH–Cu | 24.9 | +20.8 | –7.1 | –3.4 | +10.3 |
| | IH–Cu | 17.5 | +11.7 | –6.4 | +1.1 | +6.4 |
| 13 | CH–Mn | 25.3 | +4.1 | 0.0 | +13.7 | +17.8 |
| | IH–Mn | 9.2 | +0.6 | +0.2 | +1.0 | +1.8 |
| 14 | CH–Ag | 51.8 | +4.5 | –2.3 | +4.8 | +7.0 |
| | IH–Ag | 17.6 | +0.4 | –2.5 | +7.7 | +5.6 |
| 15 | CH–Al | 6.4 | +3.2 | –3.2 | +0.8 | +0.8 |
| | IH–Al | 2.6 | –0.3 | –2.1 | +2.4 | 0.0 |
| 16 | CH–Mg | 7.3 | +0.6 | –3.4 | +6.0 | +3.2 |
| | IH–Mg | 3.5 | +0.2 | –1.8 | +3.4 | +1.8 |

$\Delta m$ – difference between mass loss of metal-humic chelates (or metal-humic compounds) and mass loss of humic acids

In the temperature range 100–300°C the greatest mass loss is shown by CH–Hg and CH–Cu chelates (53.9 and 24.3%). Hydration water fraction in those samples is inconsiderable (this fact is confirmed by IR spectra). Therefore mass loss in those samples should be attributed to thermal decomposition of organic matter. In case of CH–Hg chelate high mass loss in the temperature range 100–300°C is caused by mercury sublimation. When taking into consideration amounts of evaporated mercury, mass loss in CH–Hg chelate is still high and is equal to 25.0%. Thus, Hg and Cu ions considerably accelerate decomposition of humic matter in metal-humic chelates.

In the higher temperature range 500–1000°C mass loss in many CH–Me chelates such as CH–Ba, CH–Ca, CH–Mg, CH–Zn, CH–Fe, CH–Mn, CH–Cr and CH–Co are higher comparing with mass loss in humic acids (14.0%) and change in the range 17.2–29.9%. The lowest mass loss (6.8–9.1%) are shown by the chelates CH–Pb, CH–Ag, CH–Cu and CH–Hg in the above mentioned temperature range.

### *TG curves of IH–Me metal-humic compounds*

The total mass loss in IH–Me ionic metal-humic compounds in the temperature range 100–1000°C change in the range 32.1–49.5%. Predominantly in IH–Me compounds mass losses are somewhat lower comparing with the total mass loss in humic acids (44.6%).

In general, all IH–Me compounds demonstrate higher mass loss in the temperature range 100–200°C comparing with humic acids, which is connected, first of all, with elimination of hydration water. The highest mass loss in the above mentioned temperature range is shown by IH–Me compounds, to which the following metal ions were introduced: Fe (6.9%), Ni (5.6%), Mg (4.8%), Co (4.5%) and Cr (4.5%).

Similarly to CH–Hg and CH–Cu chelates, IH–Hg and IH–Cu compounds are characterized by the highest mass loss (49.9 and 17.2% respectively) in the temperature range 100–300°C.

In the temperature range 100–500°C mass losses in IH–Me compounds are included in the range 22.5–33.6% and similarly as the total mass loss they are, in general, lower comparing with humic acids (30.6%).

In the higher temperature range 500–1000°C mass loss in IH–Me compounds change in the range 9.6–17.9%. The lowest mass losses which are 9.6, 9.9, 11.7 and 12.5% are demonstrated by IH–Pb, IH–Hg, IH–Ba and IH–Cu compounds. In the remaining IH–Me compounds mass losses in the above mentioned temperatures are predominantly somewhat higher concerning mass changes which take place in humic acids.

### *Discussion of thermogravimetric analysis results*

If mass losses in CH–Me and IH–Me metal-humic compounds appearing in TG curves are converted to organic matter, taking into account contents of individual metals in compounds investigated, the real influence of metal ions on thermal decomposition of humic matter becomes visible. In Table 1 differences between mass loss of humic matter in metal-humic compounds and mass loss in humic acids ($\Delta m$), in different temperature ranges are shown.

It is visible from Table 1 that in CH–Me chelates in the temperatue range 100–500°C in general all metal ions increase the process of thermal decomposition of humic matter to a higher or a lower degree. Ca, Ba and Mg ions, which inhibit that process, are exceptions.

Hg and Cu ions increase intensity of thermal decompositon of humic matter to a highest degree and even already at very low temperatures 100–300°C. Mass loss of organic matter in CH–Hg chelates is higher by more than 35% and in CH–Cu chelates by more than 20% comparing with the mass loss of humic acids. Ni and Co ions also affect the intensity of thermal decomposition of humic matter in CH–Me chelates to a high degree in the temperature range 100–500°C. The $\Delta m$ value for those chelates is 15–17% in the range.

In the temperature range 500–1000°C high $\Delta m$ values for CH–Ca, CH–Ba, CH–Zn and CH–Cd are involved in the intensification of thermal decompositon of humic matter to a lower degree, and are caused mainly with thermal dissociation of carbonates ($CaCO_3$ and $BaCO_3$) or with reduction of metal hydroxides or oxides to metals and evaporation of them (Zn and Cd).

If thermal decomposition of CH–Me chelates is complicated by the presence of metal hydroxides or oxides in their contents, as for IH–Me samples we could only talk about influence of metal ions on humic matter decomposition. However, because of more than two times lower contents of metal ions in IH–Me compounds their influence on thermal decomposition of humic matter is less distinct.

In the temperature range 100–500°C thermal decomposition of humic matter in IH–Me compounds is inhibited by ions of the following metals: Ca, Ba, Mg, Al, Zn and Ag, but the remaining metal ions increase intensity of thermal decomposition of humic matter.

The $\Delta m$ value for those samples is within 0.0–6.6%. The highest $\Delta m$=25.6% concerns IH–Hg compound.

In the temperature range 500–1000°C all metal ions in IH–Me compounds (excluding Hg ions) increase intensity of thermal decomposition of humic matter. The $\Delta m$ values for those compounds are within 1.0–7.7%.

Similarly to CH–Hg and CH–Cu chelates, Hg and Cu ions also increase the intensity of thermal decomposition of humic matter to the highest degree in IH–Hg and IH–Cu compounds, shifting the thermal decomposition to the low temperature range (100–300°C).

In IH–Me compounds only Ba and Al ions have a neutral influence on the course of thermal decomposition of humic matter in the whole temperature range 100–1000°C. The remaining metal ions increase the intensity of thermal decomposition of humic matter.

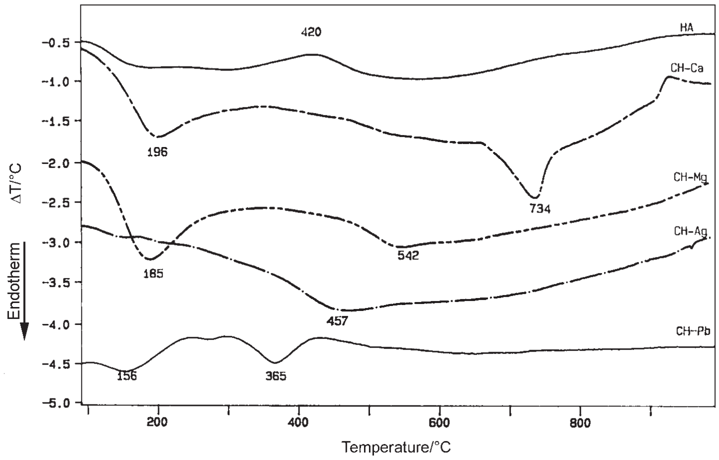


**Fig. 1** DTA curves of humic acids HA and metal-humic chelates: CH–Ca, CH–Mg, CH–Ag and CH–Pb

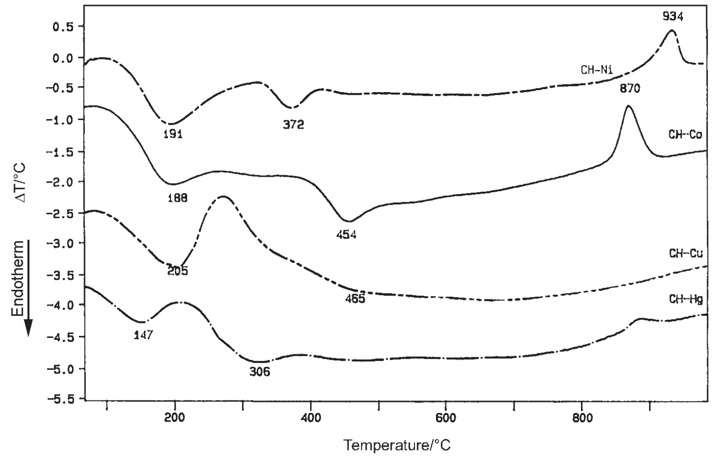


**Fig. 2** DTA curves of metal-humic chelates: CH–Ni, CH–Co, CH–Cu and CH–Hg

### *DTA curves of CH–Me chelates*

In general, DTA curves of CH–Me chelates in air dry conditions show two basic endothermic peaks: the first one is connected with evaporation of hygroscopic water, existing in the low temperature range and the second endothermic peak in the temperature range 450–650°C connected with thermal decomposition of humic matter of chelates. Instead, the thermal decomposition of humic acids (Fig.1) on DTA curves is accompanied by exothermic effect with its maximum at the temperature 420°C.

On DTA curves of CH–Me chelates in air-dried (at 20°C) conditions the endothermic peak connected with evaporation of hygroscopic water is in the temperature

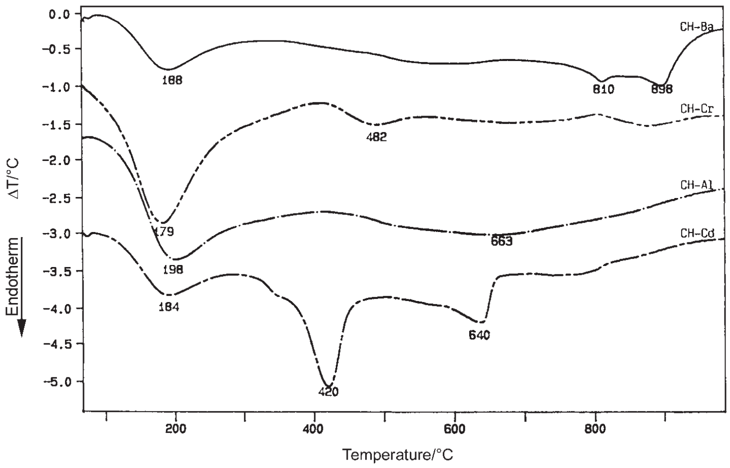


**Fig. 3** DTA curves of metal-humic chelates: CH–Ba, CH–Cr, CH–Al and CH–Cd

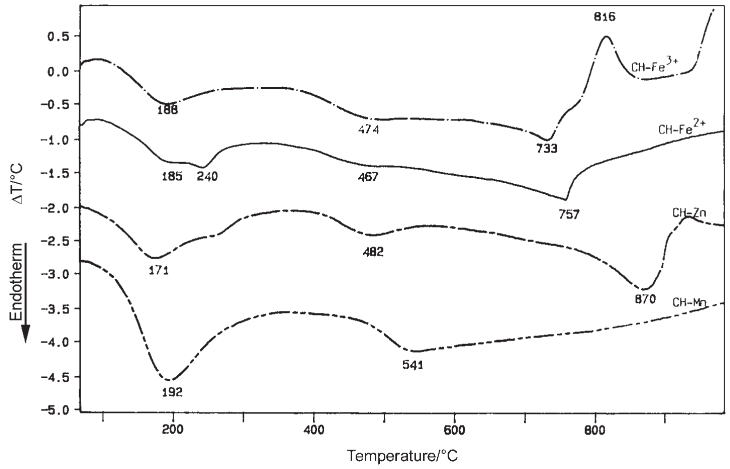


**Fig. 4** DTA curves of metal-humic chelates: CH–Fe$^{3+}$, CH–Fe$^{2+}$, CH–Zn and CH–Mn

range 119–184°C. In the figures enclosed (Figs 1–4), which show DTA curves of dried at 105°C, CH–Me chelates, at 105°C the endothermic peak is reduced almost twice and its minimum is shifted to higher temperature range 147–240°C, mainly 180–200°C. These peaks on DTA curves of dry CH–Me chelates are connected with elimination of hydration water, or with decomposition of hydroxides of some metals such as: Zn, Cr, Fe, Co, Mn.

Contrary to the thermal decomposition of humic acids, which takes place with exothermic effect with maximum at temperature 420°C, thermal decomposition of CH–Me chelates is accompanied by endothermic effects, occurring in the temperature range 450–650°C. Additionally, on DTA curves of the following chelates:

CH–Hg, CH–Pb, CH–Cd, CH–Ni, CH–Ca, CH–Ba, CH–Zn and CH–Fe there is a number of additional endothermic peaks both in lower temperature range (<500°C) and in higher temperature range (>500°C). In connection with courses of TG curves some of those endothermic effects could be attributed to the following thermochemical change. The high endothermic peak at temperature 734°C on CH–Ca chelate curves could be attributed to the thermal dissociation of calcium carbonate, which is a secondary product of thermal decomposition of CH–Ca chelate, created as a result of reaction of calcium ions with carbon dioxide (Fig. 1). A similar endothermic effect with minimum at temperatures 810 and 898°C, connected with thermal dissociation of barium carbonate is shown on DTA curves of CH–Ba chelate (Fig. 3).

A high endothermic peak existing on DTA curves of CH–Zn chelate with minimum at temperature 870°C, connected with high mass loss on TG curves is probably caused by zinc evaporation, which is created in reaction of zinc oxide reduction (Fig. 4).

Endothermic effects connected with melting of metals and/or with their evaporation are visible on DTA curves of the following chelates: CH–Cd (with minima at temperatures 420 and 640°C), CH–Pb (with minimum at temperature 365°C) and CH–Hg (with minimum at temperature 306°C).

Two endothermic peaks on DTA curves of CH–Fe(III) chelates with minima at temperatures 733 and 757°C respectively, which are accompanied by mass loss on TG curves, are probably caused by the reduction of ferric oxides. The ferric oxide $Fe_2O_3$ is reduced to oxides FeO and $Fe_3O_4$, and FeO oxide is subject to farther reduction to metal (Fig. 4).

On DTA curves of CH–Ni chelate endothermic peak with minimum at temperature 372°C is probably caused by the decomposition of nickel hydroxide (Fig. 2).

In high temperature range on DTA curves of some chelates there are rather big exothermic effects. These are peaks on DTA curves of the following chelates: CH–Co (870°), CH–Ni (934°C), CH–Fe(III) (816°C), CH–Cr (788°C) and CH–Hg (885°C). Peaks of such types do not occur on DTA curves of IH–Me compounds, therefore presence of such peaks may be involved in precipitation of metal hydroxides in course of preparation of CH–Me chelates and thermal change of those compounds.

### *DTA curves of metal humic IH–Me compounds*

On DTA curves of dry compounds endothermic peaks connected with elimination of hydration water occur in the temperature range 147–250°C, most frequently in the range 180–190°C.

On some DTA curves of IH–Me compounds, particularly of those compounds which include small amounts of metals in their compositions, an exothermic peak occurs with its maximum at temperature of about 400°C. The exothermic peak passes to an endothermic peak with its minimum in the temperature range 475–590°C. Sometimes the endothermic peak minimum stretches to higher temperatures of above 600°C (compounds: IH–Ba, IH–Cd, IH–Co, IH–Fe and IH–Mg).

In the low temperature range 200–300°C on DTA curves of IH–Hg and IH–Cu compounds there are high exothermic peaks with maxima at temperatures 210 and 298°C. The first of those peaks on DTA curves of IH–Hg sample passes to an endothermic effect with minimum at temperature of 305°C. However, on DTA curve of IH–Cu compound there are two endothermic peaks at temperatures 322 and 470°C and exothermic peak with maximum at temperature of 410°C.

Additional endothermic peaks in the higher temperature range (500–1000°C) occur only on DTA curves of IH–Zn sample (928°C), and in the low temperature range on DTA curves of IH–Pb sample (383°C). In the first case it is caused by the evaporation of metal zinc and in the second case it is caused by melting of metal lead.

## Discussion of results and conclusions

Results of thermal analysis of metal-humic compounds confirm a different mechanism of their thermal decomposition comparing with thermal destruction of humic acids themselves.

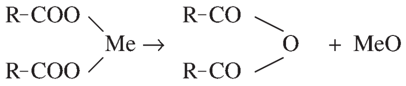
An essential stage of thermal destruction of humic acids is involved in splitting of peripheral components of humic structure, i.e. aliphatic arrangements and oxygen functional groups. This stage is in the temperature range 100–500°C. In that temperature range highest mass loss in humic acids take place –30.6%, which is about 75% of the whole mass loss. On DTA curves at temperature of about 400°C there is an exothermic peak, which most probably is connected with the condensation process of aromatic structures [14]. In the next stage of thermal destruction of humic acids (500–1000°C) mass losses are much lower (14.0%) and on DTA curves no considerable thermal effects occur.

Presence of metal ions in humic acid structure causes changes in the course of both TG curves and DTA curves. Those changes are more visible on thermal analysis curves of CH–Me chelates, containing more than twice amount of metal ions comparing with IH–Me compounds.

On DTA curves of ionic IH–Me metal humic compounds in the temperature range 100–500°C two thermal effects could be observed: weak exothermic effect with maximum at temperature of about 400°C, which passes into an endothermic effect with minimum in the temperature range 450–650°C, but on DTA curves of CH–Me chelates there is only an endothermic peak with its minimum in the temperature range 450–550°C.

In the higher temperature range 500–1000°C on DTA curves of some CH–Me chelates there is a number of endothermic peaks, which indicate a possibility that metal oxides could be created during the process of thermal decomposition of the chelates. Some of those oxides react with products of thermal decomposition of humic matter such as: $CO_2$, CO and C. As a result of those reactions carbonates are created (CH–Ca and CH–Ba chelates), reduction of metal oxide to metal (CH–Zn, CH–Cd, CH–Fe and CH–Pb chelates) and metal evaporation (CH–Zn, CH–Cd and CH–Hg) could take place.

Results of thermal analysis show that there is a high probability of thermal decomposition mechanism of metal humic compounds, which is similar to thermal dissociation of oxy-acids' salts, through the formation of metal oxides and acid anhydrides:



$$\begin{matrix} \text{R–COO} \diagdown & & \text{R–CO} \diagdown & & \\ & \text{Me} \rightarrow & & \text{O} & + \text{MeO} \\ \text{R–COO} \diagup & & \text{R–CO} \diagup & & \end{matrix}$$

In general, all metal ions increase the intensity of thermal decomposition of humic matter more or less proportionally to their contents in metal humic compounds. To metal ions which most of all accelerate thermal destruction process of humic matter in the temperature range 100–500°C belong Hg and Cu ions and next Ni and Co ions.

Hg and Cu ions shift thermal decomposition process of humic matter to the low temperature range 100–300°C. Mass loss in that temperature range in CH–Hg and IH–Hg compounds are more than 35% higher and in CH–Cu more than 20% higher comparing with mass loss of humic acids.

Ca, Ba and Mg ions belong to a small group of metal ions which inhibit humic matter decomposition in the temperature range 100–500°C.

In the higher temperature range 500–1000°C mostly all metal ions investigated (except Cu and Hg ions) increase intensity of thermal decomposition of humic matter.

DTA curves of CH–Me and IH–Me metal humic compounds confirm the presence of considerable amount of hydration water in both types of compounds and metal hydroxides in some CH–Me chelates. The hydration water is removed in the temperature range 100–200°C. Metal hydroxides, undergoing thermochemical processes exert an influence on a different course of thermal analysis curves of CH–Me chelates, especially at higher temperatures of the thermal decomposition process (500–1000°C).

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