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SIMULTANEOUS TG-DTG-DTA-EGA ANALYSIS FOR STUDIES OF KEROGEN

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ABSTRACT

The aim of this work was to study some properties of kerogen by simultaneous thermal analysis. This substance is of importance for oil prospecting in geology. Clay rock specimens of different origin containing kerogen as well as kerogen extracted from the specimens were used for studies by means of a vacuum thermoanalyser (Mettler) equipped with a mass spectrometer (Balzers). The obtained curves of TG, DTG, DTA and EGA for carbon and jurassic samples taken from various depths were very complex but it was possible to find some directional relationships along the depths of the deposit. The results obtained show that it is possible by using those methods to arrive at some conclusions about origin of the specimens as well as about the degree of transformation of kerogen.

INTRODUCTION

Studies of kerogen, an organic substance, are of great importance for oil prospecting. The substance involves formation of oil hydrocarbons. Processes occurring in organic and clay components of deposit rocks are directly connected [1,2]. Catalytic action of clay minerals results in a stepwise transformation of organic substance in deposits into oil hydrocarbons.

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This work is aimed to apply the simultaneous thermal analysis TG-DTG-DTA and EGA to study clay rock specimens of different origin containing kerogen as well as kerogen of different grade of diagenesis.

EXPERIMENTAL

The studies were performed by means of a vacuum thermoanalyser TA-1 (Mettler) equipped with a quadrupole mass spectrometer QMG-101 (Balzers). This apparatus permits simultaneous registration of the following curves : TG,DTG,DTA,EGA,T and P [3].

The following clay rock specimens from Polish deposits [2] , representing different deposits of the carboniferous period : C-1_1, C-1_2, C-1_3 (3000 m deposit depth), C-2 (2000), C-3 (1000 m), the upper Jura period : J-1, the middle Jura period : J-2, the lower Jura period J-3_1, J-3_2 as well as of the extracted kerogen : K-1, K-2, K-3 were studied. The preliminary chemical as well as transmission electron microscopy analyses of clay rock specimens taken for studies indicate the presence of the kerogen substance of carbon type. The obtained electron pictures of the produced kerogen are very like those published in [4] .

All analyses TG-DTG-DTA-EGA were done at 10^{-5} Tr within the temperature limit 298-1273 K with the heating rate 6^{o}/min (thermocouple Pt-Pt Rh 10 %) using identical weighed portions of the same granulation. The samples were heated in Pt crucibles. Mass spectra were registered at the analysis rate of 1M/s, for the mass range of 1-100 M/e. In addition the studies of kerogen specimens were made with TG-DTG-DTA at the air atmosphere.

RESULTS

The first series of studies was performed with the carboniferous deposit specimens. All the obtained TG-DTG-DTA curves indicate a complex character of the studied processes with some distinct effects appearing within 500-1000 K temperature range. It was found that the deeper the deposit the lower the temperature of the effects on the curves as well as the higher the weight loss of specimen observed. For the simultaneous EGA analysis curves the variation of the peak heights corresponded to the following M/e values : 1,2,12,14,16-20,22,26-29,31,32,34-40,42,44-49,51-54,56, 58,61,65,67,69,71,78-80,83-85,93,97. It was found that for the mass spectrometry curves of carboniferous specimens the temperatures corresponding to the extrema on the EGA (T_m) curves shift along the deposit depth in direction of high temperatures for some M/e (1,16,17,18,20) values. The reverse relationship was observed for the curves with M/e values as follows: 31,32,42,45,47,49, 51,54,65,67,69 and 71.

The second series of studies was performed for the Jura deposits. Despite distinct differences shown by the TG, DTG, DTA and P curves one can notice some regularities e.g. the temperature corresponding to extrema shift in direction of higher temperatures when we follow deeper into deposit layers. The EGA simultaneous analysis curves show that along with depth of deposit the temperatures corresponding to maxima on the EGA curves (T_m) shift for some values of M/e in direction of lower temperatures while for the others in the opposite direction. This is shown in Fig.1 where the numbers 1,2,3 and 4 denote the average values obtained in succession for the specimens J-1, J-2, $J-3_1$ and $J-3_2$.

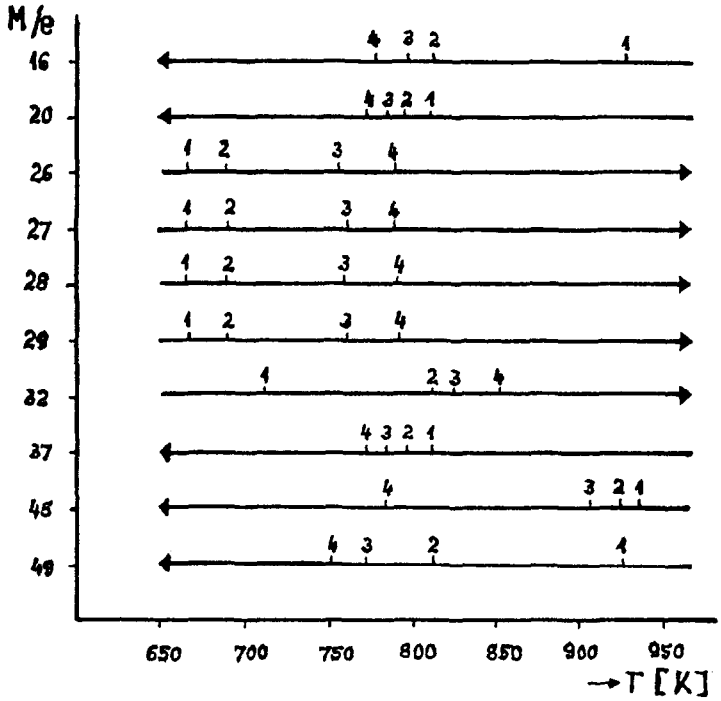

Fig.1. Scheme of the dependence of the T_m shifts on the EGA curves for Jura specimens on the deposit depth. 1,2,3 and 4 denote the average values obtained in succession for the specimens J-1, J-2, $J-3_1$ and $J-3_2$.

The analogous studies were performed for the kerogen specimens extracted from the upper, middle and lower Jurassic deposits corresponding to the K-1, K-2 and K-3 series in sequence. All the obtained TG, DTG and DTA curves have similar shape. They show two characteristic effects. The first and second extrema

are within 753-773 K and 813-833 K temperature range, respectively. It is characteristic that the temperatures T_m corresponding to these effects shift in direction of higher temperatures with the depth of the deposits. The results of the mass spectrometry studies enabled the drawing of 33 EGA curves for each kerogen series. The comparison of the EGA curves indicates some regularities shown in Fig.2. It is evident that with regard to kerogen the temperatures T_m on the EGA curves shift to low values when one goes deeper into the deposit. The shape of the EGA curves is related to the grade of diagenesis of kerogen so it could be taken as a basis to determine the studied specimens.

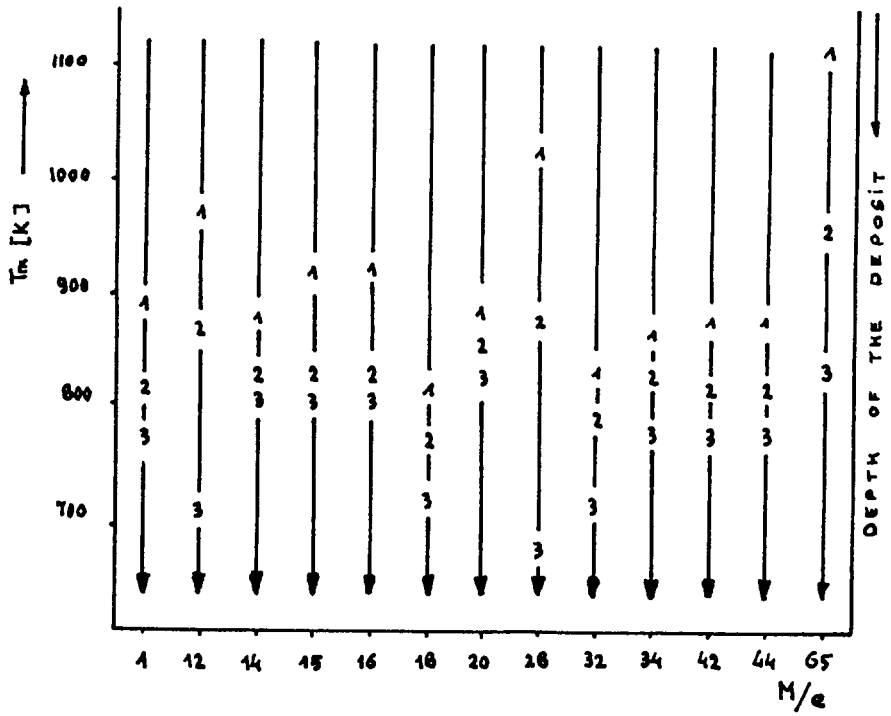

Fig.2. Scheme of the dependence of the T_m shifts on the EGA curves for kerogen specimens on the deposit depth.

All the TG, DTG and DTA curves of kerogen submitted to heating in air atmosphere exhibit two effects overlapping one another. Fig.3. for instance, presents a set of the DTG curves. The temperatures of extrema for both the effects for the K-1, K-2 and K-3 specimens shift to the lower temperatures region. In the same order from K-1 to K-3 the first effect surface area (S_1) (the hatched area in Fig.3.) decreases while the second effect surface area (S_2) increases.

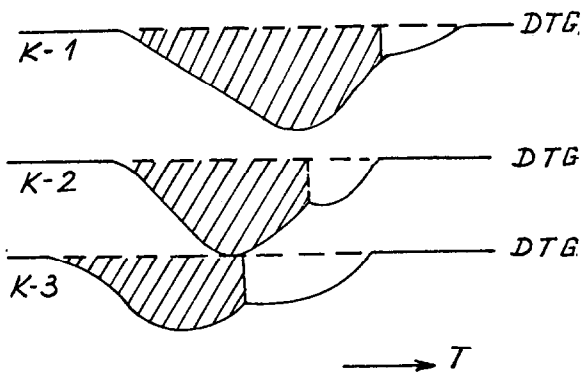

Fig.3. The DTG curves for specimens : K-1, K-2 and K-3 heated in air atmosphere.

CONCLUSIONS

A comparison of the obtained results indicates a definite trend of the character of the thermoanalytical curves with the depth of the deposits. For the specimens coming from the carbon deposits the extrema of the overall effects on the DTA, DTG and

P curves shift in direction of lower temperatures with the depth of the deposits opposite to the tendency observed for the Jura specimens. The oriented trend of the shifts of the maxima on the EGA curves along the deposit depth was noted too.

It was found that the shape of all curves obtained from the thermal analyses for 3 series of K-1, K-2 and K-3 specimens depends on the grade of diagenesis of kerogen. The shape of the TG, DTG and DTA curves for kerogen depends apparently on the kind of atmosphere. At the oxidative atmosphere one can observe a substantial (up to 80 K) shift of the curves in direction of lower temperatures when compared with the vacuum measurements. There are two distinct, overlapping in part one another effects on the DTA and DTG curves for kerogen. The curves shift along the grade of diagenesis in the direction of higher temperatures. However, for the simultaneous EGA curves one observes some distinct shifts of the temperatures corresponding to the maxima on the curves (T_m) in the direction of lower temperatures along the increase of the grade of diagenesis for kerogen.

The distinct trend of the above described effects on the DTA and DTG curves for kerogen heated in air atmosphere shows that the value of the S_1/S_2 ratio could be taken as a measure of the grade of diagenesis for kerogen substance ; the lower the S_1/S_2 value the higher the grade of diagenesis of kerogen.

The analysis of the presented curves obtained by all the TA methods points out that the characteristic effects with their directionality can be taken as a basis for resolution of different specimens as well as for determination of the grade of diagenesis of kerogen.

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