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THERMOANALYTICAL AND THERMOGASTITRIMETRIC INVESTIGATION OF OIL-SHALES

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From thermoanalytical curves (DTG, TG) recorded in an oxygen atmosphere, the moisture and carbonate contents of oil-shales were determined with acceptable accuracy. The nature of the carbonates was predicted from the shape of the DTG curves above 550°C Dolomite (ankerite) as found in Gérce oil-shale, and calcite in Pula–9 oil-shale. The clay content was determined from the signal of a water-detector recorded in a nitrogen atmosphere. The peaks at 80°C and 150°C for Gérce oil-shale were attributed to montmorillonite, and the sharp peak at 525°C for Pula–9 oil-shale to kaolinite.

The volatile and fixed carbon contents of the oil-shales were calculated from the thermogastitrimetric curves.

Oil-shale (mineralogically called alignite) has been defined as a compact laminated rock of sedimentary origin which contains 15–50% organic matter [2]. The organic matter can at best be only slightly extracted with ordinary solvents for petroleum [1]. If the organic matter is subjected to heat it yields shale-oil, the composition of which depends on the atmosphere used [3, 4].

Distillation [5], thermogravimetry [2, 6] and NMR spectrometry [7] are commonly used for quantitative determination of the utilizable organic matter, with organic elemental analysis for determination of the total content.

The present paper describes thermoanalytical investigations on raw oil-shales, in which the mass change and the carbon content of the evolved organic matter were determined simultaneously. The investigations were carried out in inert (nitrogen) and in active (oxygen) atmospheres. The total carbon content of the gaseous products (in the presence of the carrier gases mentioned above) was completely converted to carbon dioxide by means of postcatalytic combustion [8, 9] and continuously titrated.

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Experiments

Materials

Two kinds of raw, powdered Hungarian oil-shale, found in the vicinity of Gérce and Pula, in Transdanubia, were investigated.

Their total carbon contents (organic and inorganic) were determined with an elemental analyser (CHN-I, Laborator Pristoje, Prague). The total carbon contents (organic and mineral) of the oil-shales were 7.68% (Gérce) and 12.95% (Pula-9). Their mineralogical compositions were estimated with an X-ray diffractometer (Philips, PM 8203, CuK_α line). The minerals found were as follows:

Gérce: quartz, chlorite, muscovite, ankerite (dolomite), gypsum, chabazite, calcite and feldspar;

Pula-9: aragonite, quartz, calcite, dolomite, feldspar, mica, montmorillonite and kaolinite.

Instruments

A derivatograph (MOM, Hungary) was used for the thermoanalytical studies. A gas-collecting adapter [10], installed in the oven of the derivatograph, allowed the continuous introduction of carrier gases and the transfer of the gaseous products into the absorbers of the titration apparatus.

A thermogastitrimeter (MOM, Hungary) was used for continuous titration of the carbon dioxide content of the gaseous products. In certain measurements the amount of water released during heating in a nitrogen atmosphere was followed with a water-detector [11].

Thermoanalytical methods

1. The air-dried samples were ground and sieved through a 50 μm sieve. About 150–300 mg of oil-shale was spread on the platinum plates of the "multi-plate" sample holder [12]. During the entire operation, a carrier gas input flow of 25–30 l/h and a suction flow rate of 6–10 l/h were maintained. A heating rate of 9 deg/min was applied up to 900°.

2. The gaseous products evolved in a nitrogen atmosphere were sucked through the water-detector [11] attached to the derivatograph and the amount of water released was continuously recorded.

Thermogastitrimetric methods

A. The combustion products evolved in an oxygen atmosphere were passed through a catalyst compartment containing a red-hot platinum spiral [9] and were sucked into the absorbers of the gastitrimeter. The absorbed carbon dioxide was continuously titrated with 0.1 *N* natrium hidroxide as titrant to pH 9.3 as end-point. A known amount of $KHCO_3$, spread on the plates of the "multi-plate" sample holder and heated up to 300°, was used to standardize the titrant solution.

B. For determination of the total carbon-content of the gaseous products evolved in a nitrogen atmosphere, oxygen was mixed into the gaseous products leaving the gas-collecting tube, and they were then sucked over the red-hot platinum spiral [9]. The amount of carbon dioxide formed was titrated as in point *A*.

Results

The thermoanalytical curves (DTG, DTA, WATER, TG) of the raw oil-shales in a *nitrogen* atmosphere can be seen in Figs 1 and 2.

When Gérce oil-shale was subjected to heat in a nitrogen atmosphere (Fig. 1), water was released in two steps, at 90° and 150°. The endothermic peaks at 440, 470 and 510° in the DTA curve might be attributed to the alteration and decomposition of the organic matter.

Above 550° the inorganic carbonates decomposed. This process ended at 860°, as the DTG curve indicated, but the TG curve was not yet horizontal, due to the slow decomposition of the carbon residue and heavy hydrocarbons. This decomposition of organic matter was accompanied by the signal of the water-detector (Fig. 1, broken line).

From the sample of Pula–9 oil-shale (Fig. 2) the adhesive water was released first in one step, followed by decomposition of the bulk of the organic matter (at 320° and 440° at highest rate). This process ended at 480° (DTG). Decomposition of the carbonate continued up to 800°, but the TG curve showed further weight loss above this temperature.

The water released on the decomposition of organic matter was indicated by the signal of the water-detector (Fig. 2, broken line). The sharp peak at 525° might be assigned to the clay content of the oil-shale.

The thermoanalytical curves (DTG, DTA, TG) of the raw oil-shales in an *oxygen* atmosphere can be seen in Figs 3 and 4.

When the Gérce oil-shale was heated in an oxygen atmosphere (Fig. 3), water was released first in two steps (90 and 160°). The oxidation of organic matter started at

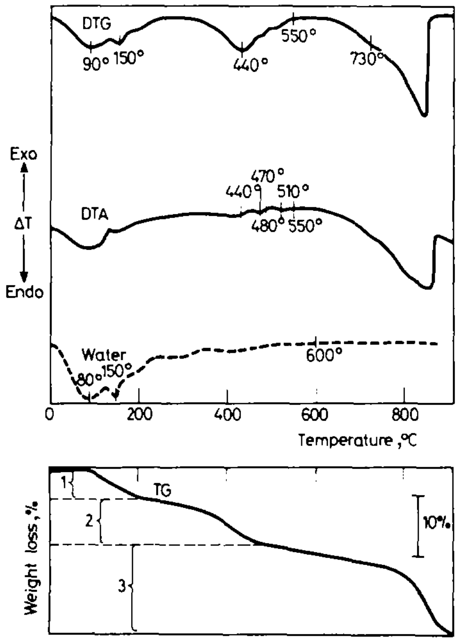

Fig. 1 Thermoanalytical curves (DTG, DTA, WATER, TG) of Gérce oil-shale taken in nitrogen atmosphere. Heating rate: 10 deg/min. 1 humidity; 2 decomposition of organic matter; 3 decomposition of organic matter and ankerite

200°, with highest rate at 280°. The oxidation of the bulk of the organic matter ended at 430°. Decomposition of the mineral carbonate occurred in the range 550–760°. After this process the TG curve became horizontal.

When a sample of Pula–9 oil-shale was heated in an oxygen atmosphere (Fig. 4), water was lost first, and the bulk of the organic matter was oxidized at 200–430°. Oxidation of the organic matter continued in further steps (450, 510 and 550° in the DTA curve). The decomposition of calcite started at 550° and ended at 800°. Above 800° the TG curve was horizontal, indicating that all organic matter burned, without leaving any residue.

The weight loss data calculated from the thermoanalytical curves taken in nitrogen and oxygen atmospheres are listed in Table 1.

The thermogastitrimetric (TGT) curves of the raw oil-shale samples can be seen in Figs 5 and 6.

The carbon content of the gaseous products of the Gérce oil-shale (Fig. 5, curve TGT–I) released in a nitrogen atmosphere between 300 and 550° is derived from the volatile organic matter. Between 550 and 900°, the carbon dioxide content of the gas products is derived from the decomposition of ankerite. Curve TGT–I was not yet

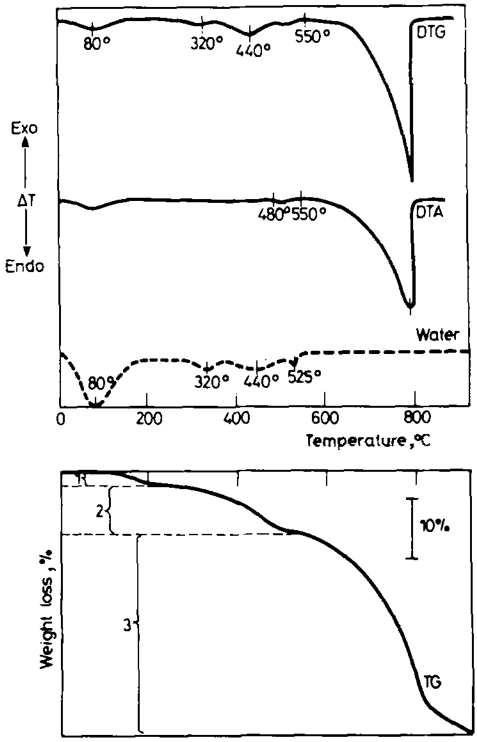

Fig. 2 Thermoanalytical curves (DTG, DTA, WATER, TG) of Pula-9 oil-shale taken in nitrogen atmosphere. Heating rate: 10 deg/min. 1 humidity; 2 decomposition of organic matter; 3 decomposition of organic matter and calcite

Table 1 Percentage weight losses (Δm%) of oil-shales in oxygen and nitrogen atmospheres (20–900°)

Sample	Atmosphere	Δm% 20–200°	200–550°	550–900°	Total
Gérce	oxygen	4.8	9.1	10.6	24.5
	nitrogen	4.8	7.4	13.5	25.7
Pula-9	oxygen	2.4	9.6	27.9	39.9
	nitrogen	2.5	6.9	31.8	41.2

horizontal above 900°, indicating the further departure of carbon-containing products.

When the Gérce oil-shale was heated in an oxygen atmosphere (Fig. 5, curve TGT–II), the carbon dioxide was already measurable at 200°. The oxidation of the bulk of the organic matter ended at 430° and curve TGT–II indicated further

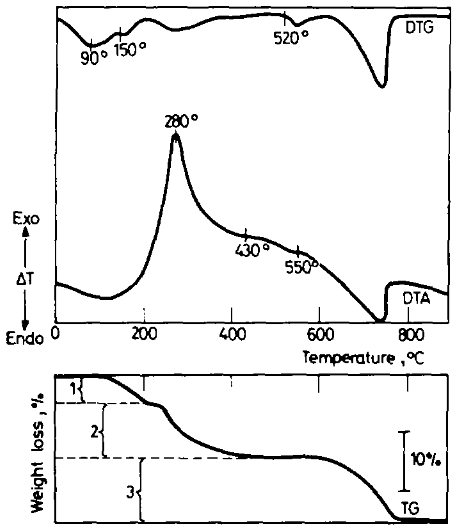

Fig. 3 Thermoanalytical curves (DTG, DTA, TG) of Gérce oil-shale taken in oxygen atmosphere. Heating rate: 10 deg/min. 1 humidity; 2 oxidation of the organic matter; 3 decomposition of ankerite

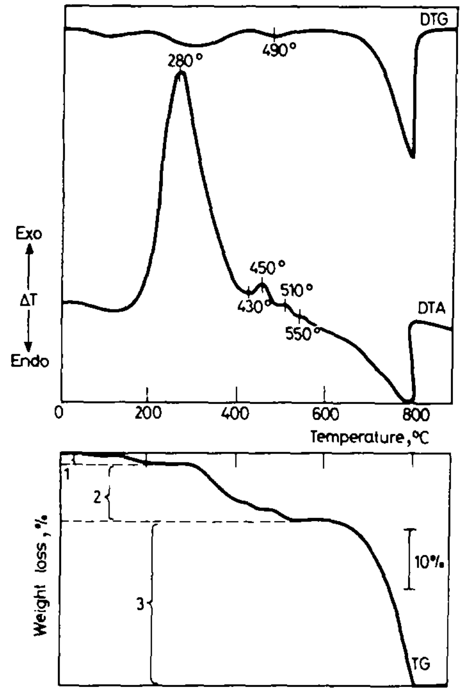

Fig. 4 Thermoanalytical curves (DTG, DTA, TG) of Pula 9 oil-shale taken in oxygen atmosphere. Heating rate: 10 deg/min. 1 humidity; 2 oxidation of the organic matter; 3 decomposition of calcite

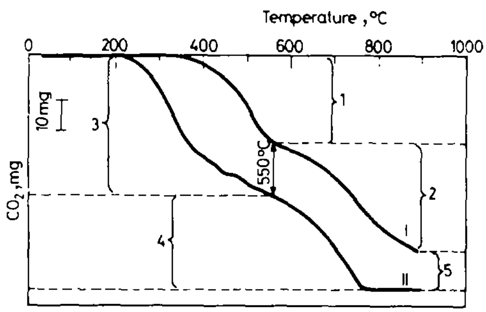

Fig. 5 Thermogastitrimetric carbon-dioxide curves (TGT) of Gérce oil-shale (267 mg). TGT–I: taken in nitrogen atmosphere; TGT–II: taken in oxygen atmosphere; 1 CO_2 derived from organic matter volatiled up to 550°; 2 CO_2 derived from organic matter volatiled 550–900° and decomposition of ankerite; 3 CO_2 derived from oxidation of the organic matter; 4 CO_2 derived from decomposition of ankerite

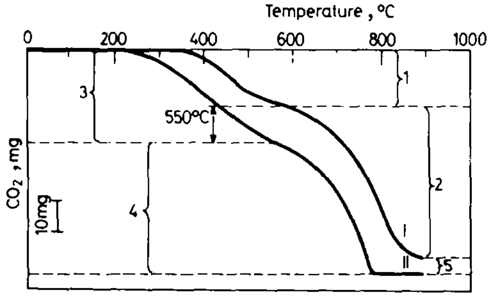

Fig. 6 Thermogastitrimetric carbon-dioxide curves (TGT) of Pula-9 oil-shale. TGT–I: taken in nitrogen atmosphere; TGT–II: taken in oxygen atmosphere; 1 CO_2 derived from organic matter volatiled up to 550°; 2 CO_2 derived from organic matter volatiled 550–900° and decomposition of calcite; 3 CO_2 derived from the oxidation of the organic matter; 4 CO_2 derived from decomposition of calcite

oxidation steps at 450° and 500°. Between 550 and 760° the carbon dioxide content of the gaseous products is derived only from the decomposition of ankerite. Above 760°, curve TGT–II became horizontal, indicating no further loss of carbon-containing gas products.

The carbon dioxide content of the gaseous products of the Pula–9 oil-shale heated in a nitrogen atmosphere (Fig. 6, curve TGT–I) between 300 and 550° is derived from the volatile organic matter; and between 550 and 900° from the volatile organic matter and the decomposition of calcite.

The oxidation of the organic matter of the Pula–9 oil-shale heated in an oxygen atmosphere started at 230° (Fig. 6, curve TGT–II) and ended at 550°. Above 550° the carbon dioxide content is derived only from the decomposition of calcite.

The percentage carbon contents of the air-dried oil-shale samples are given in Table 2.

Table 2 The carbon contents (C%) of the oil-shales, determined by titration on the gaseous products in oxygen and nitrogen atmospheres

Sample	Atmosphere	C%		Total
		200–550°	550–900°	
Gérce	oxygen	5.0	2.9	7.9
	nitrogen	2.1	3.6	5.7
Pula–9	oxygen	5.4	7.6	13.0
	nitrogen	3.15	8.9	12.05

Discussion

The investigations led to the following findings.

a) The quantity of mineral carbonates in the oil-shale could be determined from the TG data (Table 1) or the TGT curves recorded in an oxygen atmosphere between 550 and 900°. The mineral carbonate contents of the Gérce and Pula–9 oil-shales were found to be 2.9% and 7.6% C, respectively.

b) The quantity of organic matter volatilized up to 550° could be determined from the TGT curves recorded in a nitrogen atmosphere (Figs 5 and 6, 1). These carbon contents of the Gérce and Pula–9 oil-shales were found to be 2.1% and 3.15% C, respectively.

c) The quantity of organic matter volatilized between 550 and 900°, expressed as C%, could be calculated from the TGT curves recorded in a nitrogen atmosphere by subtracting the C% corresponding to the carbonate contents (Figs 5 and 6, 2–4, Table 3).

d) The fixed carbon content (not volatilized up to 900° in a nitrogen atmosphere) could be calculated from the difference in carbon dioxide contents measured in oxygen and in nitrogen atmospheres (Figs 5 and 6, 5, Table 3).

Table 3 Volatilized and fixed carbon contents of the oil-shales, expressed as C%:

Sample	Volatile organic matter, C%		Fixed carbon, C%
	200–550°	550–900°	
Gérce	2.1	0.7	2.2
Pula–9	3.15	1.3	0.95

The ratios of the C% content and the weight loss between 200 and 550° in a nitrogen atmosphere are given in Table 4. These quotients well characterize the organic matter contents of the oil-shales.

Table 4 Ratio of weight loss (Δm%) and carbon content (C%) $\left(\frac{\Delta m\%}{C\%}\right)$ in a nitrogen atmosphere between 200 and 550°

	Gérce	Pula–9
$\frac{\Delta m\%}{C\%}$	3.52	2.19

The total carbon contents of the samples, as determined by elemental analysis and by titrimetry, are close to each other: 7.68% and 12.95%; and 7.9% and 13.0%, respectively.

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Zusammenfassung — Feuchtigkeits- und Carbonatgehalt von Ölschiefern werden aus in Sauerstoffatmosphäre aufgenommenen thermoanalytischen Kurven (DTG, TG) mit annehmbarer Genauigkeit bestimmt. Die Natur der Carbonate wurde aus dem Verlauf der DTG-Kurve oberhalb 550 °C vorausgesagt. Dolomit (Ankerit) wurde im Gérce-Ölschiefer, Calcit im Pula–9-Ölschiefer gefunden. Der Gehalt an Tonen wurde aus dem in Stickstoffatmosphäre erhaltenen Signal eines Wasserdetektors bestimmt. Die Peaks bei 80 und 150 °C in der DTG-Kurve des Gérce-Ölschiefers werden Montmorillonit, der scharfe Peak bei 525 °C im Falle von Pula–9-Ölschiefer Kaolinit zugeschrieben. Die Gehalte der Ölschiefer an flüchtigem und fixiertem Kohlenstoff werden aus gastitrimetrischen Kurven berechnet.

Резюме — Из термоаналитических кривых (ДТГ, ТГ) нефтеносных сланцев, измеренных в атмосфере кислорода, с приемлемой точностью определено содержание в них влаги и карбонатов. Тип карбонатов был установлен на основе вида кривых ДТГ выше 550°. В нефтеносном сланце месторождения Герце был найден доломит (анкерит), тогда как в образце Пула–9-кальцит. Содержание глины было определено из сигнала детектора для воды и измеренного в атмосфере азота. В случае образца месторождения Герце, наблюдаемые пики при температуре 80 и 150° были отнесены к монтмориллониту, а реазкий пик при 525° в случае образца Пула–9 — к каолину. Исхода из термогазотитриметрических кривых нефтеносных сланцев, было вычислено содержание в них летучего и связанного углерода.