

## CONTRIBUTIONS TO THE KNOWLEDGE OF THE HUNGARIAN OIL SHALE KEROGEN II

RESULTS OF PRELIMINARY DTA AND IR-INVESTIGATIONS  
ON THE KEROGEN OF THE OIL SHALE OCCURRENCE AT PULA

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### INTRODUCTION

The geological conditions and general characteristics of oil shales discovered in 1973 in Transdanubia (Hungary) were first reported by Á. JÁMBOR and G. SOLTÍ [1974]. The petrographical description of the oil shales was carried out by Cs. RAVASZ [1974]; J. MEZŐSI and M. MUCSI [1976] dealt with the sedimentology and mineralogy of the occurrence at Pula (Put-7 boring). According to the palynological investigations [Hungarian Geological Institute, E. NAGY, 1974] most part of the insoluble organic material of the sediments consists of *Botryococcus braunii* changing in amount layer by layer besides other organic material (pollens, coalified plant remnants etc.).

In connection with the detailed investigation of the oil shale occurrence of Upper Pannonian age at Pula the necessity of the examination of the kerogen content has also arisen. The following questions may arise: *a)* to what extent the peaks in the DTG and DTA curves attributable to the organic material are modified by inorganic components in the derivatograms of average samples; *b)* what kind of differences appear in the derivatograms of kerogen concentrates isolated by using physical and chemical methods, respectively, *c)* whether or not the type of kerogen from the different layers of Put-7 boring shows changes depending on the depth, sedimentation cycle, rock type; *d)* in what manner the single steps of thermal decomposition of the kerogen concentrates can be characterized by IR-investigations in comparison with the results of derivatographic examinations.

### CHARACTERIZATION OF SAMPLES INVESTIGATED

The samples used for investigations from the borehole Put-7 in neighbourhood of village Pula are given in Table 1.

The air dried samples were ground and the carbonate CO<sub>2</sub> content of the samples was determined by gasvolumetric method. The total organic carbon content was determined by ignition in oxygen stream in portion of samples free of carbonate. The soluble organic material of the samples was extracted in a SOXHLET-apparatus in two steps, first by chloroform applying an exhaustive extraction, later continuing it by extraction with benzene-acetone-methanol mixture. Data obtained are shown in Table 2.

*Fig. 1* shows the change of total carbon content through the section of boring Put-7, and that of the value of the FISCHER-assay, the latter expressed in per cent. It may be established that a fairly strong positive correlation exists between the two series.

TABLE 1

*Samples investigated*

Sample	Depth	Characterization of the layer
A—14	9,5—10,0 m	alginitic aleurite
A—15	10,0—10,5	aleuritic alginite
A—18	11,5—12,0	thin-layered type
A—24	14,5—15,0	rich in alginite
A—26	15,5—16,0	
A—27	16,0—16,5	without fine-layering, with a few carbonate
A—28	16,5—17,0	
A—32	18,5—19,0	alginite in a lesser amount, without layering, with more carbonate
A—33	19 0—19 5	
A—35	20 0—20 5	alginite with alternating carbonate content, built up from layered sections and sections without layering
A—38	21 5—22 0	
A—42	23 5—24 0	
A—45	25 0—25 5	rich in alginite, without fine-layering
A—49	27,0—27,5	alginite with carbonate, layered type
A—52	28,5—29,0	alginite with more carbonate, layered type
A—73	39,0—39,3	alginite with more carbonate without layering

TABLE 2

*Some characteristic data of samples*

Sample	Carbonate CO <sub>2</sub> %	$\Sigma C_{org}$ (%)	Organic material soluble (%)				
			in chloroform	in solvent mixture	total soluble		
A—14	9,5	11,30	1,40	+	0,54	=	1,94
A—15	8,2	11,70	2,34	+	0,43	=	2,77
A—18	16,1	7,70	0,84	+	0,55	=	1,39
A—24	6,7	32,56	3,61	+	2,04	=	5,65
A—26	3,6	45,61	5,12	+	1,73	=	6,85
A—27	4,3	45,68	3,95	+	2,01	=	5,96
A—28	4,8	28,89	4,99	+	1,54	=	6,53
A—32	15,5	11,44	1,35	+	0,79	=	2,14
A—33	21,4	9,89	0,55	+	0,49	=	1,04
A—35	22,1	11,80	1,15	+	0,32	=	1,47
A—38	14,7	16,74	3,99	+	1,10	=	5,09
A—42	17,4	18,64	1,56	+	0,95	=	2,51
A—45	11,8	30,09	2,99	+	0,85	=	3,84
A—49	16,0	21,16	4,77	+	1,49	=	6,26
A—52	17,0	8,52	1,06	+	0,48	=	1,54
A—73	29,8	6,15	0,43	+	0,23	=	0,66

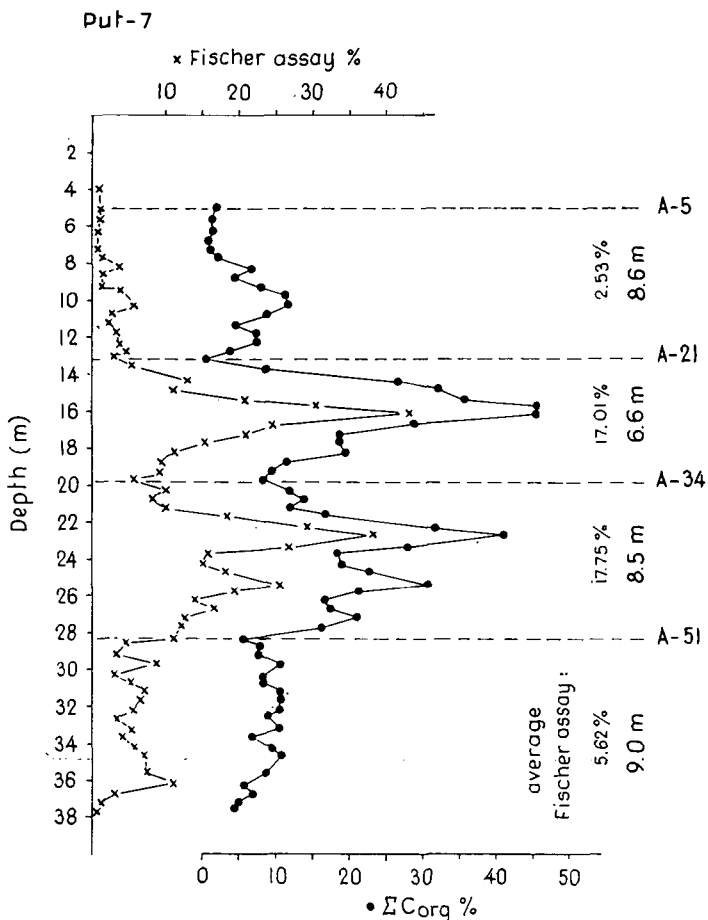


Fig. 1. Change of the  $\Sigma C_{org}$  content and the FISCHER-assay in the section of boring Put-7.

## DERIVATOGRAPHIC INVESTIGATIONS

### *Derivatographic investigation of original samples*

Investigations were carried out by an ERDEY-PAULIK-PAULIK Derivatograph in air recording the T, DTA, DTG and TG curves simultaneously under the same conditions. Heating rate  $10^{\circ}\text{C}/\text{min}$ .

Peak temperatures in DTG and DTA curves of the derivatograms of the original samples are comprised in Table 3 and 4, respectively.

The temperature of peak I (loss of water) changes from  $100^{\circ}\text{C}$  to  $130^{\circ}\text{C}$ , peak II (between  $180$ – $280^{\circ}\text{C}$ ), peak III (between  $280$ – $360^{\circ}\text{C}$ ) and peak IV ( $450$ – $480^{\circ}\text{C}$ ) represent the steps of the combustion of the organic material of the sample whereas further maxima denote partly the decomposition of phyllosilicates and that of carbonates. At any rate, in the interval of peaks V and VI an overlapping of decomposition processes of organic material and clay minerals may exist.

TABLE 3

*Temperature of maxima in the DTG curve of the original samples*

Sample	Temperature of DTG maxima							
	I	II	III	IV	V	VI	VII	VIII
A—14	130	280		460	520		700	820
A—15	125	265		460	520		680	800
A—18	130	280	(360)	(480)			700	840
A—24	100	220	300	465		(580)	(720)	820
A—26	100	220	290	460			(720)	810
A—27	100	180	280	460			760	
A—28	100	200	290	465				810
A—32	100	280		460	530		720	850
A—33	120	260		460	520	560	735	870
A—35	110	260		460	520	570	720	830
A—38	100	230	300	465		570	730	820
A—42	100	240	305	460	(540)		800	840
A—45	110	210	280	460		560	720	820
A—49	100	260	(310)	465	530		720	840
A—52	120	270		(460)			720	840
A—73	120	280		(450)			750	870
Av.:	110°	245°	301°	461°	526°	568°	726°	832°

Values in parenthesis indicate very weak effects.

TABLE 4

*Peak temperatures in the DTA curve of the original samples*

Sample	Temperature of DTA peaks						
	I	II	III	IV	V	VI	VII
A—14	155	330	(400)		495	(520)	
A—15	140	320	(420)		500		
A—18	150	335	(400)		500		560
A—24	105	270			490	535	(550)
A—26	115	275	435		480	520	
A—27	120	260			480		580
A—28	105	260	400	440	480	520	(550)
A—32	140	320			485	(510)	
A—33	145	320	(395)		485	(515)	(560)
A—35	130	300			480	(510)	
A—38	105	280	420		480	530	(555)
A—42	115	285	(410)	460	480	(520)	
A—45	120	260	(420)	435	480	530	550
A—49	120	305	390		480	500	
A—52	130	315			480	510	
A—73	125	320				530	
Av.:	126°	297°	(409°)	445°	485°	519°	558°

Values in parenthesis indicate very weak effects.

Table 4 shows first of all peaks characteristic of the organic material of the samples and peaks belonging to the decomposition of carbonates at higher temperatures are neglected. It is to mention that in derivatograms (DTA curve) of some samples fairly intensive exothermic peaks appear in closest neighbourhood of the endothermic peak of carbonate decomposition as shown in Fig. 2, C.

Samples of type "A" and "C" represent the extreme types whereas samples of "B" type may be considered as intermediate ones.

Comparing the DTA curves of samples of the "A" and "C" type the differences at higher temperatures are especially striking. The DTA curves of samples of the "C" type show expressed exothermic peaks at 760–860° C (average 796°) and 840–900° C (average 865° C) immediately before and behind the carbonate endo-

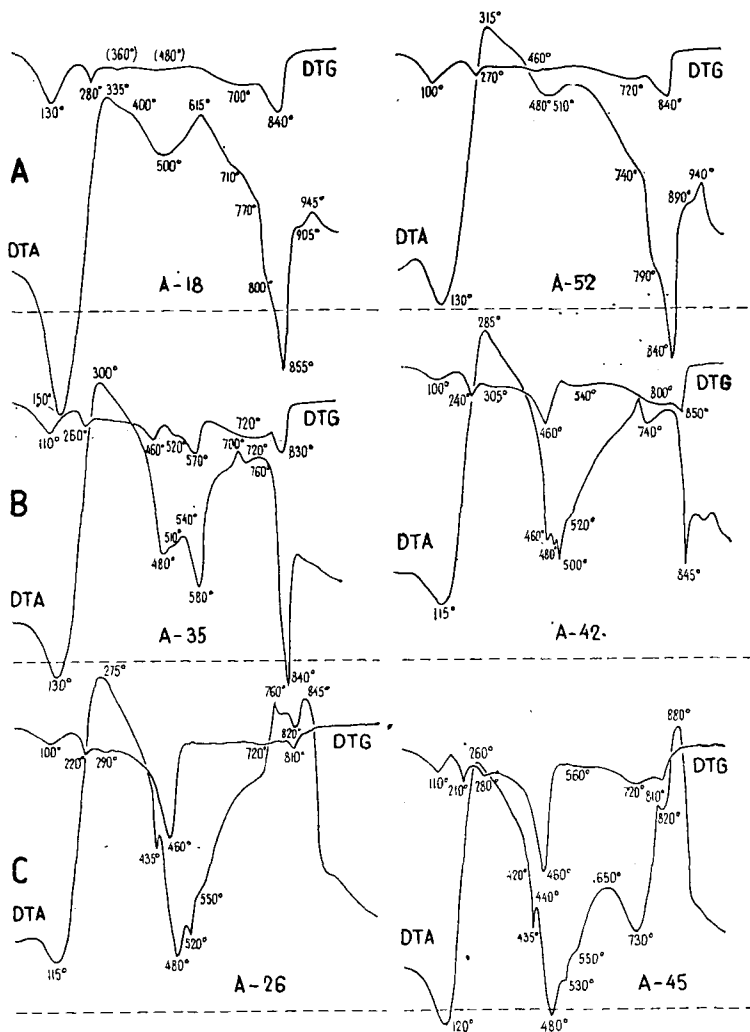


Fig. 2. DTA and DTG curve of some samples from boring Put-7. A: A-18 and A-52, B: A-35 and A-42, C: A-26 and A-45.

thermic peak at 815°–865° C (average 830). The DTA curves of samples of the “A” type don’t show any exothermic effects within the temperature intervals mentioned. In the DTA curves of samples belonging to the intermediate type “B” an exothermic peak at about 700–800° C can also be established, however, it always precedes the well developed carbonate endothermic peak. The main types naturally cannot be sharply delimited. The character of the DTA curves is determined by the changing amount of the organic material as well as by the changing ratio among the amount of organic material, phyllosilicates and carbonates and by the interaction between organic and inorganic components. The organic material content is the highest in samples of the “C” type and the lowest in samples of the “A” type.

As to the DTG curves, the three maxima following the first one (loss of water) denote the decomposition of the organic material. The first of them from 180° C to 280° C is generally small, however, sharp. The maximum from 280° C to 360° C is hardly or not observable in the curves of most of the samples. The last maximum from 450° C to 480° C, belonging to the decomposition of the organic material shows the relatively lowest variation.

In the DTA curves the temperature of the first endothermic peak varies between 105° C and 155° C, on average 126° C. It is immediately followed by a strong exothermic peak from 260° C to 335° C. In the descending part of this exothermic effect further one or two smaller peaks can be observed in the DTA curve of some samples. The last peak (endothermic) belonging to the decomposition of the organic material appears within the range 480° C to 500° C.

This last peak both in the DTA and DTG curves shows a fairly small variation within a narrow temperature interval of 20°–30° C independent of the depth, the rock type as observed in the case of all samples and merely its intensity is changing depending upon the amount of the organic material.

The first and strong exothermic peak temperature, however, shows a greater variation both in the DTA and DTG curves. Its temperature is the lower the higher is the organic material content.

According to the connection shown by *Fig. 3* the samples investigated may be divided into three groups. Samples A – 14, – 15, – 18, – 32, – 33, – 52, – 73 belong to group “A”; samples A – 35, – 38, – 42, – 49 to group “B” and group “C” includes the samples A – 24, – 26, – 27, – 28, – 45 with the highest organic carbon content.

The increase of the peak temperature in connection with the decrease of the organic carbon content is the consequence of the fact that the decrease of the amount of organic material means at the same time the increase of the amount of inorganic

TABLE 5

*Mean values of the first exothermic DTA peak, the total organic carbon and the soluble organic material of groups A, B and C*

Group	Temperature of the first exothermic DTA peak	$\Sigma C_{org}$ %	Total soluble organic material %
A	323° C	9,53	1,64
B	292	17,10	3,83
C	265	36,56	5,76

The connection of the mean value of the first exothermic peak temperature with that of the  $\Sigma C_{org}$  in the single groups is also shown in *Fig. 3* (—A—A—).

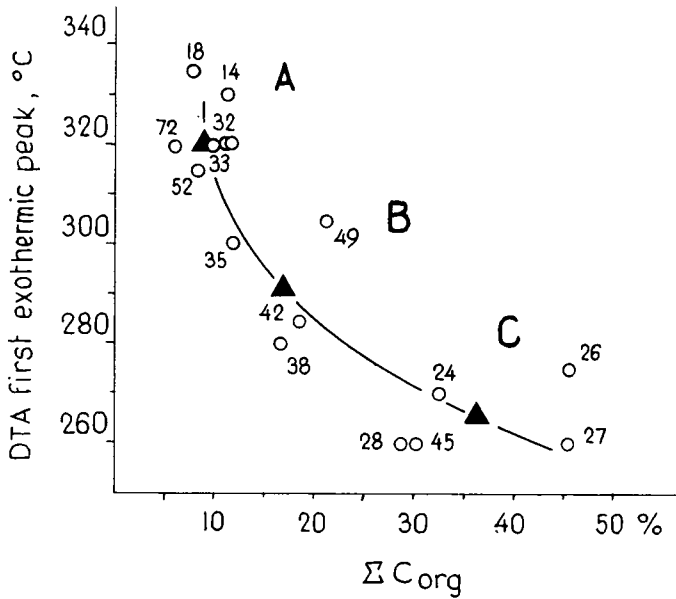


Fig. 3. Connection of the temperature of the first exothermic DTA peak with the total organic carbon content of the samples.

components (clay minerals, carbonates) and the thermal decomposition of kerogen particles surrounded by clay minerals and carbonates is retarded, whereas, in presence of organic material of greater amount the ratio of organic material/inorganic components is shifted towards the organic material and the thermal decomposition proceeds already at lower temperatures.

Under similar conditions the derivatograms of a Green River oil shale sample of Eocene age (Tosco Mine, Rio Blanco County, Colorado, USA) and of a torbanite sample (Newness, near Glen Davis, N. S. Wales, Australia) of Permian age were also recorded as shown in Fig. 4.

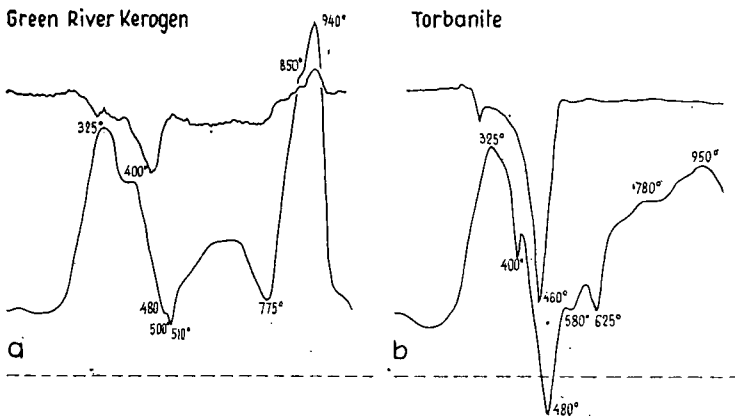


Fig. 4. DTG and DTA curves of a Green River oil shale (a) and torbanite from Australia (b).

In the DTG curve of the Green River oil shale maxima can be observed at 325° C, 360° C and the most intensive maximum at 460° C. The corresponding peaks in the DTA curve are at 325° C and 400° C as well as the peak triplet at 480–500–510° C. This endothermic peak is coupled with the highest loss of weight.

In the DTG curve of the torbanite also the maximum at 460° C is dominant and correspondingly the endothermic DTA peak at 480° C is also dominant and is incident to the greatest loss of weight (49.6 per cent) as registered in the TG curve within the temperature limits from 380° C to 520° C. The temperature of the first exothermic peak in the DTA curve is also 325° C as in the case of the Green River oil shale. On the descending side of this peak a further smaller but definite peak can be observed.

The derivatograms of these two oil shale samples show a very close similarity to those of the Pula oil shale samples rich in organic material. The similarity is especially striking between the Green River oil shale and the samples of Pula belonging to group "C", the DTA curves of both show a strong exothermic peak at higher temperatures indicating the final combustion of the fixed carbon. Similarity appears also in that respect that the temperatures (on average) both in the DTG and DTA curves of the comparative samples and the Pula samples, indicating the process of the greatest loss of weight, get on well together (DTG: 461°C, DTA: 485°C).

Differences between the derivatograms of the comparative oil shale samples and those of the samples from boring Put-7 appear in the temperature of the first exothermic peak. The first sharp maximum appears at 280°–290°C in the DTG curve of the comparative samples, whereas, this peak temperature can be observed in the DTG curves of samples from Pula, having a lower organic material content. The temperature of this first maximum in the case of samples rich in organic material (group "C'") varies from 180° C to 220° C. Consequently the temperature of the first exothermic DTA peak is lower in the case of samples of Pula varying from 260° to 335° C (on average 297° C) instead of 325° C observed at the comparative samples. The peak temperature varies from 260° C to 275° C in the case of samples rich in organic material (group "C").

The differences mentioned may be interpreted that the oil shale of Pula contains more organic components volatile at a lower temperature and since the temperature of the first characteristic peak should be shifted toward higher temperatures by the increase of the grade of coalification, hence, the alginite from Pula younger than the comparative samples, and originating from shallow depth (10–30 m from the surface) are still in the initial stage of their evolution.

It was established that the temperature of maxima, indicating the largest loss of weight both in the DTG and DTA curves of the samples from Pula and the comparative samples, agree well (461° C and 485° C on average, respectively, at samples from Pula and 460° C and 480° C, respectively, in the case of the Green River oil shale and the torbanite). This fact may be interpreted that this peak temperature is already independent of the age, the type and amount of the organic material, the type of the sediment, thus, the investigation of processes taking place at lower temperature, and indicated by DTG and DTA peaks in the lower temperature interval is more essential from the point of view of the evaluation of the original type and thermal transformation of the kerogen of the sediments. The characteristic peaks in the derivatogram are influenced by the original state of the kerogen at lower temperatures, however, after the decomposition processes having taken place by increasing temperature, the originally existing differences among kerogens are



disappeared so, in consequence nearly the same temperature values can be observed as shown above.

D. R. WILLIAMSON [1964] gives an overview on the results of investigation regarding the peculiarities and beneficiation of oil shales. From the viewpoint of the present investigations the statement seems to be essential that no kerogen is converted to soluble material below 325° C [ROBINSON and HUBBARD see WILLIAMSON] and that according to DULHUNTY [see WILLIAMSON] a sharp increase in the rate of production of soluble bitumen occurs at 360° C, and the rate decreases sharply at 380° C. According to GUTHRIE [see WILLIAMSON] heavy oil vapors and gas begin to be formed and distilled and at about 500–600° C the production of condensable oil vapors ceases.

Considering the samples investigated, rich in organic material (group "C") the greatest loss of weight starts at 330–345° C (on average 340° C) and ends at 505–550° C (on average 527° C). The corresponding DTG and DTA maxima are 460° C and 485° C, respectively. The highest loss of weight can be observed from 380° C to 530° C (the loss of weight is 49.6%) at the torbanite and from 380° C to 520° C (10.8%) in the case of the Green River oil shale.

The highest loss of weight and the corresponding temperature limits in the case of samples from Pula (group "C", rich in organic material) are as follow:

Sample	Step in the TG curve	Loss of weight %
A—24	from 335 °C to 540 °C	26,5
A—26	340 °C 550 °C	31,2
A—27	300 °C 520 °C	38,7
A—28	330 °C 520 °C	29,7
A—45	330 °C 535 °C	24,8

#### *Derivatographic investigation of kerogen concentrates*

First the soluble organic material of the samples was extracted and the kerogen of 11 samples by physical method and that of 5 samples by chemical method was concentrated. Kerogen concentrates obtained by physical method have higher ash (inorganic component) content, however, no change in the structure and composition of the original kerogen occurs. Concentrates obtained by chemical method have lower ash content, however, the kerogen undergoes some changes. Regarding the isolation of the kerogen of the Hungarian oil shales we refer to the paper of M. HÉTÉNYI and I. VARSÁNYI [1976].

For isolation by physical method the kerogen was treated first by chloroform and the further concentration of the fraction rich in organic material was carried out by treatment (fractionation) with methanol-chloroform mixtures of successively decreasing specific gravity.

Isolating the kerogen by chemical method, first the carbonates were removed and after that the chloride-free washed sample was homogenized by zinc chloride solution (sp. gr. 1.92) and centrifuged. The fractions were separated and the separation of the lowermost fraction was repeated. Finally the corresponding fractions were united washed and dried at 60° C. The further treatment was carried out according to LÜCK [1969] using acid treatment with hydrofluoric acid and alternating

treatment with dilute hydrochloride acid and ammonium hydroxide and finished the isolation with washing and drying the concentrate.

The derivatograms of the concentrates were recorded under similar conditions as those of the original samples only a special sample holder was used which results in a better separation of the peaks.

Table 6 shows the values of ignition residue of the original samples and the corresponding concentrates, respectively in the case of samples isolated by physical and chemical method. The samples were heated to 1000° C.

TABLE 6

*Ignition residue of original samples and kerogen concentrates*

Sample	I g n i t i o n   r e s i d u e		
	original sample	%	concentrate
A—14	61,41	concentrated by chemical method	6,70
A—15	63,29		7,20
A—18	62,94		1,00
A—52	61,82		0,00
A—73	57,86		2,70
			4.12
A—24	44,12	concentrated by physical method	7,67
A—26	38,75		8,75
A—27	33,96		8,50
A—28	42,17		7,86
A—32	62,15		8,75
A—33	60,15		7,20
A—35	54,96		2,00
A—38	41,05		8,00
A—42	51,97		6,88
A—45	43,37		7,40
A—49	52,20		12,67
			7,14

The characteristic peaks in the DTG and DTA curves of the concentrates are comprised in Table 7.

According to the thermogravimetric measurements the very first part of the TG curve ends on average at 170° C and is accompanied with a very low loss of weight, followed by two more expressed sections in the case of kerogens physically concentrated. Thus, the second and significant step begins at 170° C and ends at 376° C on average and is accompanied with a loss of weight of 35.52 per cent on average. The third considerable step begins at 376° C and ends at 636° C and the average loss of weight is 53.19 per cent. Within the two large steps smaller ones can be observed.

The first step in the TG curve of the concentrates obtained by chemical method ends at 155° C and represents 5.33 per cent loss of weight (on average), the second intensive step ends at 373° C and is accompanied by a loss of weight of 30.89 per cent. The last step is terminated at 615° C on average leading to a loss of weight of 58.08 per cent. The combustion processes stop at that temperature and in the curves no more changes can be observed.

Fig. 5 shows the DTA and DTG curves constructed on the basis of the mean values of temperature and loss of weight, respectively, both for kerogens physically and chemically concentrated.

TABLE 7

*The characteristic peaks in the DTG and DTA curves of the concentrates*

a) Peak temperatures in the DTA curve (°C)

Kerogen concentrated by physical method

	I	II	III	IV	V	VI	VII
A-24	225	300		375	440	(500)	
A-26	250	(290)	(340)	380	450	(510)	(580)
A-27	205	285	(350)	385	450	(520)	
A-28	230	300	(340)	370	450		
A-32	235	290	(350)	385		(500)	
A-33	235	300	(340)	375		(480)	(555)
A-35	220	300	(350)	385		(510)	(605)
A-38	230	310	(355)	390	460		(570) (595)
A-42	230	290	(340)	375		(485)	(580) (650)
A-45	215	295	(340)	365	435	(500)	(580)
A-49	260	(290)	(350)	380		(490)	
Average:	230°	295°	(345°)	378°	460°	(499°)	(573°) (616°)

Kerogen concentrated by chemical method

A-14	285	(335)	385	465	(510)	(580)
A-15	300	(340)	380	450		
A-18	320	(355)	400	425	490	570
A-52	310	(350)	370	400	440	550
A-73	300	(360)	380	420	450	555
Average:	303°	(348°)	383°	432°	472°	563°

b) Temperature of maxima in the DTG curve

Kerogen concentrates by physical method

	I	II	III	IV	V	VI	VII	VIII	IX	X
A-24	220		300	340		(440)		500		
A-26	230		310	340		(450)		470		580
A-27	180		285	350						620
A-28	220		300	370		(450)		485		
A-32	220		300	340		(460)		500		580
A-33	230		300	340		(440)		480		560
A-35	220		300	340		(440)		530		615
A-38	220		300	355				500		595
A-42	210		300	350		(450)		500		630
A-45	200		295	340		(440)		500		580
A-49	240		320	350		(450)		500		560

Average: 217° 301° 347° (447°) 496° 591°

Kerogen concentrates by chemical method

A—14	265	(320)	480	520	
A—15	280	(340)	470	540	
A—18	300	(355)	440	520	600
A—52	280		400	465	570
A—72	270	(350)	420	440	515

Average: 279° (341°) 410° 459° 522° 585°

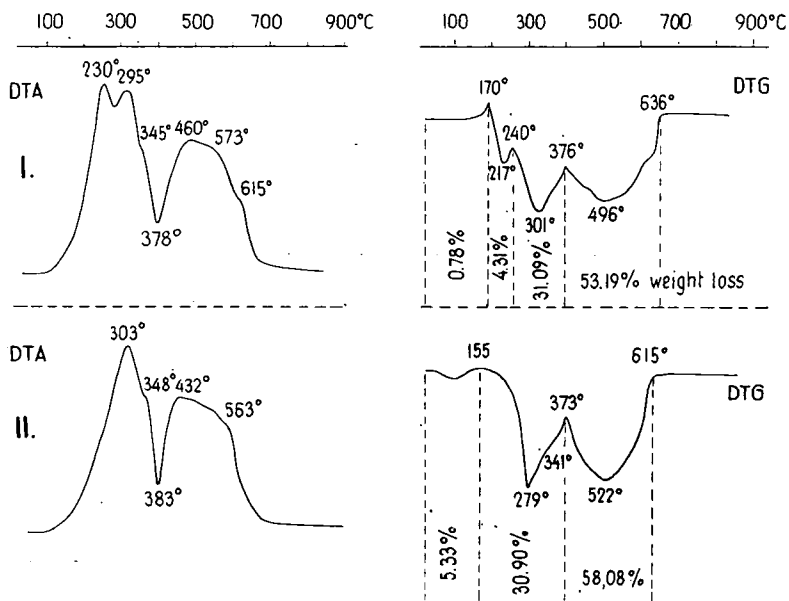


Fig. 5. DTA and DTG curves constructed on the basis of the mean value of experimental data  
 I: concentrate by physical method;  
 II: concentrate by chemical method.

From the data in Table 7 and the temperature limits of the steps in the TG curves as well as the loss of weights accompanied with them, the following conclusions may be drawn regarding the kerogens isolated from oil shale from Pula:

(i) Kerogens isolated by the two ways mentioned are similar in that respect that heating them on the air the combustion of the organic material is divided into two large sections (steps). The first one including 2 or 3 smaller steps, too, terminates nearly at the same temperature in case both of kerogens concentrated physically and chemically (376° C and 373° C). Similarity can also be established so far as the first reactions result in expressed, sharp peaks in the DTA and DTG curves, whereas, the second effect is broad and vaulted without any sharp peaks. The first represents the lower and the second section the larger loss of weight. Within the second section smaller but uncertain steps (peaks) may be observed. The combustion of the kerogen concentrated physically stops at 636° C and at 615° C in the case of kerogen isolated by chemical method. Summarizing the partial losses of weights during the first reac-

tions taking place to 376° C, nearly the same values are obtained: 36.18 per cent in the case of kerogen concentrated by physical method and 36.23 per cent at the kerogens isolated by chemical way.

(ii) Difference between the kerogens concentrated in the two manners mentioned appears definitely in processes occurring at lower temperatures. The TG curve of kerogens physically concentrated hardly shows any loss of weight to 100–120° C, even a very small increase of weight can be observed up to 160–170° C which may be interpreted as an oxidation process. The TG curve of kerogens isolated chemically starts with an expressed step representing a loss of weight larger than that observed in the TG curve of kerogens physically isolated.

The DTA curve of kerogens concentrated in physical manner is characterized by an intensive, sharp exothermic peak from 205° C to 260° C (on average 230° C) which is totally lacking in the DTA curve of kerogens concentrated by the other way. In the DTA curve of the latter the first sharp exothermic peak appears at 303° C coinciding with the second exothermic peak of kerogens physically isolated, occurring at 295° C. Consequently, a sharp maximum appears in the DTG curve of kerogens concentrated by physical way at 217° C (on average), which is lacking in the DTG curve of the kerogens chemically concentrated. This maximum corresponds to the first exothermic DTA peak.

On the second broad exothermic peak somewhat higher temperature values can be observed in case of kerogens concentrated by physical method. The character of this second broad and vaulted section is very similar in the case of kerogens isolated by the two different methods.

(iii) It may be supposed that during the concentration by chemical method some structural changes occur (rupture of bonds, oxidation etc.), whereas the original structure of kerogen remains intact by isolation physically, and the decomposition of kerogen starts only under the influence of heat. E.g. we can consider decarboxylation, followed by oxidation of the terminal methyl groups to carboxyl and with the repetition of this process similar to the decomposition mechanism described by B. LÓRÁNT [1972] in his study on the thermal decomposition of fatty acids.

The aim of further investigations is to establish the connections between the possible steps of decomposition of the kerogen from Pula and the effects observable in the derivatograms.

(iv) It seems that the type of kerogens from the different levels of the oil shale occurrence at Pula can be considered as nearly identical, because the kerogens from different layers of the occurrence gave very similar derivatograms (Fig. 6). The bulk of the organic material is built of *Botryococcus braunii* and the deviations among the derivatograms are due to the presence of other organic material (pollens, coalified plant remnants etc.) besides the *Botryococcus*.

(v) The effects appearing in the derivatograms of the original samples at lower temperatures, and accompanied presumably by the decomposition of more volatile organic material are characteristic, however, they are influenced by the inorganic components, hence, the DTA curves of the original samples represent the effects of this interaction. In the DTA curve of some samples (e.g. Group "C") a fairly strong exothermic peak appears at higher temperature, whereas, the DTA curve of kerogen concentrated from the same samples did not show any similar effect, the combustion process is finished at 620–640° C.

Since the particles of the organic material are included in clay minerals and carbonates, respectively, and the bonding between organic and inorganic components apparently can be strong [WILLIAMSON, 1964], the combustion of the organic material

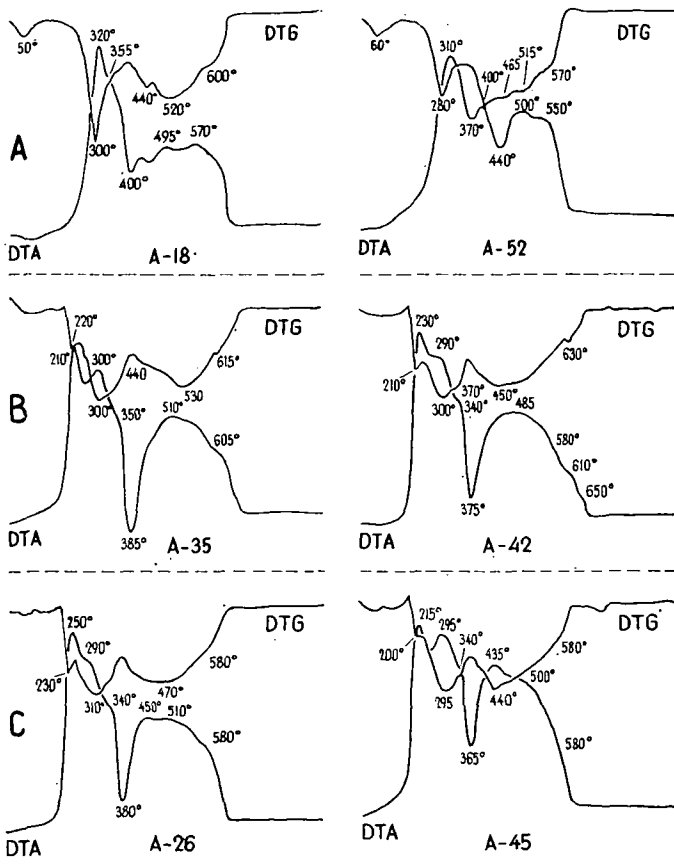


Fig. 6. DTA and DTG curves of kerogen concentrates isolated from samples denoted

at lower temperatures is retarded. Thus, after the decomposition of the organic material, what is finished very soon above  $460^{\circ}\text{C}$  in the case of the original samples according to the DTA curves, the final combustion of the fixed carbon is shifted towards higher temperatures accompanied by the decomposition of the phyllosilicates and carbonates, respectively. It is especially striking in the case of samples rich in organic material, however, it may be observed to a lesser extent also in case of samples of medium organic material content.

### IR-SPECTRA OF KEROGEN CONCENTRATES

#### *Comparison of IR-spectra of kerogens concentrated by physical and chemical methods*

IR-spectra of the kerogen samples were recorded by Zeiss UR-20 spectrophotometer from  $4000$  to  $600\text{ cm}^{-1}$  wave number, in KBr pellet (KBr: 800 mg, sample 5.0 mg). Fig. 7 shows well the differences between the IR-spectra of kerogens physically (*kerogen I*) and chemically (*kerogen II*) concentrated.

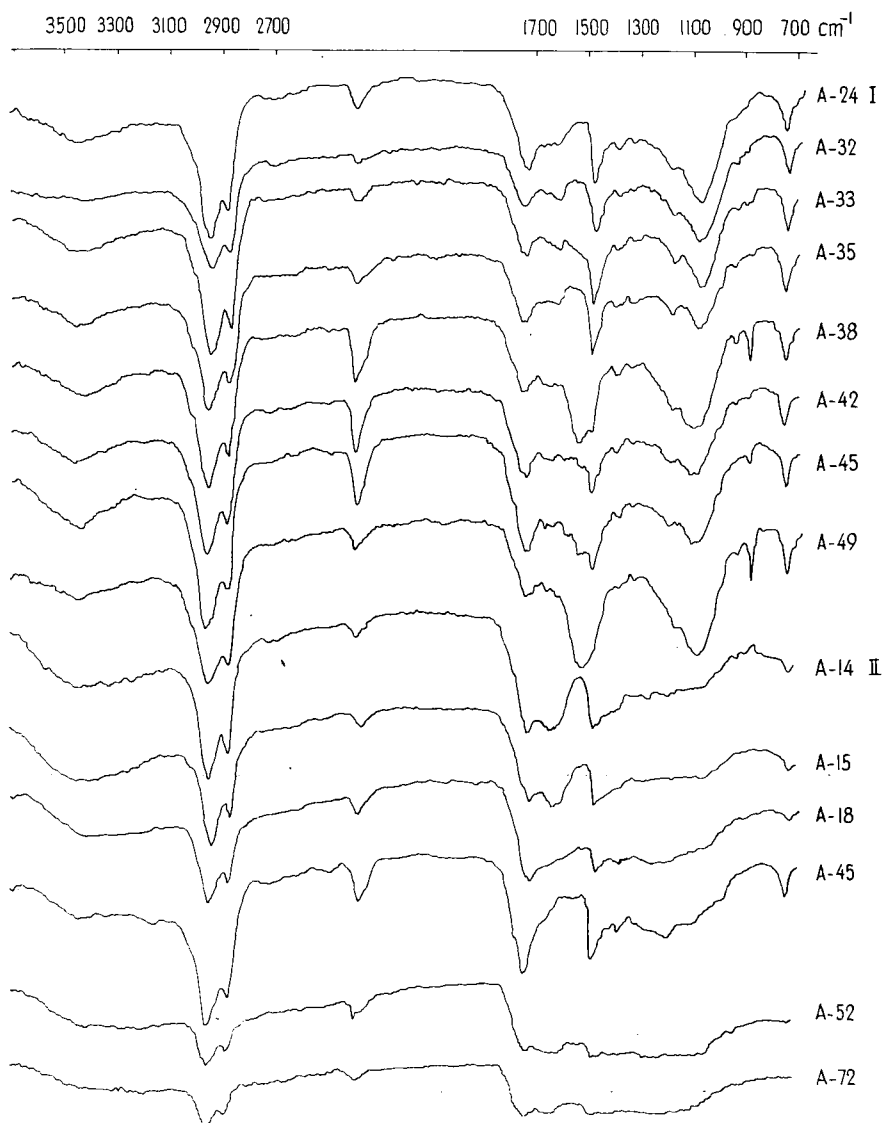


Fig. 7. IR-spectra of the kerogen samples.

Considering the characteristic absorption bands, the following can be established:

(i) In the case of *kerogen I* concentrates, the broad absorption band at 3700–3200  $\text{cm}^{-1}$  may be assigned to OH stretching vibration originated from alcoholic and/or phenolic OH-groups, and moisture, respectively. The latter may be suggested from the symmetric shape of the curve. This absorption band of *kerogen II* concentrates at 3700–3100  $\text{cm}^{-1}$  is broader and non symmetric. The weak band at 1400–1350  $\text{cm}^{-1}$ , hydroxyl in-plane deformation vibration also points to the presence of OH-groups.

Absorption bands in the IR-spectra of kerogen I and kerogen II samples

Kerogen I		Kerogen II	
Wave number cm <sup>-1</sup>	Intensity	Wave number cm <sup>-1</sup>	Intensity
3700—3200	m, (broad)	3700—3100	m, (broad)
2950	vs	2950	vs
2870	s	2870	s
2720—2680	vw	2720—2680	vw
2450	s	2450	m
1750	s	1750	s
1720	s	1720	s
1600	w	1600	m
1550	w	—	—
1480	s	1480	m
1400—1350	w	1400	w
1180	m	—	—
1080	s	—	—
950	vw	—	—
920	vw	—	—
720	m	720	vw

vs: very strong; s: strong; m: middle; w: weak; vw: very weak

(ii) The most intensive bands of the spectra at 2950 and 2870 cm<sup>-1</sup>, respectively, can be assigned to the symmetric and asymmetric stretching vibration of methyl and methylen groups. The overlapping of 2–2 bands point to the complex structure of the samples investigated.

In spectra of the *kerogen I* concentrate the intensity of these bands is stronger than those of the *kerogen II* concentrate and it suggests the assumption that the amount of methyl and methylen groups decreased due to oxidation during the chemical treatment. A similar phenomenon can be observed also in the case of the band at 1480 cm<sup>-1</sup> assigned to the in-plane deformation vibration of methylen groups. The *xy*-deformation vibrations and the in-plane deformation vibrations of methyl and methylen groups coincide with the in-plane deformation vibrations of the OH-group (1400–1350 cm<sup>-1</sup>).

The band at 720 cm<sup>-1</sup> may be explained as an in-plane deformation vibrations of groups containing side-chains with four or more carbon atoms. The intensity of this band is stronger in the spectra of the *kerogen I* concentrate.

(iii) The bands at 1750 and 1720 cm<sup>-1</sup> can be originated from the symmetric and asymmetric vibrations of carbonyl-groups. In spectra of *kerogen II* concentrate the intensities of these bands are nearly equal with those of the methyl and methylen groups at 2950–2870 cm<sup>-1</sup>, whereas, the intensity of carbonyl groups is decreased in the case of *kerogen I* concentrate.

(iv) The absorption band at 1600 cm<sup>-1</sup> can be assigned to the aromatic and/or unsaturated parts of the kerogen molecule.

(v) There are some bands (1180, 1080, 950, 920 cm<sup>-1</sup>) observed only in spectra of the *kerogen I* concentrate, which may be originated partly from aliphatic and



aromatic esthers and aliphatic ethers partly from the mineral constituents not eliminated by the isolation process.

At  $2450\text{ cm}^{-1}$  a strong band in the case of *kerogen I*, and a middle strong in the case of *kerogen II* could be observed. It may be assumed that it is a combination band of C—O stretching vibration and OH in-plane deformation vibration.

### *Changes in the IR-spectra of kerogen concentrates heated to different temperatures*

Portions of sample No. 45 concentrated by physical and chemical method, respectively, were heated to given temperatures in the Derivatograph and the IR-spectra of products obtained at different temperatures were recorded by Pye Unicam SP 1100 spectrophotometer. The actual temperature values reached were read from the T curve of the derivatogramme:

*Kerogen I*:  $260^\circ$ ,  $310^\circ$ ,  $370^\circ$ ,  $430^\circ$  and  $575^\circ\text{ C}$ ,

*Kerogen II*:  $260^\circ$ ,  $310^\circ$ ,  $395^\circ$ ,  $450^\circ$  and  $600^\circ\text{ C}$ .

The increase of the temperature resulted changes in the IR-spectra as follows:

(i) The intensity of OH absorption band gradually decreases. At  $450^\circ\text{ C}$  it can already not be observed in the case of *kerogen II* samples, whereas, in the case of *kerogen I* samples in spite of a strong decreasing tendency, it can be observed still at the highest temperature applied. This fact may be interpreted that the decomposition of the structure of the phyllosilicates (clay minerals) present is not yet completed at this temperature. The band  $900\text{--}850\text{ cm}^{-1}$  appeared only in the spectra of physically concentrated kerogens and does not show any change during the increase of the temperature.

(ii) The intensity of bands at  $2950\text{--}2870\text{ cm}^{-1}$  decreases by increasing temperature in both set of kerogen-concentrates, and it shows minimum already at  $370\text{--}395^\circ\text{ C}$ . A similar decrease of intensity can be observed in the case of bands at  $1480\text{--}1460\text{ cm}^{-1}$  belonging to the methyl-methylen groups.

The intensity of the band at  $740\text{--}720\text{ cm}^{-1}$  shows a decrease parallel to that of the methyl and methylen groups.

(iii) The intensity of bands at  $1750\text{--}1720\text{ cm}^{-1}$  (C=O of carbonyl and carboxyl groups) first increases by increasing temperature, however, from  $370\text{--}395^\circ\text{ C}$  a decrease of the intensity can be stated.

(iv) The absorption band at  $1610\text{--}1600\text{ cm}^{-1}$  shows an increasing tendency in both set of kerogen concentrates and it is the strongest band of the spectrum at  $370\text{--}395^\circ\text{ C}$ .

(v) The intensities of bands at  $1140\text{--}1000\text{ cm}^{-1}$  observed only in the spectrum of the *kerogen I* samples remained unchanged during the heat treatment, thus, they can be originated from inorganic components.

The change of the intensity ratios of absorption bands assigned to the different groups, in function of the temperature, was also considered.

The  $E_{2900}/E_{1600}$  ratio shows a sharp decrease in both set of kerogen concentrates up to  $370\text{--}395^\circ\text{ C}$ , and from this temperature the curve is flattened showing only a slight decrease.

The change of the  $E_{2900}/E_{1700}$  intensity ratio is very similar to the former.

Comparing the change of intensity ratios of  $E_{1700}/E_{1600}$  in the spectra of the *kerogen I* and the *kerogen II* concentrates, it can be established that the curve for the *kerogen I* exhibits a more or less uniform decrease, especially up to  $420\text{--}430^\circ\text{ C}$ ,

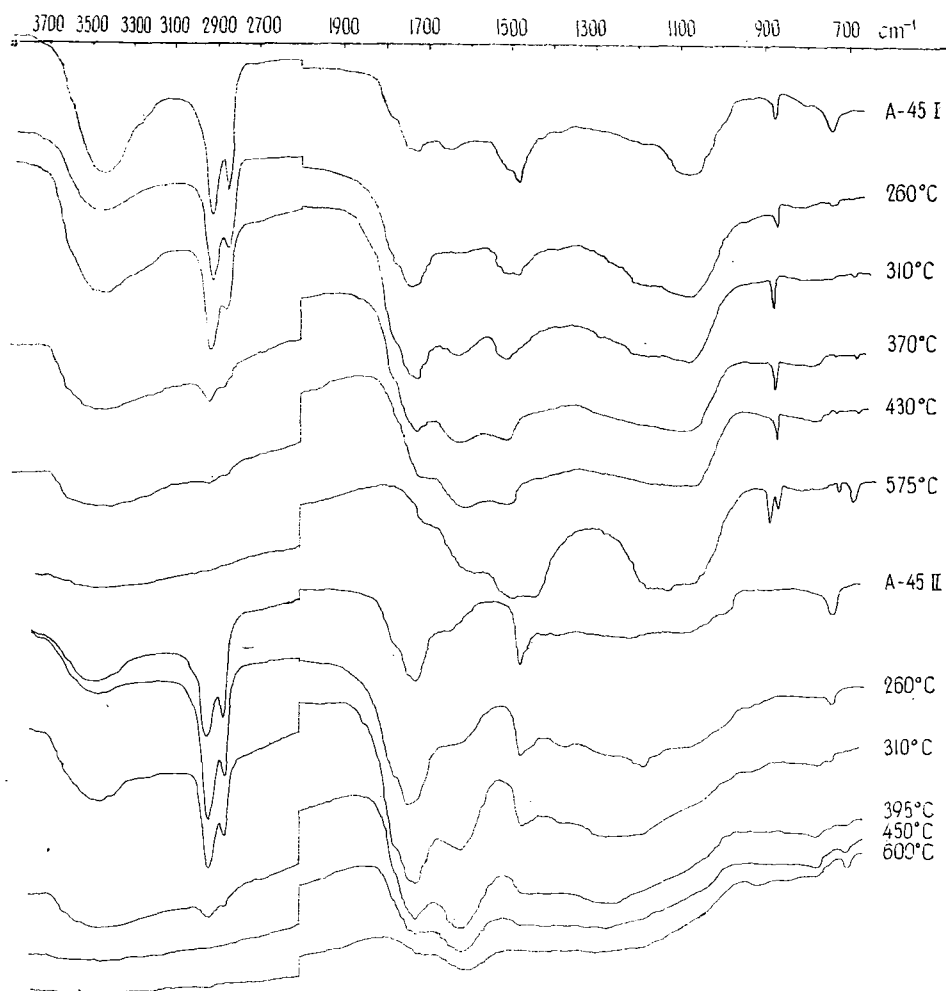


Fig. 8. IR-spectra of kerogen concentrates heated to different temperatures.

and the first section of the curve for the *kerogen II* is somewhat steeper, however, between 300 and 430° C the two curves are nearly parallel to each other.

In comparing the intensity ratios observed in the case of samples heated to 260° C, it can be established that the ratios  $E_{2900}/E_{1600}$  and  $E_{1700}/E_{1600}$  are higher in the spectra of kerogen chemically concentrated, whereas, in that of isolated by physical method the  $E_{2900}/E_{1700}$  ratio shows a higher value. It may be assumed that the methyl-methylen groups remained rather unattacked during the isolation by physical method, whereas, the isolation by chemical processes resulted in at least partial oxidation. The aromatic part of the structure of the kerogen molecule seemingly remained unchanged either using the physical isolation or the chemical one. The amount of aromatic part shows merely a relative increase due to the gradual decomposition of other functional groups under the influence of heat.

The H/C atomic ratio exhibits a decrease in function of the temperature as it is seen in Fig. 9, and no essential difference occurs between kerogen samples isolated by physical and chemical method, respectively.

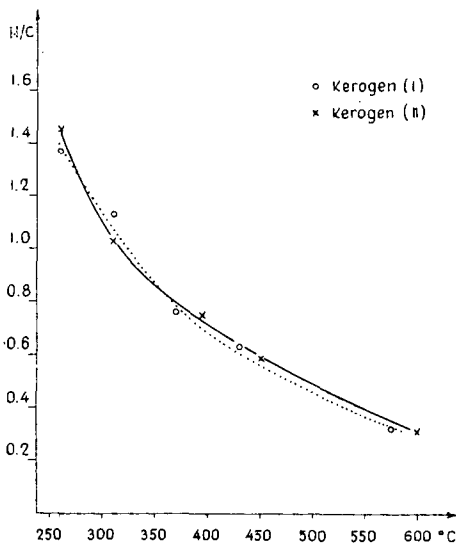


Fig. 9. Change of the H/C atomic ratio of kerogen I and II under the influence of heat.

The analytical determination of the amount of functional groups in the kerogen samples heated to different temperatures and the study of the pyrolysis in nitrogen stream presumably will lead to a more detailed picture.

### CONCLUSIONS

Comparing the change of the intensity ratios of different IR-absorption bands in function of the temperature with the experiences of the derivatographic examinations the following conclusions may be drawn:

(i) The validity of the decomposition mechanism according to LÓRÁNT is very probable regarding the methyl-methylen as well as the carboxyl groups.

(ii) The first section of the DTG curve up to 376°C may be characterized by the gradual oxidation of methyl-methylen groups and decomposition of the carboxyl groups, in accordance with the character of the change of  $E_{2900}/E_{1700}$  and  $E_{2900}/E_{1600}$  ratios exhibiting a fairly steep decrease up to 370–395°C.

(iii) The intensity of the absorption band assigned to aromatic part of the structure is fairly weak and its change under the influence of heat is far not so expressed as the change of the intensities of the bands belonging to the methyl-methylen and carbonyl-carboxyl groups.

(iv) The methyl-methylen bands can be observed in spectra of kerogens heated to 395°C but they are lacking already in the spectra of samples heated to 450°C. At the same time, the band belonging to the carbonyl-carboxyl groups, weak but well observable at 395°C, can be detected also at 600°C. Furthermore, the intensity of the aromatic band shows an increasing tendency up to 395°C, then between 450–600°C decreases, but even at 600°C remains well observable.

These facts suggest that the second section of the DTG curve (from 376° to 636° C in the case of the *kerogen I* concentrate and from 373° to 615° C in that of the *kerogen II* sample, on average) represents the decomposition of the carbonyl-carboxyl groups not yet decomposed and dominantly that of the aromatic structures. In the first section of the DTG curve (and similarly, of the DTA curve) well defined, sharp peaks appear, the rate of reactions taken place within this temperature interval is faster than that of the reactions in the second DTG (and DTA) section. The second section of the DTG curve extends over a somewhat larger temperature interval than the first one, and individual peaks can not be distinguished in it, they are united in a broad maximum. These facts are in accordance with the rate of changes of intensity ratios of characteristic absorption bands.

#### ACKNOWLEDGEMENT

The authors express their gratitude to DR. Á. JÁMBOR making available for them the samples investigated and the data of the FISCHER-assay and to DR. J. KONDA, Director of the Hungarian Geological Institute encouraging and assisting this research work.

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*Manuscript received, September 30, 1977*

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