CHARACTERIZATION OF INSOLUBLE ORGANIC SUBSTANCE OF SEDIMENTS BY THERMAL AND INFRARED INVESTIGATION

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INTRODUCTION

According to Forsman and Hunt [1958] three different types of the kerogen, in organic solvents insoluble organic matter of the sediments, may be distinguished. Two of these types, except the coaly type kerogen, may be considered as an important step toward oil formation. The investigation of the horizontal and vertical distribution of these kerogen types as well as recording of this distribution on geological sections presumably contributes to indicate and outline the sediments to be considered as mother rock.

The total organic carbon (C_{org}) content of the sediments investigated is fairly low. It changes between 0.14 and 0.83 per cent on the basis of investigation of several cores from different borings. The very low organic matter content also resulted in that only a low grade enrichment of organic material could be obtained by the izolation method generally used.

Concerning the characterization of the insoluble organic matter of the sediments — taking into account the low grade enrichment, too — the question arose first of all whether it would be possible to distinguish by a simple method the insoluble organic matter of coaly character and that showing probably kerogen-like properties.

The question may be presumably answered by infrared spectroscopic and derivatographic investigations.

PREPARATION AND CHARACTERIZATION OF THE SAMPLES

The samples are originated from the boring cores of the Lower Pannonian sediments of the southern part of the Hungarian Gieat Plain. The samples are mostly of marly, lime-marly character with more or less dolomite and Mg-limestone, respectively.

The soluble organic content of the samples ground below 0,06 mm grain size was extracted in Soxhlet-extractor and after removing the carbonates the silicates of the samples were decomposed by hydrofluoric acid-treatment and removed by repeated washing and centrifugation. The process was continued by sodium carbonate treatment followed by repeated washing and centrifugation. The humic acids were removed from several samples by digestion with 0,5 N NaOH on water-bath.

The total organic carbon content of the samples was determined by Dr. Kaschka (Ernst—Moiitz—Arndt University, Department of Geology, Greifs-

wald, GDR). Further, the chloroform-soluble organic material (Bitumen A) was also determined and the bitumen coefficient of the samples calculated on the basis of the following equation:

$$\text{bitumen coefficient} = \frac{\text{Bitumen A \%}}{C_{org}\% \cdot 1{,}7},$$

where 1,7 is the factor to recalculate the C_{org} content to organic material according to Rodionova.

To support the identification of insoluble organic substance concentrated the infrared spectroscopic and thermal investigation of different coaly organic materials was also carried out.

*Samples of investigation, their location and depth as well as the $C_{org}\%$,***
Bitumen A % and the bitumen coefficient

Sample №	Location and depth (m) of boring		$C_{org}\%$	Bit. A%	Bit. koeff.
S-1	Kelebia	545,4—645,5	0,39	0,03	4,69
S-5	Kelebia	842,4—842.5	0,58	0,11	11,43
S-6	Kelebia	898,4—899,4	0,14	0,12	49,16
S-7	Kelebia	947,3—947,8	0,58	0,08	7,75
S-8	Kelebia	1000,5—1001,5	0,43	0,09	12,19
S-9	Kelebia	1052,5—1053,0	0,52	0,23	26,47
S-10	Kelebia	1085,0—1085,4	0,66	0,13	11,25
S-12	Ásotthalom	987,0—987,2	0,43	0,14	19,45
S-14	Ásotthalom	1079,2—1079,5	0,27	0,05	10,43
S-16	Kkdorozsma	2155,0—2156,0	0,46	0,05	6,28
O-21	Pföldvár	1474,0—1477,0	0,58	0,14	13,97
O-22	Pföldvár	1526,0—1529,0	0,39	—	—
O-24	Pföldvár	1397,0—1400,0	0,43	0,27	36,98
O-28	Pföldvár	1383,0—1386,0	0,46	0,17	22,05
O-33	Pföldvár	1819,0—1820,0	0,54	0,12	12,61
O-40	Pföldvár	1978,0—1979,0	0,50	0,16	19,17
O-46	Pföldvár	1774,0—1775,0	0,50	0,06	7,53
O-48	Pföldvár	1747,5—1751,5	0,23	—	—
O-49	Pföldvár	1715,0—1718,0	0,54	0,26	28,47
O-50	Pföldvár	1778,0—1779,5	0,47	0,15	19,00
O-51	Pföldvár	1780,0—1784,0	0,50	0,46	54,47
O-53	Pszőlős	1690,0—1691,5	0,29	0,11	22,65
O-54	Pszőlős	1702,0—1704,0	0,31	0,21	39,24
O-56	Pszőlős	1764,0—1769,0	0,36	0,—	—
O-57	Pszőlős	1769,0—1773,0	0,35	0,22	38,13
O-66	Pszőlős	1773,0—1777,5	0,51	0,03	3,91
O-67	Pszőlős	1556,0—1562,0	0,39	0,08	12,27
O-71	Pszőlős	1040,0—1046,0	0,45	0,05	6,84
O-73	Pszőlős	1770,0—1774,0	—	—	—
O-80	Battonya	1004,0—1009,5	—	—	—
O-94	Pszőlős	1770,0—1771,5	—	—	—

** C_{org} means the total organic carbon content determined by combustion above 1000 °C in oxygen stream.

Many authors have dealt with infrared spectroscopic investigation of different organic materials as this method proved to be very useful in identifying the functional groups of organic substances of different kind.

The infrared spectra of the comparison material and the samples investigated were taken by a Unicam SP 200 type spectrophotometer in the range of 650—5000 cm^{-1} vawe number.

The intensive absorption bands in the spectrum of the Estonian kukersite at 2.900, 1.700 and 1.460 cm^{-1} point to the dominating character of aliphatic structure.
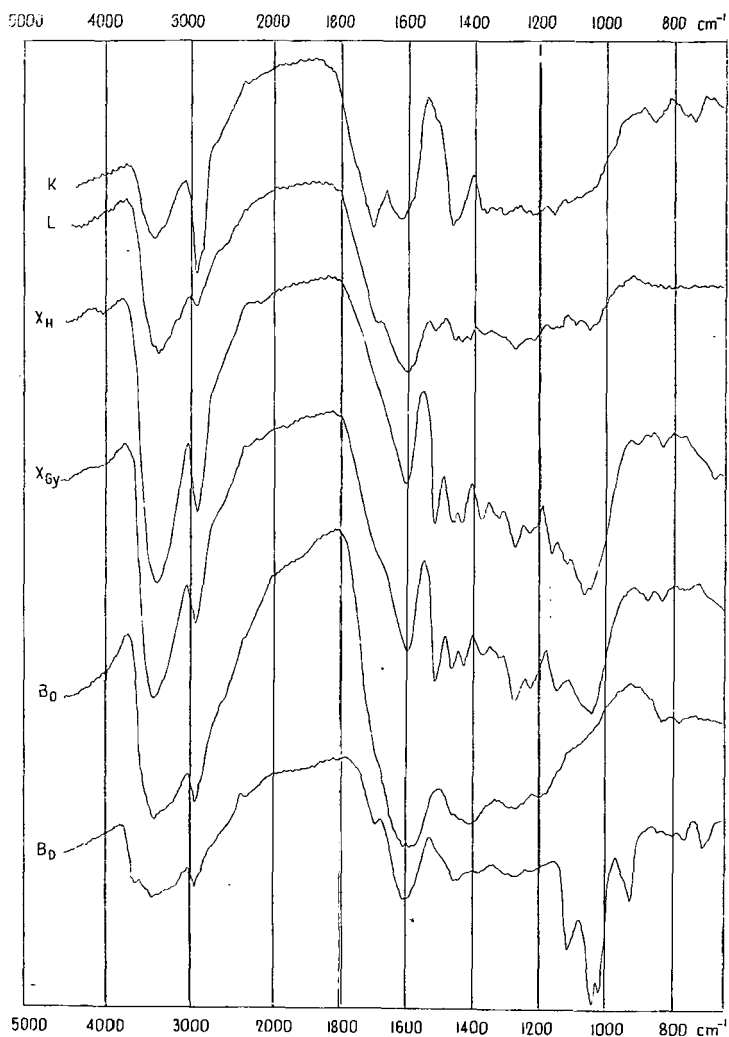
Fig.1. Infrared spectra of materials for comparison. K = kukersite (Estonian SSR), L = lignite, K$_H$ = xilite (Herend, Hungary), X$_{Gy}$ = xilite (Gyöngyös-Visonta, Hungary), B$_O$ = brown coal (Orosz-lány, Hungary), B$_D$ = brown coal (Dorog, Hungary).

243

While investigating the Green River oil-shale kerogen FORSMAN and HUNT [1958] from the significant intensity of bands at 2.857 and 1.449 cm^{-1} also found in this keiogen the presence of less aromatic and more aliphatic structure. The absorption band at 1.613 cm^{-1} may be attributed to a C=C bonding or to conjugated carbonyl-groups, according to KINNEY and SCHWARTZ [1957]. Investigating the infrared spectrum of the Green River oil-shale kerogen, ROBINSON [1969] attributed the intensive bands at 2.900 cm^{-1} and 1.460 cm^{-1} to methyl- and methylen-groups and interpreted the strong absorption in the range 1.680—1.720 cm^{-1} by the presence of carbonyl-groups. According to CALIKOWSKI and GONDEK [1968] the intensive absorption bands at 2.926 cm^{-1}, 2.853 cm^{-1} and 1.470 cm^{-1} point to methylen-groups whereas the bands at 2.926 cm^{-1} and 1.383 cm^{-1} to methyl-groups.

In the infrared spectrum of xilite samples shown in *Fig. 1* the significant absorption at 1.520 cm^{-1}, 1.600 cm^{-1} and 2.900 cm^{-1} indicate that they are mostly of aromatic structure with aliphatic side-chains. The bands between 1.000—1.500 cm^{-1}
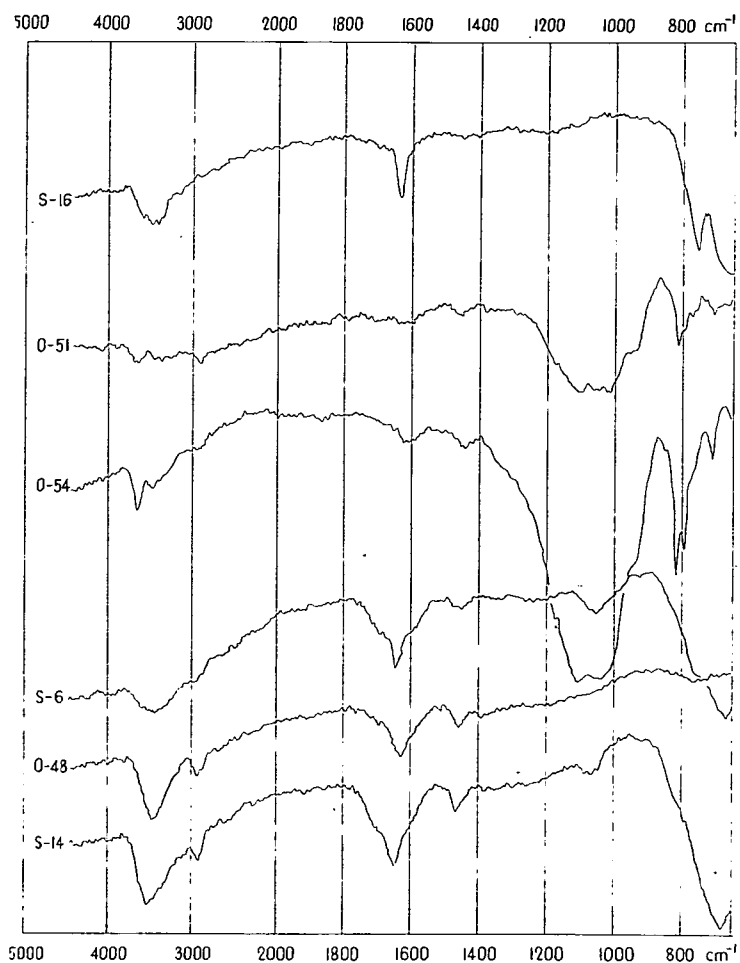
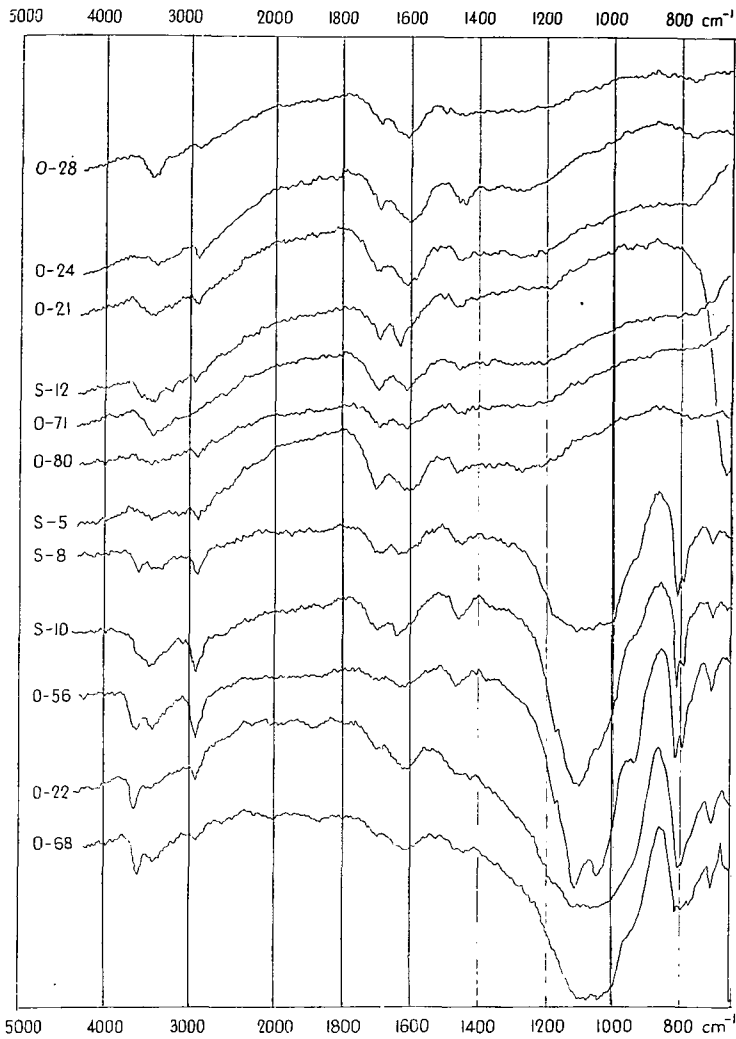*Fig. 2.* Infrared spectra of samples belonging to Group I

244

Fig. 3. Infrared spectra of organic substances belonging to Group II

may be originated by alcoholic OH-groups and substituted aromatic rings. In the spectrum of the xilite samples investigated the lack of absorption at $1.700 \ cm^{-1}$ is characteristic whereas at this wave number a definite absorption may be established in the spectrum of the Estonian kukersite kerogen. The same is clearly seen in the spectrum of lignite as well as in that of the brown coal samples, though with lower intensity. The infrared spectrum of the lignite, xilite and brown coal samples shows an intensive absorption at about $1.600 \ cm^{-1}$.

Comparing the infrared spectra of the samples investigated and grouping those samples showing similarity in their main features, three groups may be distinguished.

In the spectra of samples of Group I the absorption band in the range 3.450—3.640 cm^{-1} attributed to OH-group appears with variable intensity, weak or no absorption may be established at 2.920—2.960 cm^{-1}, definite absorption may be observed at 1.625—1.642 cm^{-1} in the spectrum of several samples and a weak absorption at 1.440—1.460 cm^{-1} with about the same intensity as the band at 2.920 cm^{-1}. The lack of absorption at 1.700 cm^{-1} is characteristic to Group I as it was characteristically lacking also in the spectra of xilite samples and did not appear or merely with very weak intensity in the spectra of lignite and brown coal samples whereas was very definite in the spectra of Estonian kukersite kerogen.

The infrared spectra of the samples belonging to Group II shows an absorption in the range 3.450—3.680 cm^{-1}, however, with weaker intensity than the spectra of samples of Group I. On the contrary, the intensity of the absorption in the range 2.920—2.960 cm^{-1} is greater in most of the samples of Group II as compared to the intensity of the former band than in the case of Group I. Especially characteristic of Group II
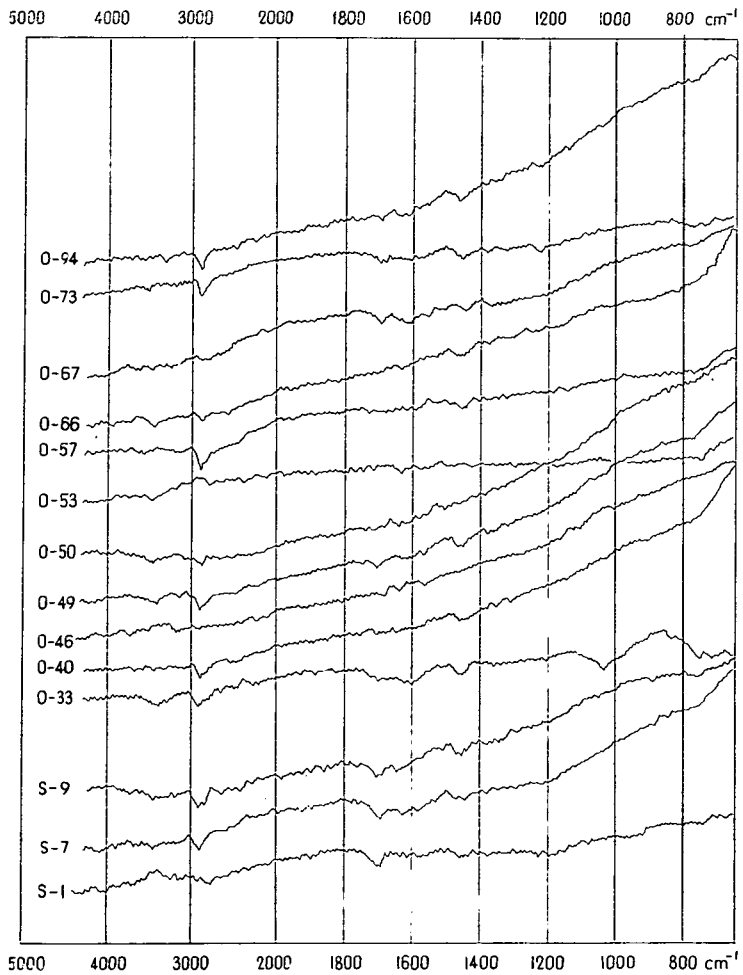

Fig. 4. Infrared specta of organin substances of group III

of less volatile compounds and the "fixed" carbon, respectively. According to the derivatograms the combustion of the organic material cannot be taken as complete till 600—700 °C since the TGA curves show a further if small loss of weight at higher temperatures, too.

In identifying the organic substance beside the DTA curves especially the consideration of the peculiarities of the DTGA and TGA curves may be helpful. Disregarding the very first endothermic effect at about 100 °C, the more pronounced the DTGA maximum between 200—300 °C and the corresponding TGA step showing to a significant loss of weight, the greater is the proportion of high volatile compounds, whereas, by decreasing amount of high volatile components the second DTGA maximum above 350 °C shifts toward higher temperatures and will be more intensive and, correspondingly also the TGA step of a more pronounced loss of weight shifts toward higher temperature ranges.

D. R. WILLIAMSON [1964] summing up several data concerning the thermal decomposition of Estonian oil shale kerogen, stated that the softening of the kerogen and the lost of the high volatile compounds begins at about 320—340 °C, whereas the decomposition of the less volatile components requires about 450 °C. In his paper, referring to the results of several authors, it is mentioned that the kerogen does not transform into soluble material below 325 °C and that the rate of the
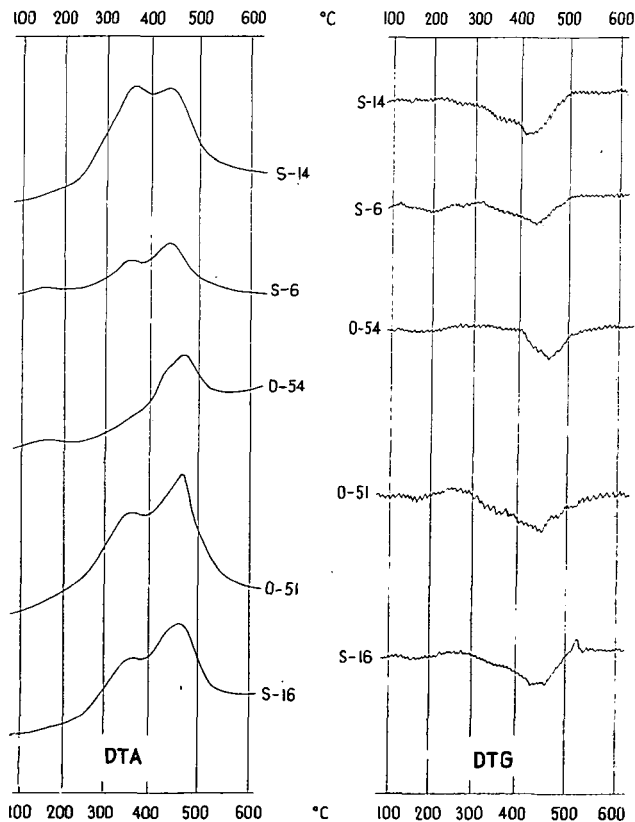

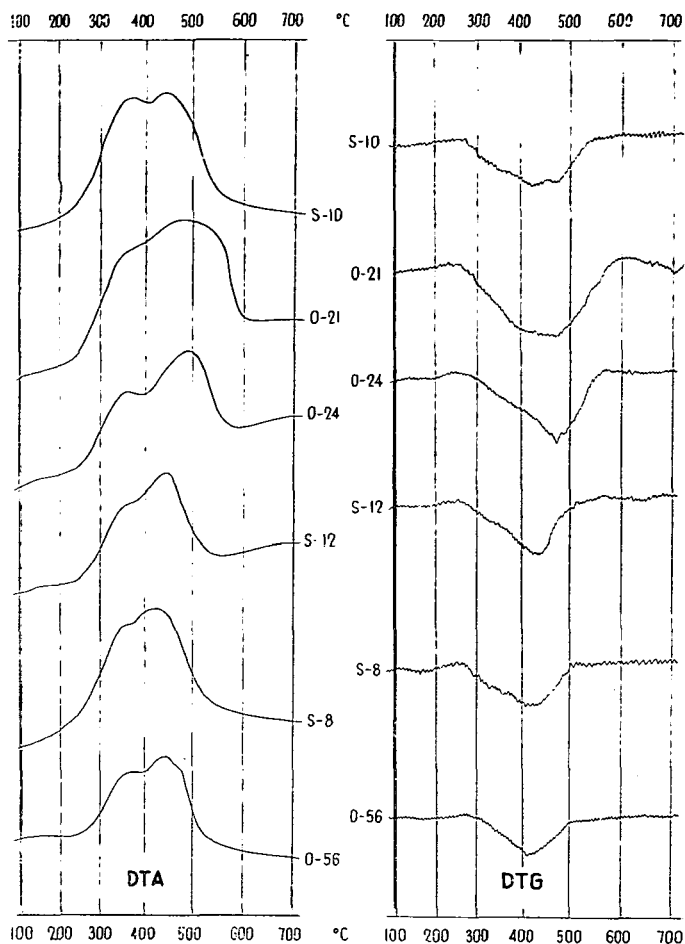Fig. 6. Exothermic effects on the DTA and DTGA curves of samples of Group I

Fig. 7. Exothermic effects on the DTA and DTGA curves of samples of Group II

decomposition of the kerogen is nearly the same in 350—437 °C and 437—525 °C ranges and finally, an expressed change may be established in the rate of decomposition at 437 °C. Naturally, deviations from the values mentioned both toward the lower and the higher temperatures are possibly depending on the character of the kerogen sample.

The steps mentioned can also be recognized on the derivatogram of the kukersite kerogen used for comparison (in the figure showing only the DTA and DTGA effects in connection with the decomposition of the organic material) with more or less temperature deviations. On the TGA curve a very pronounced step appeared in the range 235—360 °C which equals to about 17 per cent loss of weight, the next two TGA steps at 360—460 ° and 460—580 °C are of the same intensity and the two corresponding DTGA maxima have also nearly the same character. The former step means 37 per cent and the second 39 per cent loss of weight. It seems that the evaluation of the character of the TGA and DTGA curves i. e. that of the

250

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