

IR AND NMR CHARACTERIZATION OF OIL GENERATED FROM SOME HUNGARIAN OIL SHALE AT 773 K

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INTRODUCTION

Near Pula (Transdanubian Central Mountains, Hungary) oil shale beds were found filling one of the Upper Pannonian basalt crater [JÁMBOR and SOLTI, 1975]. Subsequently to this discovery several oil shale beds were found which can be assigned to two genetic groups [JÁMBOR, 1980]:

1. Beds accompanying the Pliocene basalt volcanism filling the craters: e.g. Pula, Gércse, Várkesző, etc.

2. Oil shales occurring in the areas of Neogene lagoons of foothills: e.g. the indications of Várpalota, Budajenő, Kaposcs, etc.

Though these oil shales are of low grade, their organic matter content is higher than that of the sediments of the Great Plain of similar age. Thus, these provide favourable possibility to produce pure kerogen of greater quantities, consequently to carry out investigations serving the more precise knowledge of the kerogen features.

The thermal behaviour of the organic matter of oil shales is significant from two points of view: first of all from that of the industrial utilization since nowadays the aboveground or in-situ retorting are the most common utilization of oil shales [DINNEEN, 1976]; the second reason is the better knowledge of the formation conditions and evolution of the components of organic matter, first of all those of hydrocarbons [TISSOT *et al.*, 1971, 1974, 1978].

In our department the investigation of kerogen characteristics deriving from the Pula oil shale is in progress for several years [GRASSELLY *et al.*, 1977; HETÉNYI *et al.*, 1977, 1978, 1979]. Since the features of kerogen deriving from a given area are affected by numerous factors (quality of precursors, mineral composition, environmental effects, etc.), the researches on kerogen are rather complex, thus all the plus information may promote the knowledge of this inert matter being important not only from the theoretical but also from the economic point of view. Thus, in addition to the investigation of kerogen, the features of the soluble matter suitable to direct analyses and degrading from the kerogen itself, are also studied.

EXPERIMENTAL

Analyses were carried out at different temperatures and durations on some oil shales of Hungary. Their characteristic data are comprehended in Table 1. In the following only the shale oils generated at 773 K during 1 hour will be dealt with.

Thermal treatment was carried out in a Heraeus-furnace controlled by thermostat in oxygen-free nitrogen gas flow. The liquid products, i.e. oil and water

Characteristic data of some Hungarian oil shales

TABLE 1

Locality	Age	Bitumen content %	Ash %	CO ₂ %	C _{org} %
Várkesző	Pliocene Upper Pannonian	6.80	68.5	2.7	13.4
Pula	Pliocene Upper Pannonian	4.60	46.3	9.7	27.3
Várpalota	Miocene Badenian	6.6	62.4	3.1	20.1
Mecsek	Miocene Carpathian	0.3	71.9	16.8	4.3

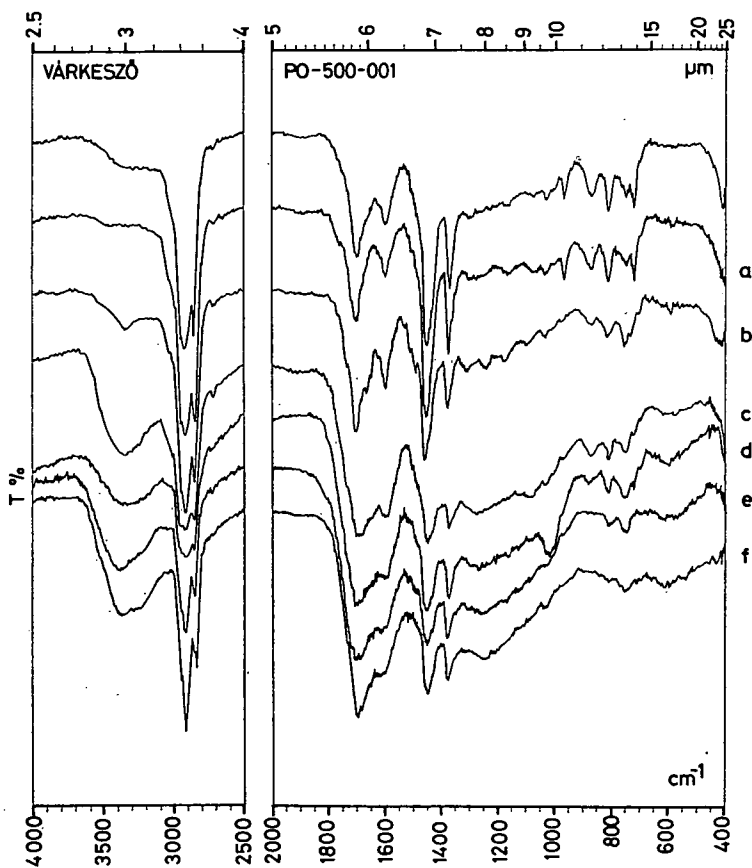


Fig. 1. The IR spectra of crude shale oil from Várkesző and that of its column chromatographed fractions

TABLE 2

Column chromatographic results of some Hungarian shale oils and crude oil from Algyő

Sign of the fraction	Solvent	Várkesző		Pula		Várpalota		Mecsek		Algyő-2	
		Quantity (g) of the fraction	Proportion (%)	Quantity (g) of the fraction	Proportion (%)	Quantity (g) of the fraction	Proportion (%)	Quantity (g) of the fraction	Proportion (%)	Quantity (g) of the fraction	Proportion (%)
a	hexane	0.4180	73.22	0.6590	73.47	0.6914	62.73	0.5138	78.56	0.6783	72.00
b	hexane: benzene 1:1	0.0127	2.22	0.0710	7.92	0.0600	5.44	0.0307	4.69	0.0150	1.59
c	benzene	0.0272	4.76	0.0580	6.47	0.0879	7.97	0.0275	4.20	0.0450	4.78
d	chloroform	0.0190	3.33	0.0335	3.73	0.0775	7.03	0.0210	3.21	0.0090	0.95
e	acetone	0.0140	2.45	0.0480	5.35	0.0202	1.83	0.0030	0.46	0.0040	0.42
f	methanol	0.0083	1.45	0.0090	1.00	0.0167	1.52	0.0070	1.07	0.0050	0.53
		0.4992	87.43	0.8785	97.94	0.9537	86.52	0.6030	92.19	0.7463	80.27

were trapped in a tank adjusted to the end of the heating tube. The shale oil was separated by shaking in chloroform in a separating filler. The solvent was evaporated at 333 K in drying oven, then the crude shale oil was chromatographed on alumina as reported earlier in the column chromatography of bitumen of the Pula oil shale [PÁPAY, 1979]. The column chromatographic data of different shale oils, as well as of the petroleum deriving from the Algyó-2 Upper Pannonian reservoir are shown in Table 2. (The volatile components of the oil were eliminated at 323 K under water-jet vacuum.) It is characteristic of all the oils that the hexane fraction is of highest amount and, as it has been expected, these fractions consist mainly of apolar compounds, thus the efficiency of chromatography is high.

To determine the qualitative composition of the oils the IR records of the starting oils and fractions were carried out by means of a Specord 75 IR spectrometer in the range of $4000\text{--}400\text{ cm}^{-1}$ wavenumber. Spectra were recorded by means of film record of 0.02 mm in case of the crude oils and of the first three fractions, while in case of the fractions *d*, *e* and *f* spectra were recorded by means of the KBr-method (pellets of 20 mm diameter were pressed at about 18 MPa under vacuum).

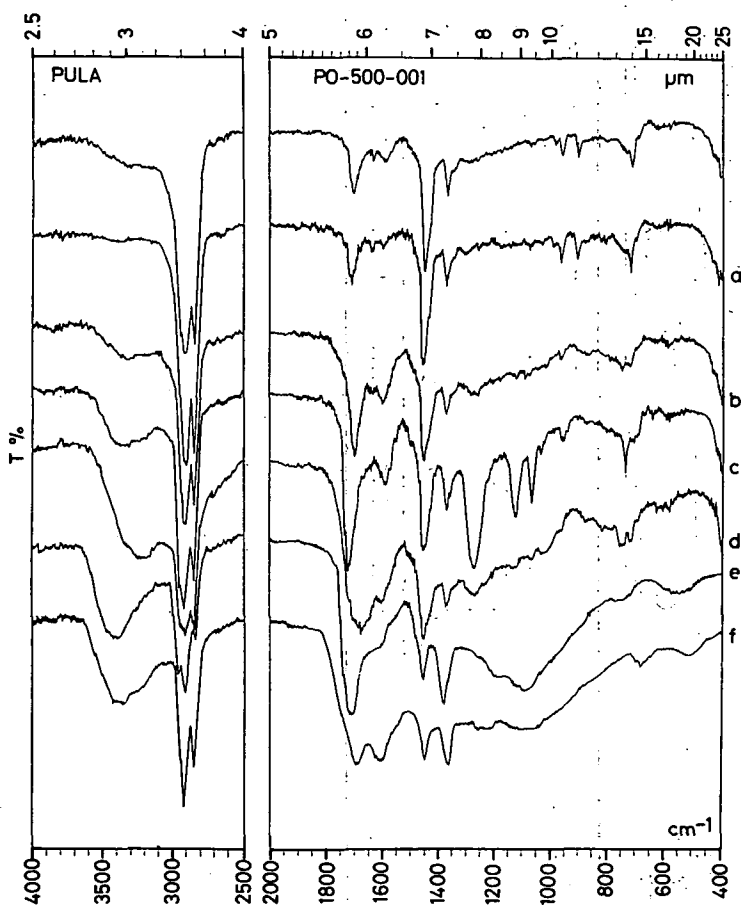


Fig. 2. The IR spectra of crude shale oil from Pula and that of its column chromatographed fractions

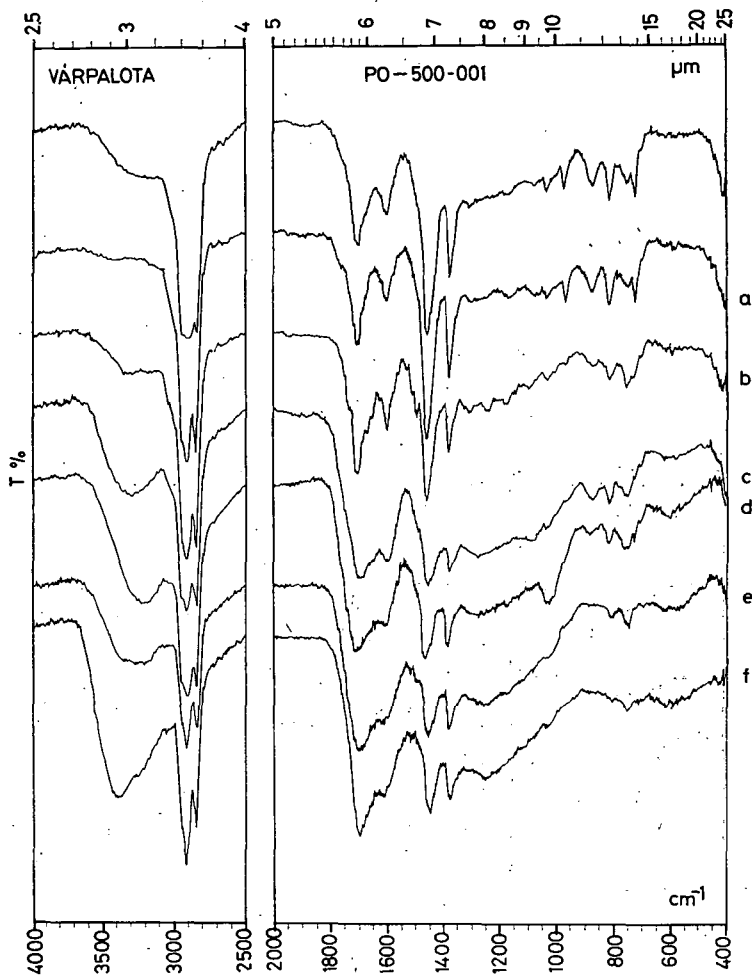


Fig. 3. The IR spectra of crude shale oil from Värpalota and that of its column chromatographed fractions

It is seen in the IR records of shale oils (Figs. 1—4) that the crude oils and their hexane fractions are qualitatively rather similar, only the νOH band is lacking in the hexane fractions. Some differences in the intensities of the bands relate to slight quantitative differences. In addition to the long unbranched paraffins ($\nu_s \nu_{as} \text{CH}_2$, CH_3 2960—2850 cm^{-1} , $\delta_{as} \text{CH}_3$ and $\beta_s \text{CH}_2$ 1460 cm^{-1} , $\delta_s \text{CH}_3$ 1370 cm^{-1} and β_{as} 720 cm^{-1}) bands relating to the presence of mono- and di-substituted aromatic hydrocarbons are also found in the spectrum (1600—1500 cm^{-1} : aromatic νCC , γ (=CH) 810 and 750 cm^{-1} , γCC 700 cm^{-1}). The νCO band at 1710 cm^{-1} occurs in all records with low intensity, but the quantity of carbonyl is very low. In addition to the bands mentioned above, in the spectra of the shale oils of Pula (Fig. 2) and Värpalota (Fig. 3) weak νCC at 1640 cm^{-1} and γ (=CH₂) at 990, 910 cm^{-1} can be observed being characteristic of the terminal vinyl groups. Taking into account the

relative intensity of the band at 720 cm^{-1} indicating the chain length of paraffins, the shale oil of Várkesz6 shows the shortest chain.

In fractions *b* (hexane:benzene 1:1) the quantity of oxygen increased indicated by the appearance of slight intensity of the νOH and by increase of intensity of the νCO band. In the Várpalota sample (Fig. 3) small ester bands occur in the "finger print" range ($1300\text{--}1000\text{ cm}^{-1}$). The increase of quantity of the aromatic compounds is indicated by the intense band at 750 cm^{-1} . Concerning their quality, in this range also mainly hydrocarbons are found.

In the *c* (benzene) fractions the νOH and νCO bands are intense. In case of the Mecsek sample (Fig. 4) ester bands are found at 1280 , 1130 and 1070 cm^{-1} . The proportion of aromatic compounds is considerable.

According to the functional groups in the fraction *d* (chloroform) mostly long-chain alkyl-aryl ketons and alcohols are found. In the Mecsek sample the band of 720 cm^{-1} occurs as a shoulder on the band of 750 cm^{-1} indicating that among the chloroform fractions of the samples the carbon chains of this sample is the shortest.

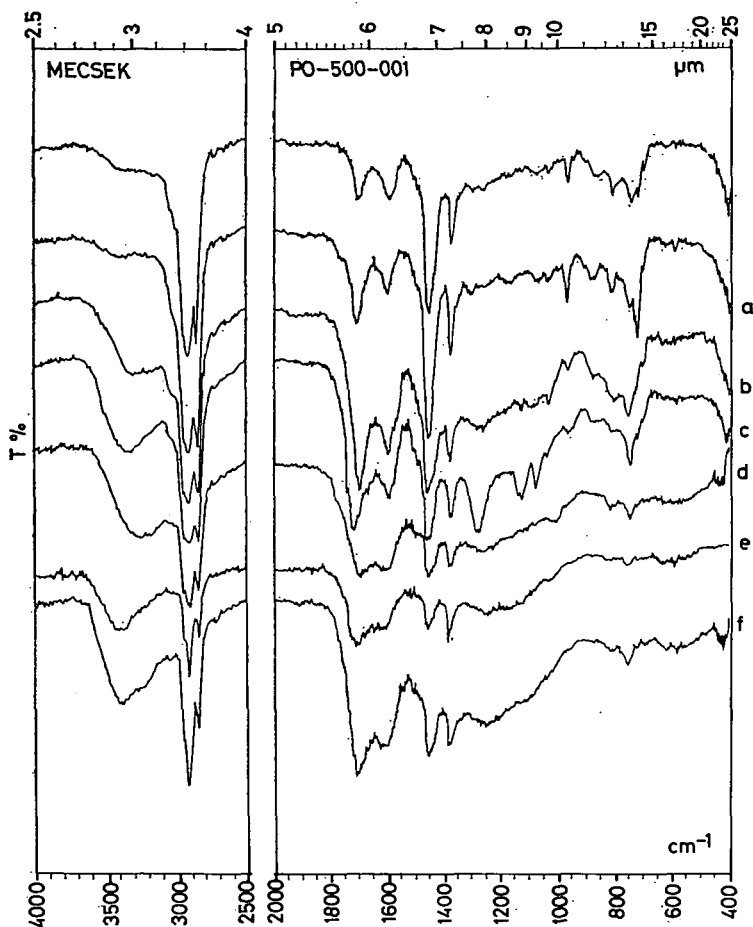


Fig. 4. The IR spectra of crude shale oil from Mecsek and that of its column chromatographed fractions

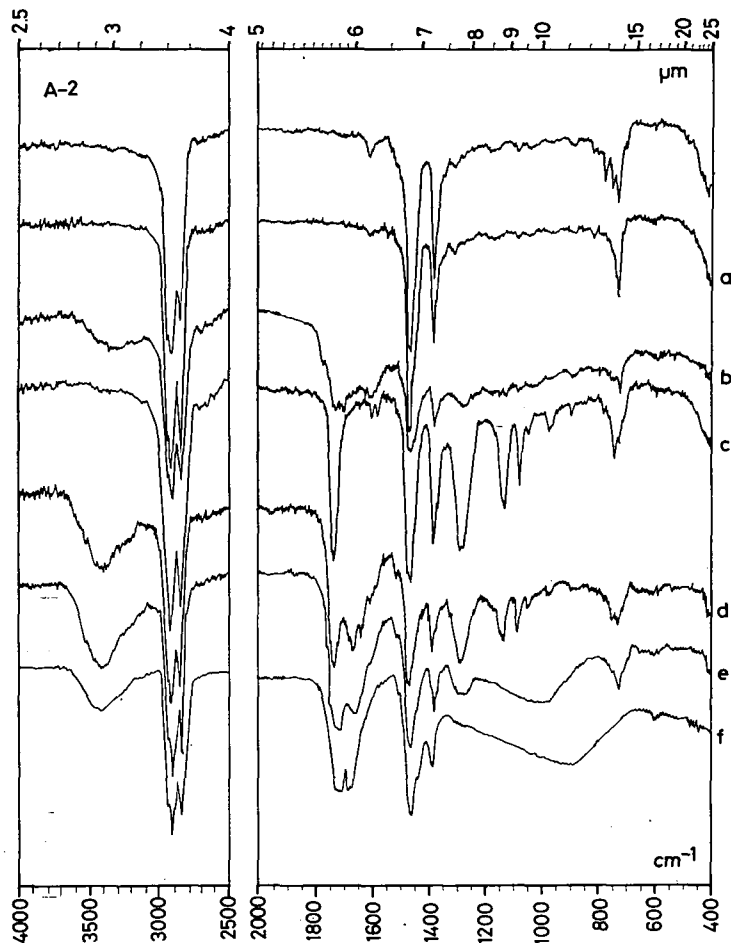


Fig. 5. The IR spectra of crude oil from Algyó and that of its column chromatographed fractions

Spectra of the fractions *e*. (acetone) and *f* (methanol) are of similar character. The νOH and νCO bands are intense. In the spectra of both fractions bands relating to the presence of more or less aromatic compounds are found. The band of 720 cm^{-1} is usually absent or appears as a weak shoulder on the aromatic oscillations. The intensity of the band 1370 cm^{-1} is the same or somewhat higher in most of the spectra. Consequently, in these fractions first of all branched as well as aromatic compounds are found.

In Fig. 5 the IR spectra of the paraffinic oil and of its column chromatographed fractions are shown, the oil deriving from the Algyó-2 Upper Pannonian reservoir. The features described in case of shale oils are valid also of the crude oil, but some differences can also be observed. As compared to the shale oils, in the fractions *a* of the oil and in the oil itself the carbonyl band is absent and occurs only from the *b* (hexane:benzene 1:1) fraction. Consequently, oxygen-bearing compounds occur also in the oil in slight amounts, but their quantity is less than in shale oils.

Further, in the spectra aromatic bands are indicated which is lacking in the hexane fraction and occurs only in the subsequent fractions.

The IR records provide information on the character of the functional groups. Nevertheless, information on the differences, of quality (e.g. distribution of the aliphatic and acyclic compounds, the average chain length, the approximate distribution of the quality of carbon chains) can only be obtained by NMR records (POPLE *et al.*, 1959; JACKMAN and STERNHELL, 1969]. NMR records were made by a JEOL C-60 HL type spectrometer, in carbon tetrachloride. The values of crude oils and of their hexane fractions (h.) calculated from NMR records are shown in Table 3.

TABLE 3
Characteristic values of oils and their hexane fractions calculated from NMR records

Locality	Length of the average paraffinic carbon skeleton	Quality of the carbon skeleton		
		Aliphatic %	Alicyclic %	Aromatic %
Várkesző	C ₁₀	48	31	21
Várkesző h.	C ₉	52	26	22
Pula	C ₁₆	60,5	30	9,5
Pula h.	C ₁₃	60	30	10
Várpalota	C ₁₃	55	27	18
Várpalota h.	C ₂₀	54	31	15
Mecsek	C ₁₆	39	35	26
Mecsek h.	C ₁₇	35	35,5	29,5
Algyő-2	C ₈	80	7	13
Algyő-2 h.	C ₉	94	6	—

Accordingly, the average chain length is greater in the shale oils than in crude oils, except the case of Várkesző. The gas chromatographic analyses of some oil proved that data calculated from the NMR records are correct as tendency but the average paraffin chains are somewhat longer. This difference is caused by the fact that the NMR instrument does not make difference between the shorter lateral chains of the aromatic compounds and the paraffins, so the chain length of paraffins is longer by 2 to 4 carbon atoms. When calculating the paraffin content, however, this increase would mean a change of only 3 to 4%. According to the NMR data it is characteristic of the quality of shale oils that these consist of paraffin (40—60%), cycloparaffin (relatively constant value of about 30%) and of aromatic compounds (10 to 26%). The quantity of aromatic compounds is lowest in the oil shale of Pula and highest in the Mecsek sample.

The oil of Algyő is rich in paraffins, the quantities of acyclic and aromatic compounds is subordinated. According to the gas chromatographic analyses the aromatic compounds consist three kinds of xylol isomers and of ethyl-benzène.

SUMMARY

According to the IR and NMR analyses of the oils generated at 773 K from oil shales of Hungary, the shale oils consist in 70 to 80% of hydrocarbon mixtures of paraffins, cycloparaffins and aromatic compounds. The other part of shale oils contains hetero-atomic compounds, first of all oxygen, in form of ketons, alcohols, esthers, etc.

When studying the data as a function of geological age, it can be stated in the oils generated from oil shales containing organic matter of the same type that in addition to the alicyclic compounds of relatively constant and high amount the quantity of paraffins is lowest and that of aromatic compounds is highest in the oldest Mecsek sample (Carpathian). As the geological age becomes younger, the quantity of paraffins increases, that of the aromatic compounds decreases. The IR records show that the oxygen content is relatively highest in the Upper Pannonian samples and relatively lowest in the samples of Carpathian stage.

These statements concern the oils containing organic matter of the same type since, in harmony with the investigations carried out so far, the kerogen of the Upper Pannonian oil shales of Pula and Várkesző is of different type. Thus, the oil shale of Pula is assigned to the group I of the VAN KREVELEN diagram (algal origin) while that of Várkesző is presumably a mixed type which contains plant remnants of higher evolution, *i.e.* more humic components, in addition to the ingredients of algal origin (personal communication of M. HETÉNYI).

These results verify the decomposition theory of TISSOT *et al.* which stated that in the course of maturation of the organic matter of sediments first the hetero-atomic bonds are broken, this is followed by the decomposition of the aliphatic chains and the state of aromatization of system increases. Based on our measurements this can be supplemented by the fact that the release of hetero-atoms (first of all of oxygen) proceeds not only by the release of compounds small molecular weight (CO_2 , H_2O , etc.), but together with these oxygen-containing compounds of greater molecular weight, *e.g.* ketons may also released. This statement is verified also by the IR records of shale oils in which the carbonyl band is always present.

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