

SEVERAL FEATURES OF THE OIL SHALE AND OIL-SHALE-KEROGEN BITUMENS OF PULA (HUNGARY)

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ABSTRACT

In favour of determining the soluble organic matter of the oil shale of Pula according to the main chemical groups, bitumens were destructed to fractions by means of column chromatography, and each fraction was analyzed by infrared spectroscopy and C-H analysis, respectively. Similarly, the analysis of the soluble organic matter formed from the kerogen concentrate accumulated physically from the oil shale under thermal treatment, was also carried out. It is characteristic of all samples that these consist of oxygen-containing compounds, e.g. carbon-acid esters, ketons and alcohols. Further, the long straight-chain hydrocarbons occur first of all in the hexane fractions in different quantities while the salts of carbon acid are contained mainly by the methanol fractions.

The original bitumen of the oil shale and the bitumen formed from kerogen concentrate after thermal treatment show the most striking difference that in the latter one aromatic compounds of small quantities are found while in the oil shale bitumens these are absent. To decide whether these aryl compounds were formed from the alkyl and cycloalkyl compounds due to the catalytic effect of clay minerals or were released from the kerogen matrix, or both effects play predominant role in the formation, further investigations are in progress.

INTRODUCTION

In Hungary economically negligible but abundant organic matter containing surficial outcrop was found in Transdanubia, in the environs of Pula, in 1973, as a filling matter of a basalt crater-lake [JÁMBOR, SOLTÍ, 1975]. The section most abundant in organic matter is found between 13.5 and 19.0 m. In the samples great quantities of the plankton alga *Botryococcus braunii* KÜTZING are found in addition to the rich spore-pollen content [NAGY, 1976]. According to the palynological and diatom analyses sedimentation took place in standing water of shallow depth. The temperature of water might be 283—285 K at the time of diatom flourishing, i.e. warmer than the recent climate. These diatomaceous formations were generated in the Upper Pannonian brackish phase [HAJÓS, 1976]. The chemical analyses indicated that the sedimentary rock of Pula can be qualified as a limy-clayey oil shale the organic matter of which is a highly polymerized kerogen of algal origin [ARATÓ and BELLA, 1976].

The abundant organic matter content of the oil shales of Pula provides favourable possibilities to extract relatively pure kerogen of greater quantity, consequently to carry out investigations aiming the determination of the peculiarities of the kerogen. Such analyses are e.g. to investigate the decomposition products of kerogen produced by temperature increase and by oxidation, and the results are suitable to draw conclusions to the original organic matter components of the oil shales. The kerogen of Pula being considered to be stable at the beginning of its thermal history was treated similarly as TISSOT *et al.* [1971, 1974] have treated the kerogen of the Toarcian shale of the Parisian Basin.

Nowadays it is generally accepted the most of the oil shales have been generated by algal accumulation. It has been evidenced that in different occurrences, i.e. in the Siberian balthashite as well as in the Australian coorongite and torbanite the presence of the *Botryococcus braunii* is common [BLACKBURN and TEMPERLEY, 1936]. The polymerisation and film-producing oxidation of lipids are the chemical proves of the preservation of algae since the non-polymerized material is decomposed during the biological decomposition.

According to THORNE *et al.* [1964]: "Oil shale was formed by the deposition and lithification of finely divided mineral matter and organic debris in the bottom of shallow lakes and seas. The organic debris resulted from the mechanical and chemical degradation of small aquatic algal organisms."

The investigation results of the kerogen of oil shale of Pula of Upper Pannonian age and deriving from shallow depth provide the possibility to reconstruct the thermal history of kerogen deriving from boreholes of the Southern Great Plain, being of similar age but deriving from much greater depths. Further, taking into account the same age the role of burial depth can also be elucidated.

In literature other kinds of correlation methods are also known. The chemical analysis of the very young coorongite assumed to be the intermediary of the Australian torbanite promotes the cognition of composition of the kerogen [CANE, 1969]. The general model determined by means of mass spectrometry, pyrochromatography and of other methods is as follows: the structural backbone is a carboxylic acid terminating in long alkyl chains the chain consisting of ester and ionic functions, between the chains probably peroxide and hydroxyl groups are found. It is postulated that some of the cross links of macromolecules are oxygen bonds of ether-type. The hydrocarbon fractions of coorongite have been investigated in detail [DOUGLAS *et al.*, 1969]. Based on these investigations it is probable that the hydrocarbons of isoprene skeleton were produced by the chlorophyll of the *Botryococcus braunii* as a result of bacterial activity or autolysis. The same authors refer also to the fact that in the hydrocarbon fraction of the older Scotch torbanite and of the Scotch Westwood Shale also isoprene-skeletal alkanes were found and the latter one contains also the remains of *Botryococcus braunii*. The particular investigation of the hydrocarbon fractions is believed to be very important since this may throw light upon the formation conditions of the organic matter.

By all means, the results render probable the imagination that both the kerogen and the oil were produced by mixed lipid matter. In both of them the precursor is a material in which the difference of small measure in the structure produces very different behaviour during diagenesis and during the geological times produces different end-products. After the suitable burial period the intermediaries deriving from lipids of less ability to reactions are decomposed to oil-like molecules while from the more reactive members of the same groups produce inert kerogen through polymerisation and condensation reactions [CANE, 1976].

The analytical results of the soluble organic matter also contribute to know the inert and stable kerogen. In the non-reservoir old sediments the quantity of soluble matter amounts only to hundredth or tenth percent, in different oil shales this value is greater by an order of magnitude. In Table 1 the data of several foreign oil shale bitumen are demonstrated after YEN [1976] in addition to those of the oil shale of Pula.

Since the quantity and character of the soluble organic matter depends partly on the environmental effects and partly on the source matter, i.e. on kerogen, it

TABLE 1

*Bitumen contents of some foreign oil shales and
of the oil shale of Pula (Hungary)*

Name and location	Age	Bitumen content (%)
Torbanite, Scotland	Permian	1.6
Green River, Colo. USA	Eocene	2.0
Alginite, Australia	Permian	1.2
Coorongite, Australia	Recent	46.0
Pula, Hungary	Pliocene	4.6

proved to be expedient to analyze the soluble fractions of the organic matter of the oil shale of Pula. The interpretation of the results is simplified by the fact that the starting organic matter is autochthonous.

EXPERIMENTAL

Analyses were carried out on the average sample (alginite) of the oil shale from the Pula-region. The air-dry sample was powdered down to less than 0.15 mm, in agate mill. The soluble organic matter was extracted in the Soxhlet-equipment first by chloroform (Bit-A), then by a mixture of benzene:acetone:methanol (70:15:15), (BAM-bitumen). The ratio of solvent/solid matter was 4:1. During the thorough extraction the solvent was changed several times. The extraction time was long: to remove the Bit-A of 3.3% on the average needed 80—90 hours, while the extraction of BAM-bitumen of 1.3% on the average needed 140—160 hours when starting from 50 g dry matter.

Though the Soxhlet-equipment is widely used in several countries to extract bitumens, it seems so that in case of a sediment of such abundant organic matter content the method of extraction should be changed. Some preliminary measurements were carried out, i.e. in three-necked boiling flask the solvent and the matter to be extracted (ratio 30:1) were simultaneously mixed and refluxed. By means of this method extraction time could be decreased to the tenth.

The crude extracts were fractionated on neutral alumina of III—IV activity by means of a rapid and simple method, i.e. of the suction column chromatography. (The principle of this procedure: chromatography is carried out by means of a suction flask under vacuum. The ratio of matter/adsorbent changed between 1:70 and 1:100, respectively. The material to be fractionated was carried on the column solved in hexan, resp., benzene. The solution of each fraction was followed in UV-light. The elution of each fraction required several litres of solvent. The solution was condensed to 40—50 ml by means of distillation under decreased pressure. The remaining part was removed on steam-bath and in drying furnace at 343—353 K, respectively.)

The column chromatographic data of Bit-A and BAM-bitumens of the oil shale of Pula are demonstrated in Tables 2 and 3 below; the starting material quantities are 1.1390 and 1.1110 g, respectively. The data of the Tables indicate numerically the differences between the bitumens, the difference showing already in crude state. After the evaporation of the solvent Bit-A is solid, easily powderable and is light-brown colour, while BAM-bitumen is of brownish-black colour and slightly sticky. On the basis of the features of the extracting solvent it can be expected that the BAM-bitumen contains more polar material mixture than Bit-A. In fact, however,

Column chromatographic results of Bit-A of the oil shale of Pula

TABLE 2

Sign of the fraction	Denomination of the solvent	Quantity (ml)	Quantity (g) of the fraction	Proportion (%)
a	hexane	5300	0.0730	6.41
b	hexane: benzene 1:1	5200	0.1120	9.83
c	benzene	6400	0.1790	15.71
d	chloroform	3700	0.2690	23.61
e	acetone	3400	0.1660	14.57
f	methanol	2750	0.0815	7.15
			0.8805	77.28

Column chromatographic results of the BAM-bitumen of the oil shale of Pula

TABLE 3

Sign of the fraction	Denomination of the solvent	Quantity (ml)	Quantity (g) of the fraction	Proportion (%)
a	hexane	6200	0.0830	7.47
b	hexane: benzene 1:1	3000	0.0334	3.00
c	benzene	5000	0.0517	4.65
d	chloroform	3000	0.0850	7.65
e	acetone	4150	0.1489	13.40
f	methanol	3000	0.0850	7.65
			0.4870	43.82

the BAM-bitumen can be solved in chloroform under slight heating and this indicates that the solvent mixture dissolves the material bound more strongly at the grain's surface, but applying the suitable protic solvent mixture the soluble matter can be removed in one step. (In the literature several authors use only solvent mixtures.) It is characteristic of the chromatographed bitumen fractions that their colour is gradually deepened from the high yellow to different shades of brown. Most of the fractions are of ointment consistency at room temperature, the solid ones also melt below 373 K except the methanol-part. The composition of each fraction has been controlled by means of thin-layer chromatography. The silicagel plates of 10×20 cm (Kieselgel G nach STAHL) were activated during 2 hours at 393 K. The matter was dropped onto the starting point solved in chloroform. Development was made with benzene.

It is characteristic of the first three fractions of both the Bit-A and of the BAM-bitumen that these are mixtures of mostly apolar matter, the other fractions consist of polar compounds. The quality of the different matter was identified by means of IR-records. (The matter to be analyzed was washed down from the silicagel by means of suitable solvent, i.e. by KBr of spectroscopic purity. After evaporation of the solvent the KBr containing the matter can be pastilled and then the IR-record can be carried out.)

To determine the functional groups the spectra of the fractions of column chromatography as well as those of some spots of differing R_f value were recorded. Records were made by means of the IR-spectroscopie UNICAM SP 200. In case

of solid matter the method of KBr pastilling (200 mg KBr+2 mg matter to be analyzed), in case of greasy fractions the film-technique were used. In the course of interpretation the designation of each vibration type was carried out after the HOLLY—SOHÁR—VARSÁNYI [HOLLY—SOHÁR, 1975] system, i.e.

- ν_s : symmetric stretching vibration
- ν_{as} : asymmetric stretching vibration
- β_s : scissoring (in-plane symmetric deformation) vibration
- β_{as} : rocking (in-plane asymmetric deformation) vibration
- γ_s : wagging (symmetric perpendicular deformation) vibration
- γ_{as} : twisting (asymmetric perpendicular deformation) vibration
- δ_s : symmetric deformation vibration
- δ_{as} : asymmetric deformation vibration

In Figs. 1 and 2 the Bit-A column chromatographed fraction of the oil shale of Pula, resp., the IR-spectra of the spots of different R_f value are found.

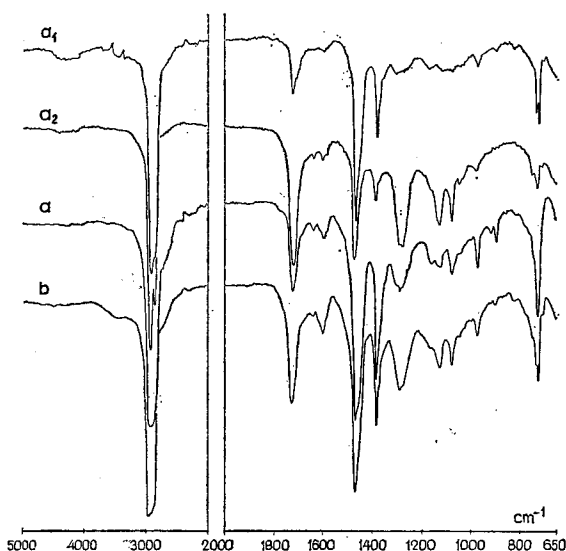


Fig. 1. The IR spectra of the spots of different R_f value and several Bit-A column chromatographed fractions

In the spectrum of the spot of $R_f=0.9$ separated on thin layer from the Bit-A fractions (a_1) the following bands are characteristic of the long chain paraffin hydrocarbons: 2900, 2850 (ν C—H), 1470 (δ_{as} CH₃, β_s CH₂), 1380 (δ_s CH₃) and 720 (β_{as} CH₂) cm^{-1} . Slight contamination is shown at 1720 cm^{-1} (ν C=O), and under-saturation at 1610 cm^{-1} (ν C=C). In the spectrum of the spot occurring in the range of $R_f=0.6-0.7$ and separated on thin layer from the Bit-A fractions (a_2) the intensity of ν CO (1720 cm^{-1}) increased, the accompanying vibrations are found in the "finger print" range. In addition to the isolated C=C (1640 cm^{-1}) the conjugated under-saturation (1600 cm^{-1}) can also be observed, the quantity of both of them is small. In this R_f range straight-chain ketons are found.

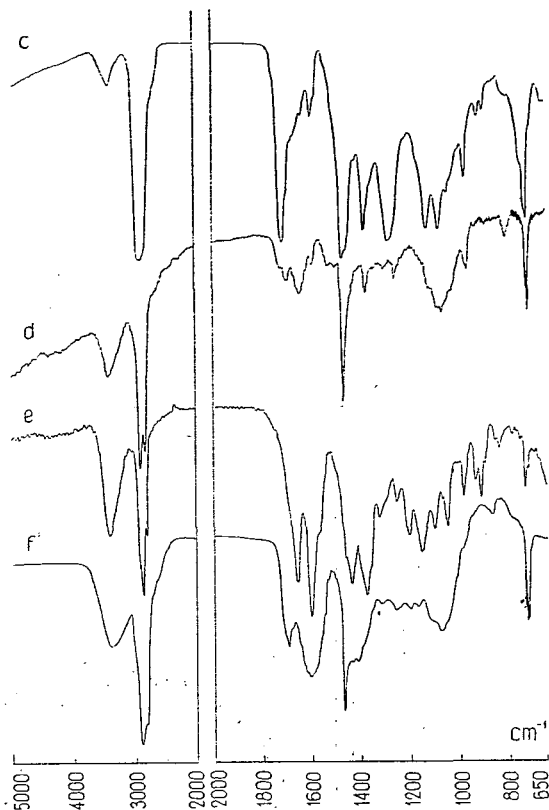


Fig. 2. The IR spectra of the further Bit-A column chromatographed fractions

It is to be noted that when evaluating the spectrum of coorongite the band-pair of 1140 and 1085 cm^{-1} was believed to be of ether-type bond which formed the cross-bonds of macromolecules [CANE, 1969]. It is probable that among the chains of the compounds constituting some, especially the *b* and *c* fractions of the oil shale of Pula C—O—C bonds are also found.

The original *a* (hexan) and *b* (hexan:benzene=1:1) fractions consist of the mixture of "pure" compounds mentioned above. The fraction *a* contains mostly aliphatic hydrocarbons while in fraction *b* the straight chain ketons are predominant. In both cases the spectra show slight undersaturation at 1640—1600 resp. 980—900 cm^{-1} (ν C=C; resp. γ C—H vinyl).

It is characteristic in general of the other fractions of Bit-A that deformation vibrations occur at 3450 cm^{-1} referring to the presence of ν OH, these occur with different intensities.

In the *c* (benzene) part the ν OH vibration appears first but considering the whole spectrum it agrees with the fraction *b* the only difference being the somewhat saturation here.

In the *d* (chloroform) fraction the carboxyl group skeletal vibration is relatively very small. The supplementary γ OH vibration of the ν OH band can be observed at 1070 cm^{-1} . The long straight chain alcohols predominate.

The spectrum of the fraction *e* (acetone) shows differences as compared to the records above mostly in the shorter wavelength range. The ν CO band is displaced by about 40 cm^{-1} and occurs at lower wave number, i.e. at 1680 cm^{-1} . The band at 1610 cm^{-1} referring to undersaturation is more intense than in the foregoing case. At the joint band of the $\beta_s\text{ CH}_2$ and $\delta_{as}\text{ CH}_3$ in this case the vibration of $\delta_s\text{ CH}_3$ is more intense. At 1160 cm^{-1} the transmittance of the $\nu_{as}\text{ C—O—C}$ band approaches that of the carbonyl group. These features together are characteristic of the branched undersaturated conjugated esters. At the same time, the fraction contains alcohol-type compounds, too, because the ν OH band is very strong. The corresponding deformation vibrations cannot be identified in the finger print range due to superpositions.

It is conspicuous in the spectrum of the fraction *f* (methanol) that it is relatively poor in bands and some bands being narrow in general became widened. In addition to the long chain alcohols mentioned above the spectrum shows the presence of carboxyl acid salt. The wide band at 1570 cm^{-1} ($\nu_{as}\text{ CO}_2^-$) and the widening at 1400 cm^{-1} ($\nu_s\text{ CO}_2^-$) can be attributed to the carboxylate ion. It proved to be successful to separate the salt of carboxylic acid which contains mainly Ca-ions. The spectrum also indicates carbonyl contamination.

The IR-records of the BAM-bitumen fractions (*Fig. 3*) indicate the presence of similar functional groups as mentioned above, but the composition of certain parts is different from those of the Bit-A fractions. Based on the spectra the following compounds can be found in the BAM-bitumen.

Part *a* (hexan) consists mostly of long aliphatic paraffin hydrocarbons but the presence of cycloparaffins can also be assumed. Slight undersaturation and carbonyl contamination also occur.

Fraction *b* (hexan:benzene=1:1) contains aliphatic saturated ketons and carboxyl acid ester.

In the fraction *c* (benzene) somewhat more undersaturation and hydroxyl contamination are found though this is very similar to the fraction *b*.

In the fraction *d* (chloroform) oxo-compound also occur in addition to the long-chain alcohols; the band of carbonyl group is widened indicating the presence of carbonyl group conjugated by C=C double bond.

The fraction *e* (acetone) contains highly undersaturated branched matter having conjugated oxo and hydroxyl which are esters and alcohols.

In the fraction *f* (methanol) compounds containing long-chain undersaturated alcoholic hydroxyl group as well as salt of carboxylic acid, resp. their mixture are found. The spectrum indicates carbonyl contamination, too.

ANALYSIS OF THE SOLUBLE ORGANIC MATTER OF THE THERMALLY TREATED OIL SHALE KEROGEN.

Major part of the organic matter of oil shales consists of kerogen being insoluble in traditional solvents and from which shale oil is produced by means of destructive distillation. Our experiments carried out at lower temperatures than pyrolysis (max. 573 K) aimed the more thorough knowledge of the decomposition processes of kerogen.

In the course of the analyses physically isolated thus unchanged kerogen concentrate was used which has been of ash content of about 9 percent. The inorganic components are first of all clay minerals, quartz, feldspar and small quantity of

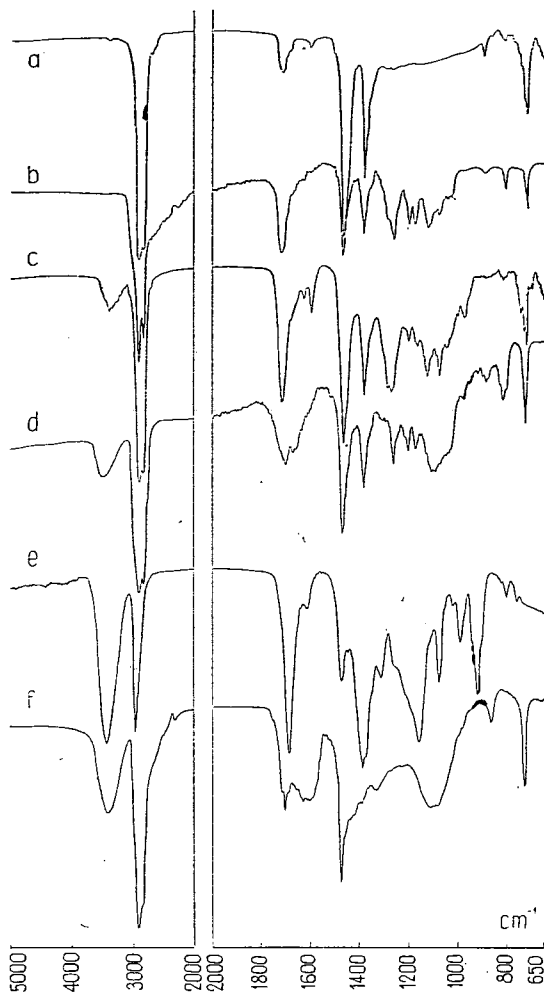


Fig. 3. The IR spectra of the BAM-bitumen column chromatographed fractions

carbonate. Experiments proved that at low temperatures (423, 473 and 573 K) soluble organic matter was formed from kerogen. The total soluble organic matter was removed from the sample treated thermally during one day at 573 K in nitrogen flow (i.e. under the expected greatest influence) by means of mixture of BAM-solvent and the analyses described in the characterization of oil shale bitumens were carried out. The material quantity to be separated (0.0740 g) was chromatographed on alumina of III—IV activity. Data of column chromatography are comprehended in Table 4.

The comparison between the data of Table 4 and the fractions corresponding to the original bitumens of the oil shale shows that the compounds formed from kerogen are mostly apolar while the quantity of the polar matter relatively decreased. More information can be obtained from the IR-spectra (Fig. 4).

TABLE 4

Column chromatographic results of the soluble organic matter
of the oil shale kerogen after thermal treatment (Pula)

Sign of the fraction	Denomination of the solvent	Quantity (ml)	Quantity (g) of the fraction	Proportion (%)
a	hexane	1400	0.0190	25.68
b	hexane:benzene 1:1	1900	0.0050	6.76
c	benzene	2900	0.0270	36.49
d	chloroform	1850	0.0020	2.70
e	acetone	1350	0.0070	9.46
f	methanol	1600	0.0110	14.86
			0.0710	95.95

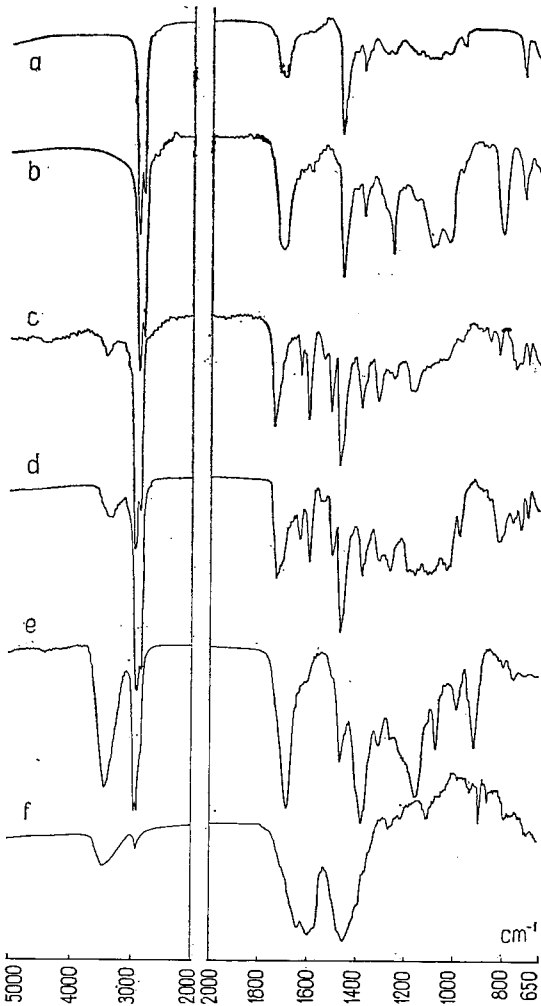


Fig. 4. The IR spectra of the thermally treated oil shale kerogen column chromatographed fractions

Having evaluated the spectra of bitumens produced by the thermally treated oil shale kerogen vibrations of qualitative new type were found in certain fractions which do not occur in the spectrum of the bitumens of the original oil shale. Depending on the quantity, in the range between 1600 and 1500 cm^{-1} small shoulders or peaks of medium intensity indicate the aromatic skeletal vibrations. The corresponding deformation vibrations are found at 750 cm^{-1} ($\gamma = \text{CH}$) and at 710 cm^{-1} (γCC).

Similarly to the recent analyses in some fractions of Bit-A of the original oil shale treated first thermally and subsequently extracted, the presence of aromatic compounds was indicated by the IR-spectra. Though the total quantity of the aryl-compounds is not predominant the exact interpretation of their formation needs further experiments.

One of the formation possibilities is as follows: aromatization takes place from the different alkyl or cycloalkyl components due to the catalytic effect of clay minerals; further it is also possible that in the easily removable parts e.g. alkyl-aril compounds are released from the kerogen matrix due to the thermal effect and by means of the breaking of bonds, and which contain also aromatic skeleton, as well.

According to the IR-records of the thermally treated kerogen concentrate the composition of each fraction is as follows:

The fraction *a* (hexan) consists mostly of hydrocarbons of long alkyl chains with slight carbonyl contamination. The wide shoulder at 1600 cm^{-1} derives rather from undersaturation than from aromatic skeletal vibrations since the complementary deformation bands cannot be observed.

In the fraction *b* (hexan:benzene=1:1) mostly the keton-type compounds predominate. The chain is long and not branched. The spectrum shows minimal aromatic contamination.

In the fraction *c* (benzene) partly alkyl-aril skeletal oxo-compounds are found with slight OH-contamination.

In the fraction *d* (chloroform) the spectrum indicates somewhat more alcoholic OH-groups, the skeleton is, however, aliphatic and of aromatic structure.

The fraction *e* (acetone) consists of esters and alcohols being conjugated, undersaturated and of branched chain.

The spectrum of the fraction *f* (methanol) indicates great amounts of inorganic matter. In addition to the salt of carboxylic acid compounds of undersaturated alcoholic functional groups are found.

In favour of obtaining further information the C—H analysis of the column chromatographed fractions was also carried out, in addition to the IR-records.

Analysis was done by means of the KÖRBL-method, in which the oxidation of carbon compounds is carried out in oxygen flow at 823 K and the active catalyzing effect of thermal decomposition products of silver permanganate is used. The quantities of carbon dioxide and water were determined gravimetrically. In Table 5 the C—H analytical results of the oil shale bitumens and of the chromatographed fractions of the bitumen formed as a result of thermal treatment from the kerogen concentrate and isolated physically from the original oil shale, are comprehended. As comparison, the quantities of elements constituting the "original" not chromatographed bitumen of the oil shale are shown below (in percent):

Bit-A:	C: 72.9	H: 11.8	S: 0.14
BAM-bitumen:	C: 72.6	H: 11.2	S: 0.17

C-H analyses of the shale kerogen bitumen fractions after thermal treatment and of the oil shale bitumens of Pula

TABLE 5

Elution agent of the fractions separated in the column	Bit-A		BAM-bitumen		Oil shale kerogen after thermal treatment	
	C %	H %	C %	H %	C %	H %
hexane	83.95	13.02	80.95	12.55	81.93	12.75
hexane:benzene 1:1	82.22	12.85	79.82	12.45	80.07	11.90
benzene	79.52	12.75	78.38	12.35	78.88	11.64
chloroform	78.50	12.51	77.72	12.40	77.36	10.86
acetone	66.75 ⁺	11.07	61.19 ⁺	10.58	64.61 ⁺	9.82
methanol	63.60 ⁺	9.62	62.02 ⁺	9.50	67.90 ⁺	10.44

⁺ Having completed the analyses incombustible matter of 1—3 percent remained.

Data of Table 5 also show that the individual fractions are mixtures and not pure materials. It is fairly evidenced by numerical data, i.e. when comparing the data of the hexan-fractions with those of the spot (R_f : 0.9) separated from the hexan fraction of Bit-A which represent C_{20} hydrocarbons: C: 84.77%, H: 13.56%.

Data of the analysis also indicate that the quantity of oxygen increases during progressive chromatography since the lacking percent is attributed to this element.

In the final fraction (*f*) the presence of inorganic matter was indicated also by the IR-spectra while the record of the fraction *e* did not show this. It is probable that also in this part small quantity of salt of carboxylic acid is found, but it can be also assumed that sulfur culminates in this fraction and is represented by thioester, in the spectrum, however, its weak bands, e.g. C—S, S=O are overshadowed by the more characteristic bands.

DISCUSSION

The data of soluble organic matter concerning the oil shale of Pula show that the major part of bitumens consists of oxygen-bearing compounds, i.e. carboxylic esters, alcohols, etc. which derive from the lipid-like material of algae. The long-chain aliphatic structure is mostly characteristic of the compounds and branched hydrocarbons occur only in smaller quantities, mainly in the acetone fraction.

The relatively high oxygen content relates to the fact that the organic matter is free of stronger effects, it is in the initial phase of its evolution. This verified also by the fact that in the oil shale, resp., oil shale kerogen samples treated at relatively low temperatures the presence of the aromatic skeleton can be determined. In case of the samples of the Southern Great Plain deriving from greater depths (1990—2100 m) and being more diagenized but of the same Upper Pannonian age the quantity of oxygen decreased according to the previous investigations and the proportion of the condensed compounds increased.

The investigation of the soluble organic matter is closely related to the investigation of the oil shale kerogen. Because of the low maturity grade the oil shale kerogen of Pula is highly suitable to follow the thermal-historic processes under laboratory conditions. The analysis of the soluble products will provide further data

concerning the changes in the kerogen structure due to thermal treatment. In the future the analysis of bitumens will be supplemented by the analysis of the oil produced under thermal treatment in favour to obtain further information on the oil shale kerogen and to make clear the genetic problems.

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