

THE IR SPECTROSCOPIC INVESTIGATION OF THE ORGANIC EXTRACT OF ROCKS

By

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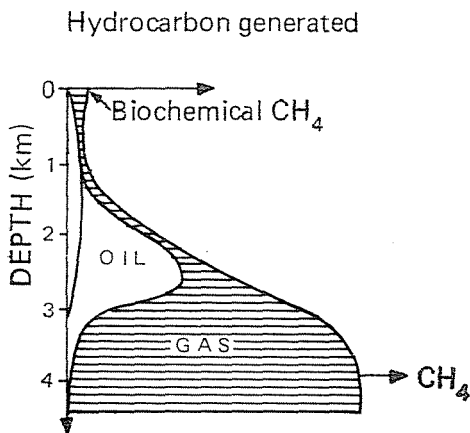
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1. Aim

The aim of this work was to elucidate hydrocarbon formation by investigating the spread organic matter in rocks found in a Hungarian neogene basin. Hydrocarbons, as energy sources, have prominent role all over the world, and thus their research is very important. The study of the bituminous substance extractable from rocks by organic solvents greatly contributes to forecasting the perspectives of mineral oil and gas streams, ultimately to the prognosis of resources. The investigation of kerogenes, the organic substances of rocks insoluble in organic solvents, has similar importance (even more so, the main emphasis has now been shifted to this substance).

Let us first review the transformation of organic substances with the increase of temperature and pressure during the progress of burying. Fig. 1 shows the general scheme of hydrocarbon formation after Tissot. The changes



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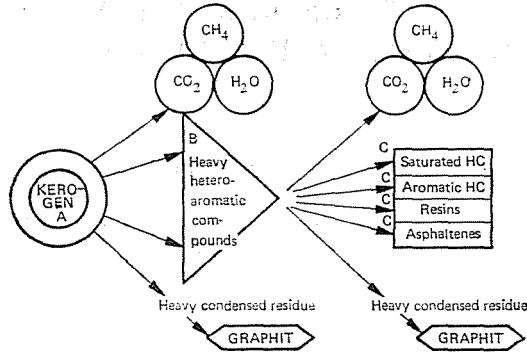


Fig. 2. General scheme of thermal degradation of organic matter in sediments

take place irreversibly in the organic material under the effect of temperature and pressure. The amount of hydrocarbons is small near the surface, consisting mainly of methane of biochemical origin. Down to 1000 m, by the diagenesis of organic matter, mainly N_2 , CO_2 , H_2S and a little amount of hydrocarbon gases are formed. These hydrocarbons preserve without change, or with minor

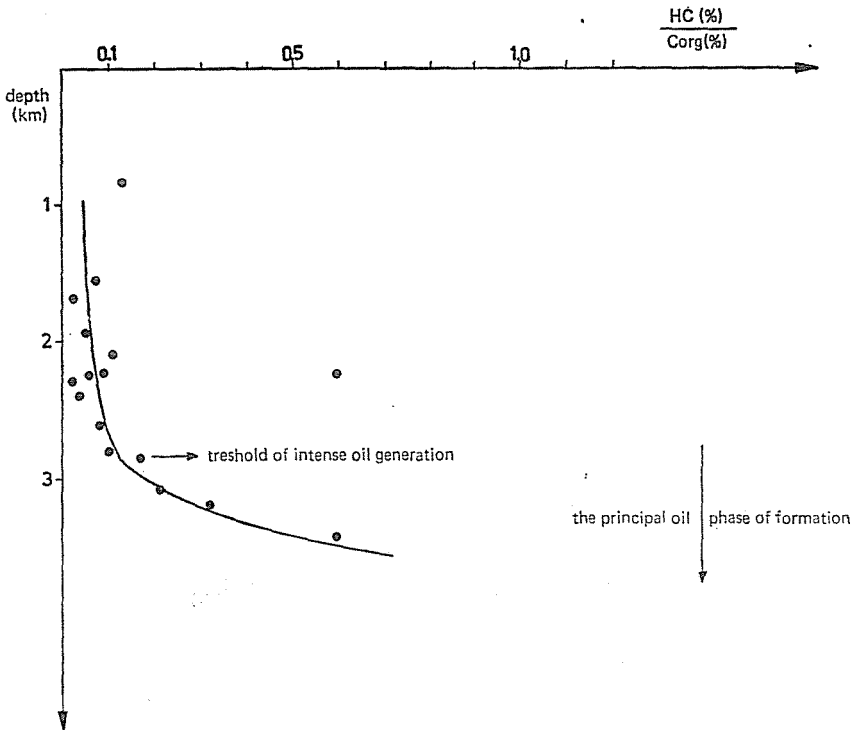


Fig. 3. Definition of intense oil generation at the Hungarian field under investigation

changes (not affecting the basic hydrocarbon chain), the characteristic molecular structures of the original, living organisms.

With further increase in depth, after a certain threshold (depending on the original organic substance, the history of burying and the geothermic gradient), the main phase of oil formation follows (Vassoievitch, 1969), in which the thermal and catalytic decomposition of organic material into liquid hydrocarbons is the dominating process. Hydrocarbons formed here have already no characteristic structures. In larger depths mainly light hydrocarbon gases are formed (equally from oil and kerogene), and at the end only methane, leaving back graphite. The products of the thermal decomposition of kerogene are shown in Fig. 2 (after Tissot).

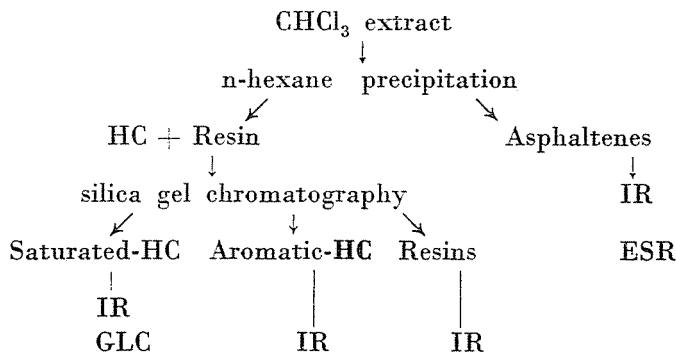
Fig. 3 shows the oil formation zone in the area investigated by us. The maximum depth of wells was 3400 m, therefore the further parts of the curves can be estimated only.

2. Material and Methods

2.1. The origin of rock samples

54 core samples were investigated, 19 of which was subjected to detailed IR analysis. According to age, all core samples were neogene, clastic rocks, sedimented from sea water or partly sweet water, respectively. They consist in part of clay rock, in part of sand rock.

2.2. The extraction of organic material and the analytical methods applied (a sketch)



2.2.1. Soxhlet extraction

Finely ground rock ($<60 \mu$) was subjected to exhaustive extraction in Soxhlet apparatus, first with chloroform, and then with 1 : 1 benzene-ethanol

mixture. Chloroform dissolves primarily hydrocarbons, resins and asphaltenes, whereas 1 : 1 benzene-ethanol mixture (later B : A) dissolves strongly polar compounds with high O, S and N content.

2.2.2. Asphaltene separation

Asphaltenes, complicated polycondensed aromatic compounds with paraffin chains and substantial heteroatom content (mainly O), were separated with large excess of n-hexane.

2.2.3. Determination of organic carbon content

From the rock, extracted with chloroform and carefully purified of inorganic carbonates, organic carbon content was determined by ignition in a Wösthoff apparatus.

2.2.4. ESR analysis

The spectra were measured on a JEOL JES-ME-3X instrument, at room temperature, with 100 kHz field modulation in the X band. The absolute spin concentration was determined by comparison with the "strong pitch" signal of Varian with known spin concentration (3×10^{15} spins/cm).

2.2.5. Column chromatographic separation

Asphaltene-free organic material was separated on silica gel column by elution technique. An eluotropic series was applied with a different number of members depending on the sample (on the amount of organic substance fed onto the column), and accordingly, different numbers of fractions were obtained. The two most frequently used eluotropic series, designed by us on the basis of the literature of column chromatography, were as follows:

a) n-hexane
benzene
ethanol

b) n-hexane
cyclohexane
carbon tetrachloride
xylene
benzene
chloroform
tetrahydrofuran
ethyl acetate
isoamyl alcohol
methyl-ethyl-ketone
acetone
ethanol
1 : 1 mixture of methanol and
pyridine

The IR spectra of the fractions were recorded, and the first fractions, eluted with n-hexane (which contain normal, branching and cyclic hydrocarbons with a very low amount of aromatic impurities), were investigated with GLC.

2.2.6. IR spectrophotometric investigations

The spectra were measured on a Spekdord IR 75 recording spectrophotometer, using KBr disc technique, and evaluated by the baseline method. Bitumens were characterized by the indices introduced and used by GLEBOSKAYA (1971), GALACTIONOVA and PROSKURYAKOVA (1971) and VYCHEV et al. (1973). These indices are as follows:

$$K_k = \frac{E_{1710 \text{ cm}^{-1}}}{E_{1470 \text{ cm}^{-1}}} \quad \text{or} \quad K_k = \frac{E_{1720-40 \text{ cm}^{-1}}}{E_{1479 \text{ cm}^{-1}}}$$

i.e. the ratios of the extinctions of the carbonyl groups and methylene groups in the given type of compound at the given wavenumbers.

Ratios

$$K_a = \frac{E_{720 \text{ cm}^{-1}}}{E_{750 \text{ cm}^{-1}}} \quad \text{and} \quad K_A = \frac{E_{1610 \text{ cm}^{-1}}}{E_{1470 \text{ cm}^{-1}}}$$

are proportional to the aromatic content.

$$K_e = \frac{E_{1380 \text{ cm}^{-1}}}{E_{1470 \text{ cm}^{-1}}}$$

is characteristic of the extent of branching of open cyclic hydrocarbons.

$$K_c = \frac{E_{720 \text{ cm}^{-1}}}{E_{970 \text{ cm}^{-1}}}$$

indicates the ratio of cyclic hydrocarbons and aliphatic hydrocarbons containing more than four methylene groups.

Of these indices, K_k has proved to be useful in the genetic qualification of bitumens (Glebovskaya, 1966). K_A and K_e are less sensitive, strongly depending on the type of parent organic material. K_a and K_c are even less sensitive, and their interpretation is much more complicated than that of the former three indices.

3. Results and Discussion

3.1. Variation of the measured organic-geochemical parameters of bitumen with depth

The problems of hydrocarbon formation and migration may be solved by investigating the variation of the measured parameters of bitumen with depth and petrological characteristics. Table 1 shows the geological and measured geochemical parameters of 19 core samples investigated in detail in our laboratory.

$$\beta = \frac{\text{Soxhlet bitumen } \%}{C_{\text{org}} \%}$$

Table 1

Number of sample	Depth (m)	Rock	Insoluble residue (%)	C _{org} (%)	Amount of Soxhlet bitumen		CHCl ₃
					CHCl ₃ (%)	B:A=1:1 (%)	
77/24	823.0—829.0	sandstone	63.6	0.09	0.03	0.03	0.38
77/7	1156.0—1161.0	sand	80.2	0.08	1.60	0.05	1.17
77/4	1574.0—1578.0	sandstone	62.0	0.27	0.05	0.04	0.20
77/6	1704.0—1708.0	marly siltstone	62.7	0.31	0.03	0.03	0.16
77/1	1952.5—1954.5	marly siltstone	73.0	0.53	0.07	0.03	0.18
77/16	2106.0—2108.0	calcareous marle	37.4	0.14	0.07	0.03	0.36
77/105	2196.0—2202.0	siltstone	77.7	0.33	0.06	0.04	0.17
77/19	2200.0—2208.0	sandstone	66.6	0.2	0.14	0.03	0.45
77/104	2226.0—2232.0	dolomit	32.2	0.04	0.04	0.02	0.57
77/41	2324.0—2330.0	sandstone	78.0	0.49	0.05	0.07	0.09
77/42	2324.0—2330.0	marly siltstone	67.6	0.59	0.07	0.05	0.11
77/14	2401.0—2404.0	marly siltstone	59.5	0.34	0.06	0.03	0.16
77/43	2676.5—2678.5	marle	43.1	0.25	0.06	0.03	0.19
77/45	2791.0—2796.0	marle	43.7	0.39	0.08	0.05	0.18
77/38	2877.0—2888.5	marle	49.8	0.51	0.14	0.07	0.22
77/34	3095.0—3097.0	marle	33.8	0.44	0.22	0.05	0.36
77/37	3120.0—3124.0	marle	39.3	0.51	0.20	0.06	0.30
77/107	3187.0—3191.0	dolomit	1.6	0.05	0.08	0.04	0.69
77 _g 27	3369.8—3375.0	argillaceous limestone	16.1	0.28	0.30	0.05	0.58

shows the extent of bituminization. In organic-geochemical literature β is a generally accepted parameter, enabling the process of oil formation to be monitored. Due to limited space, only the variation of the amount of bitumen with depth is presented here for detailed analysis (Fig. 4). The increase of the amount of bitumen with depth can be well seen in clay rocks, whereas in sand rocks no definite trend can be observed. Investigating the depth dependence of various measured parameters, two areas can be distinguished in the neogene basin studied by us. As an example, Fig. 5 is shown, in which these two areas are denoted with A and B.

This problem is not discussed here, however, since the main concern of our paper is the detailed IR spectrophotometric investigation of bitumens.

Chromatographic fractions				Absorbance ratio						N_g ($10^{12}/g$)	HC (%) Corg(%)
HC (%)	Aromatic HC (%)	Resin (%)	Asphaltene (%)	$E_{2200cm^{-1}}/E_{750cm^{-1}}$	$E_{2200cm^{-1}}/E_{1700cm^{-1}}$	$E_{1350cm^{-1}}/E_{1700cm^{-1}}$	$E_{1210cm^{-1}}/E_{1470cm^{-1}}$	$E_{1710cm^{-1}}/E_{1470cm^{-1}}$	$E_{1720-400cm^{-1}}/E_{1470cm^{-1}}$		
45.6	8.5	28.2	8.5	—	—	0.40	0.10	0.19	—	—	0.13
99.6	—	—	0.4	—	—	—	—	—	—	—	17.50
45.7	9.3	22.6	19.9	—	—	0.55	0.19	0.34	0.37	3.1	0.07
25.5	11.4	48.2	14.1	1.65	—	0.47	0.11	0.25	0.28	—	0.02
53.9	3.9	29.6	8.3	—	—	0.52	0.21	0.37	0.40	9.7	0.05
63.3	13.0	7.2	6.6	—	—	0.48	0.06	0.14	0.19	—	0.11
43.6	14.8	30.0	10.3	1.40	—	0.53	0.30	0.42	—	48.0	0.09
53.5	10.4	18.7	7.6	—	—	0.22	—	0.27	0.42	—	0.03
63.8	12.3	19.8	4.1	—	—	0.43	—	0.15	—	—	0.62
24.5	14.3	30.4	24.3	0.29	—	0.59	0.66	0.59	—	22.0	0.02
26.5	13.6	34.5	21.9	1.40	—	0.51	0.20	0.25	—	28.0	0.02
41.5	16.7	26.7	10.5	—	—	0.53	0.32	0.41	—	5.7	0.03
40.3	14.8	36.5	7.65	1.03	—	0.50	0.27	0.47	—	96.0	0.08
43.1	9.9	33.5	6.8	2.29	6.40	0.44	0.16	0.21	0.24	114.0	0.10
57.8	6.6	28.1	5.7	—	—	0.41	0.17	0.23	—	134.0	0.17
57.9	11.5	27.1	3.1	2.05	—	0.45	0.12	0.37	0.44	145.0	0.21
57.9	8.3	27.3	5.4	—	—	0.34	0.09	0.16	—	157.0	0.21
80.9	5.2	10.7	3.1	—	—	0.35	0.11	0.15	0.17	—	0.32
64.7	7.7	24.4	2.6	—	—	0.38	0.09	0.17	—	—	0.60

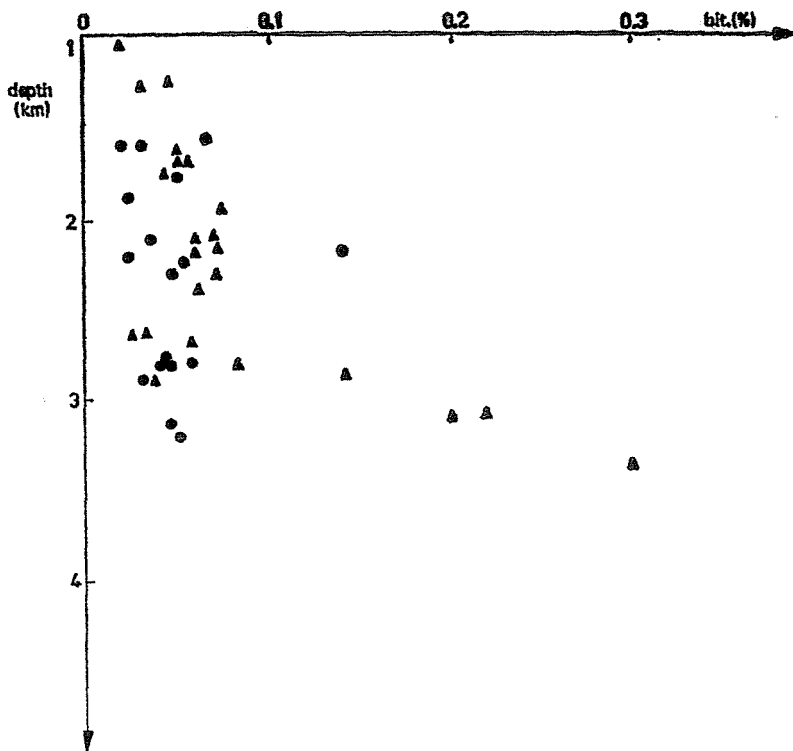


Fig. 4. Variation in amount of total chloroform extract as function of depth

3.2. Determination of the type of soluble organic substance by means of IR spectroscopy

The detailed analytical investigation of soluble organic substance and kerogene may solve the following problems: zone of hydrocarbon formation, identification of mother rock, elucidation of migration, type of the parent organic material. In order to answer these questions, it is important to know the composition and type of organic substance dissoluble by chloroform from the rock.

To study the type of bitumen and the migration, the statistical method of NERUCHEV (1969) and TÓTH and KÓKAY (1973) was applied, according to which the bitumen samples are divided in two evaluation groups in a $C_{org} - \beta$ and in a $C_{org} - \text{bit.}_{\text{CHCl}_3}$ plot.

On the basis of the IR data, plotting the ratios of absorbances in $\beta - K_k$ and $K_A - K_k$ diagrams, a line separating autochthonic and allochthonic bitumens can be drawn at $K_k = 0.4$ (Fig. 6 and 7). (*Autochthonic* is organic matter sedimented together with the rock or formed therein, *allochthonic* is organic matter migrated into the rock from other rocks.)

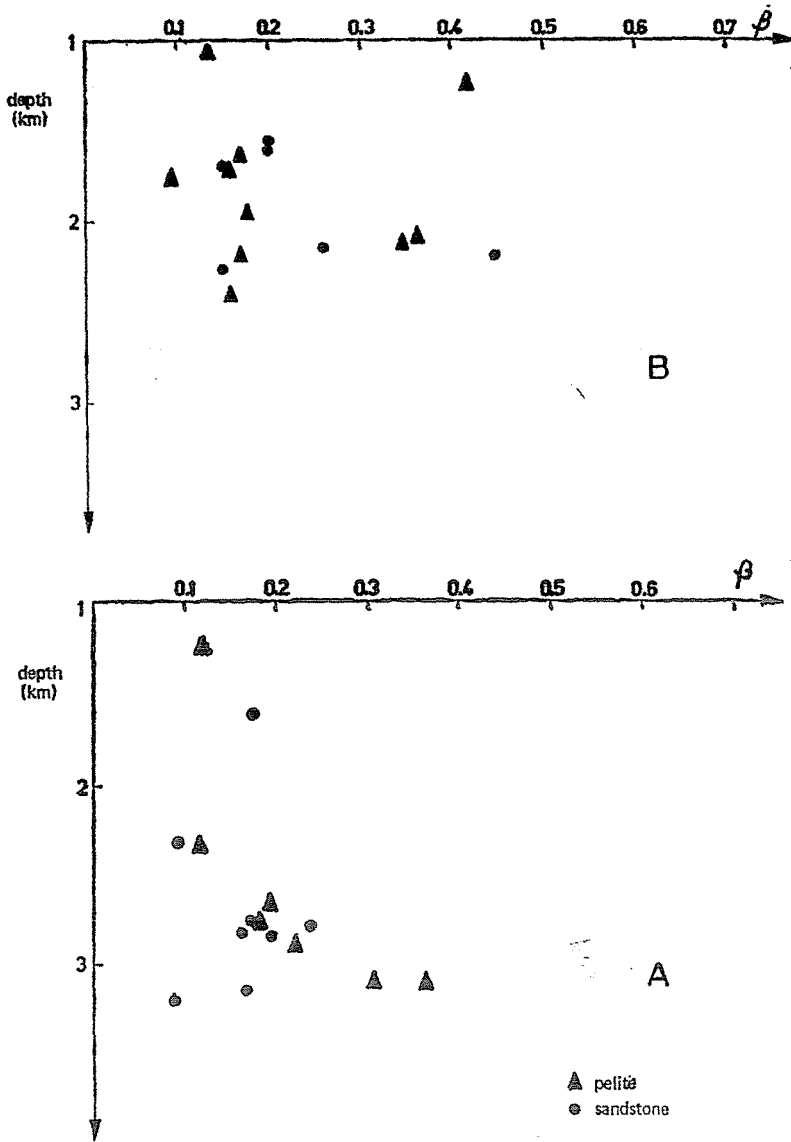


Fig. 5. Variation of β value as function of depth at B and A area

It must be stressed, however, that the results obtained on the basis of IR spectra should be compared with other measured geochemical and geological properties of the given area.

In our case, with the majority of samples, the conclusions drawn from the IR spectra were in agreement with the geological data. However, there was one area, for which the bitumenic character obtained from the IR spectra

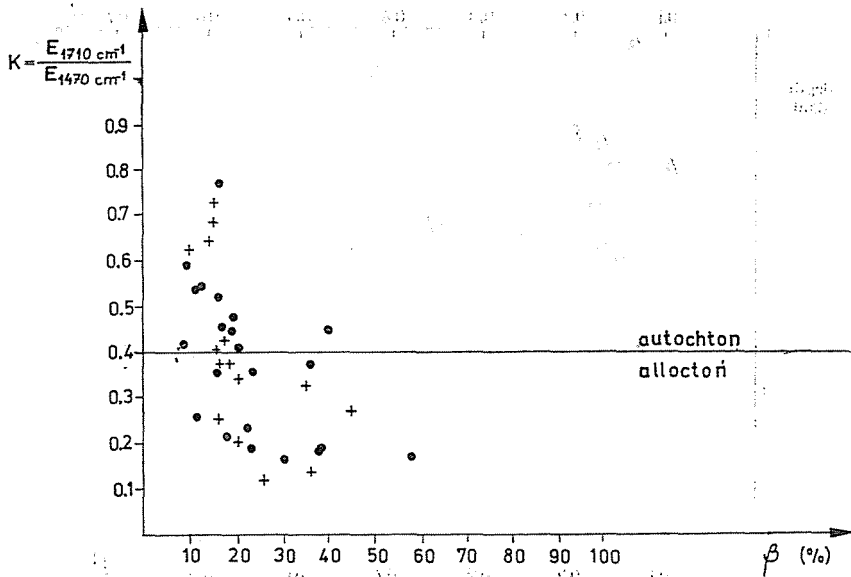


Fig. 6. Correlation between β and K_K in bitumens of the Hungarian basin under investigation

contradicted other measured organic-geochemical parameters, regarding the depth and petrological characteristics. This illustrates the limitations of the above method of analysis.

The next part of the paper is concerned with the composition of leached bitumen and its chromatographic fractions, and with the identification of

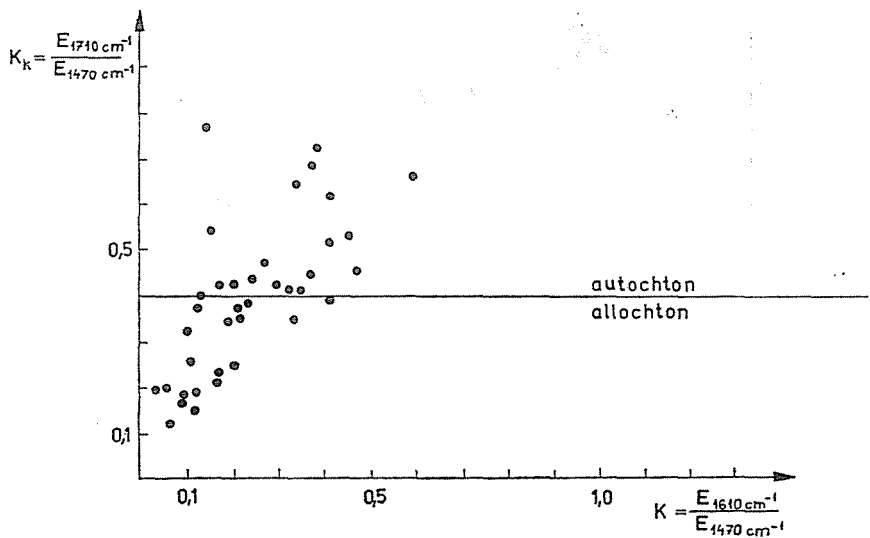


Fig. 7. Relation between K_A and K_K in bitumens of the Hungarian basin under investigation

characteristic compound types on the basis of their IR spectra. We shall analyse in detail the spectra of the CHCl_3 and 1 : 1 benzene-ethanol extracts with increasing depth. From the two areas of the basin each, one sand rock and one aleurite sample is presented here only, and the IR spectra of their chromatographic fractions will be discussed.

3.2.1. The IR spectra of the organic substance dissolved by CHCl_3 (Fig. 8/b)

Fig. 8/b shows the IR spectra of bitumens as a function of depth. (The $4000-2000 \text{ cm}^{-1}$ region of the spectra is not shown since the characteristic bands appearing here are present in all the samples, differing at most in intensities.)

In the unseparated bitumen sample the presence of functional groups shown in the Fig. 8/a could be detected. Notation system of Sohár, Holly,

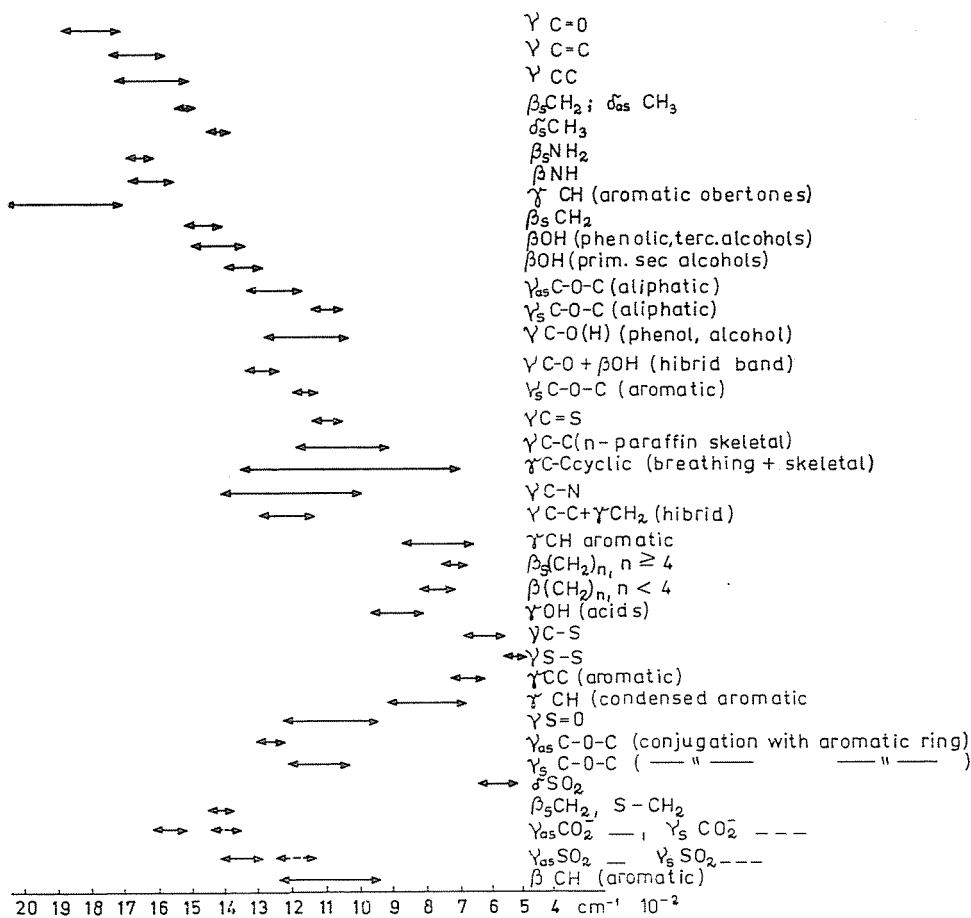


Fig. 8/a. The characteristic band and group frequencies

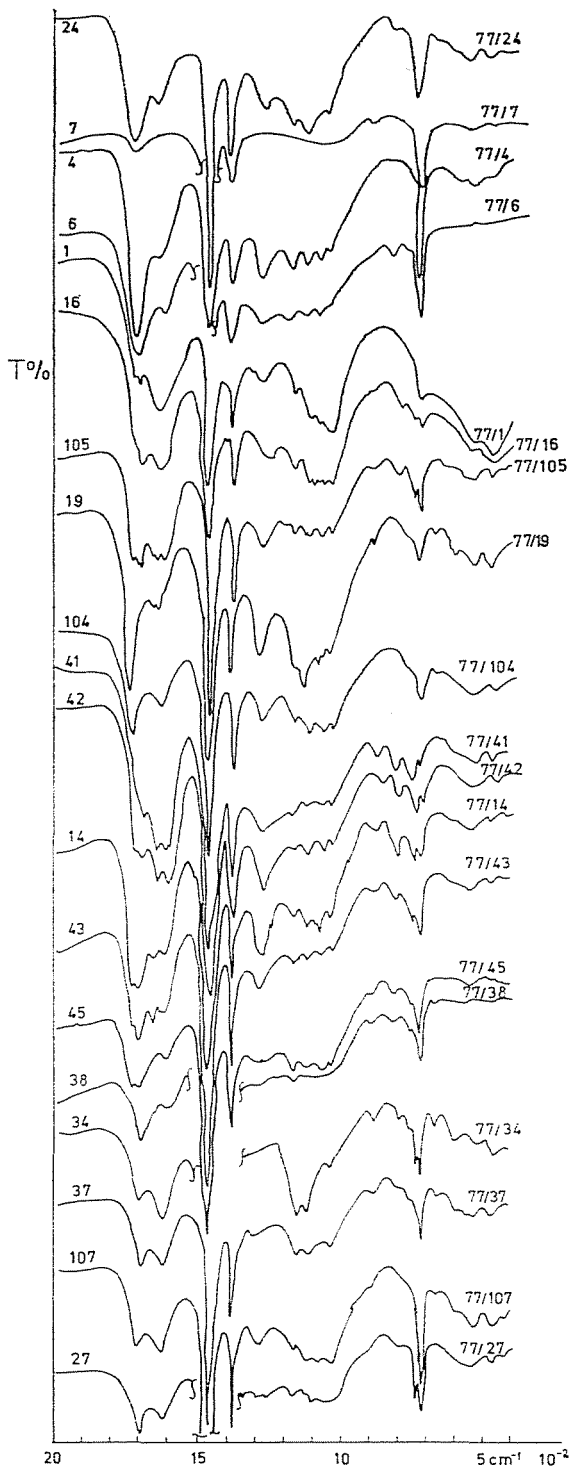
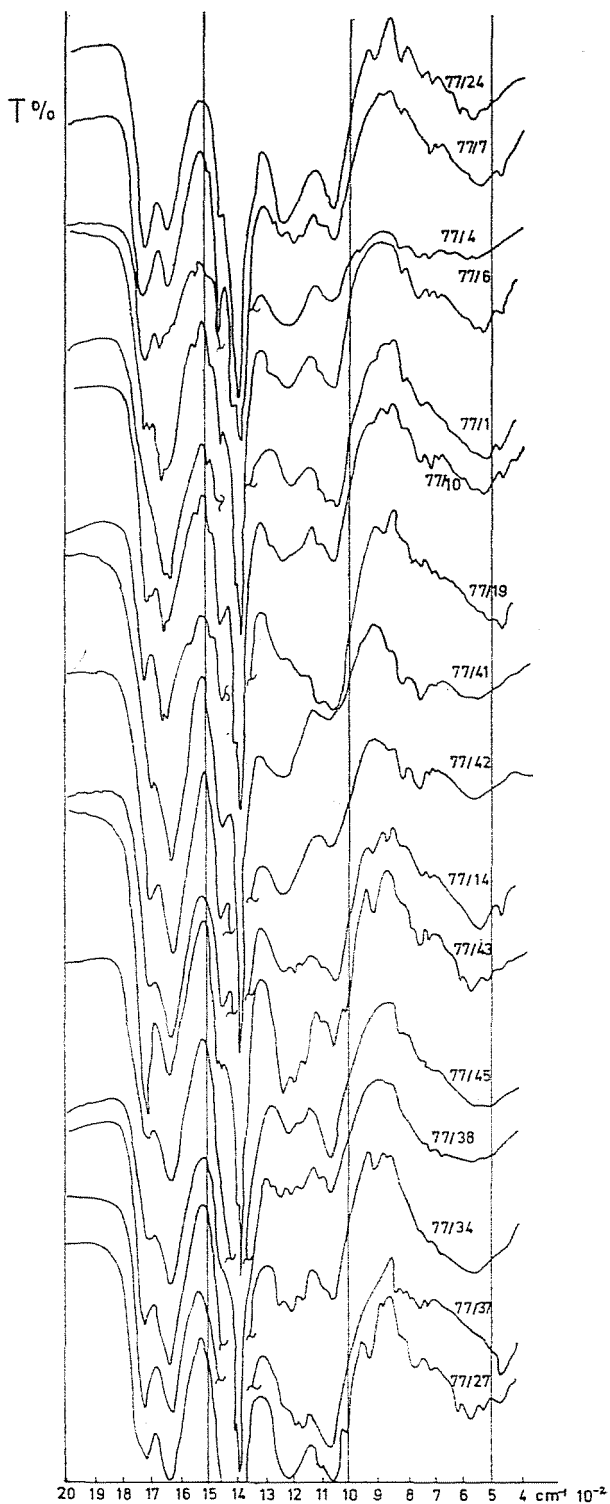


Fig. 8/b. The IR spectra of total CHCl_3 extracts from samples

Fig. 9. The IR Spectra of total
 $B:A = 1:1$ extracts from
samples



Varsányi (1969) is used in the figure. Of these, the amount of the groups of dominant character has been studied as a function of depth. The following results were obtained. The amount of *higher, aliphatic* groups (720 cm^{-1}) has no relation to depth down to 2200 m. Some samples contain large amounts of them (77/24, 77/7), whereas others much less. Below 2200 m their amount increases with depth. This phenomenon (to 2200 m) can be interpreted by migration.

The bands of *carbonyl* groups ($1750\text{--}1650\text{ cm}^{-1}$) are present in all samples, from the accompanying bands mostly the presence of ester groups can be concluded, in amounts decreasing with depth.

Aromatic groups (ca. 3040, ca. 1600 and $900\text{--}700\text{ cm}^{-1}$) appear after a certain depth; their amount is much smaller than that of aliphatic groups, and decreases with further increasing depth. The reason is the formation of *condensed ring* systems, as shown mainly by the broad band around 1600 cm^{-1} assigned to skeletal vibrations.

Sulfur compounds might be present in all samples ($600\text{--}400\text{ cm}^{-1}$); their amount varies with depth.

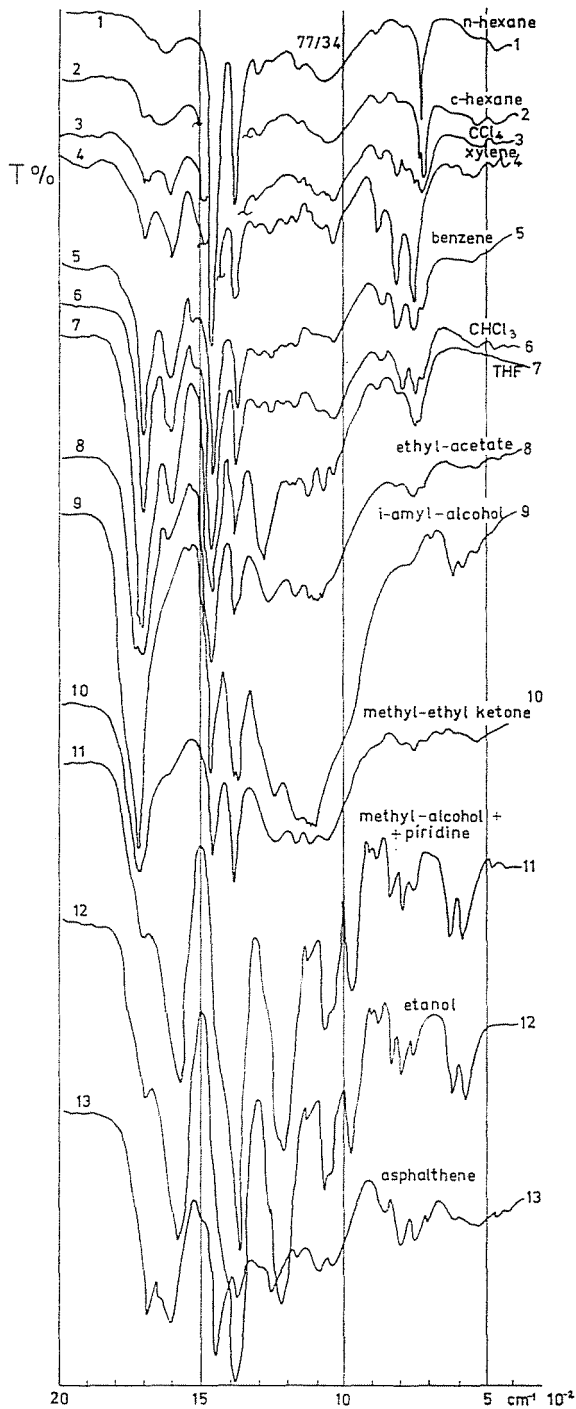
The region of the spectrum most difficult to interpret is between 1300 and 1100 cm^{-1} . This contains the C—O—C stretching vibrations of esters (occasionally ethers), and the breathing vibrations of cyclic (naphthenic) compounds. Condensed aromatic systems also have a considerable, grey-body-like absorption in this region. The intensity features of the band system appearing in this region do not show any dependence on depth, either. Investigating the other bands of the groups absorbing in this region, it can be found that at smaller depths (to 2200 m) mainly ester groups are present, then cyclic paraffins become dominant, and at great depths bitumen consists mainly of condensed aromatic systems in addition to higher hydrocarbons. Branching hydrocarbons ($1380\text{--}1360\text{ cm}^{-1}$) are not present in notable amount.

3.2.2. The IR spectra of unseparated 1:1 benzene-ethanol extracts of core samples (Fig. 9)

The IR spectra agree in main features with those of unseparated bitumen obtained with chloroform extraction, but in the OH and NH regions ($3600\text{--}3100\text{ cm}^{-1}$), as well as in the region characteristic of sulfur, aromatic and condensed aromatic compounds, stronger and more distinct absorption bands can be observed. Of the bands present in bitumen and shown in the Fig. 8/a, the following are the most important:

Aliphatic hydrocarbons ($3000\text{--}2800$, ca. 1480, ca. 1380 and 720 cm^{-1}) are present in considerable quantities, but their character is different from that found in the chloroform extract. Here the share of higher hydrocarbons is much smaller, and branching chains dominate. This is shown by the fact

Fig. 10. The IR spectra of column chromatographic fractions of sample 77/34



that the rocking vibration of methylene groups is hardly observable at 720 cm^{-1} , and the methyl deformation at 1380 cm^{-1} is split and much stronger than the deformation vibration around 1480 cm^{-1} arising from the methyl and methylene groups. The amount of aliphatic part does not vary with depth to remarkable extent, showing slight increase.

The ratio of *carbonyl groups* absorbing at $1750\text{--}1700\text{ cm}^{-1}$ (mainly esters) to *aromatic* and *condensed aromatic* systems ($1640\text{--}1600\text{ cm}^{-1}$) is, however, varying. With increasing depth the ratio of carbonyl groups decreases (except for one sample). The aromatic ratio is slightly higher here than in the case of chloroform extract.

In the $1300\text{--}1100\text{ cm}^{-1}$ region the spectra are substantially different both in band contours and in intensities. Regarding that in this region esters, cyclic and heterocyclic compounds may equally have absorptions, no safe interpretation could be given.

It can be seen that all samples contain *sulfur compounds*, in larger quantities than the chloroform extracts.

The presence of *amides* and *amines* can also be assumed, in larger quantities than in chloroform extracts ($3600\text{--}3100\text{ cm}^{-1}$).

3.2.3. The IR spectra of column chromatographic fractions of sample 77/34 (Fig. 10)

Bitumen, fed onto the column, was eluted with the series of solvents shown on the figure of spectra. The IR spectra of the fractions vary during elution. From the presence and intensities of the characteristic vibrations of the functional groups investigated (paraffin, cycloparaffin, aromatic, condensed aromatic, carbonyl and other polar groups) the following conclusions could be drawn. The first two fractions can be regarded as practically pure higher paraffin hydrocarbons (720 cm^{-1}), accompanied by a small amount of cycloparaffins (ca. 1000 cm^{-1}). In fraction 3, but mainly in 4, aromatic hydrocarbons appear in addition to the above, with different substitution patterns ($900\text{--}700\text{ cm}^{-1}$). In fractions 4–7, besides the aliphatic components, mainly monocyclic aromatic derivatives appear together with aromatic having a small number of rings. Starting at fraction 8, the bands in the CH deformation region of aromatics overlap, the intensities of skeletal stretching vibrations increase, and the bands broaden. These facts indicate that with this fraction the ratio of resin-like components increase.

Investigation of the characteristic bands of polar groups shows that OH and NH groups are present in remarkable amount in fractions 7–12 ($3400\text{--}3100\text{ cm}^{-1}$). Carbonyl groups (mainly esters) appear after fraction 4, and their amounts increase up to fraction 10. In the next two fractions already the broad aromatic skeletal band dominates this region, but the presence of

amides can also be assumed ($1650-1600\text{ cm}^{-1}$). Starting with fraction 8, the long alkyl chains are gradually replaced by branching chains. This is shown by the shoulder of the 1380 cm^{-1} band (spectrum 8), or by the splitting of this band (spectrum 9). The CH stretching region ($3000-2800\text{ cm}^{-1}$) indicates the same tendency, since the intensities of bands arising from methyl groups ($2970-2960\text{ cm}^{-1}$ and 2870 cm^{-1}) increase with increasing fraction number.

3.2.4. *The IR spectra of column chromatographic fractions of sample 77/105* (Fig. 11)

The bitumen extract of sample 77/105 was eluted with a solvent series of 7 members. The spectra of the fractions show the following features.

Fraction 1 is mainly straight-chain high paraffin hydrocarbon with a small cyclic and branching hydrocarbon content. In fraction 2, besides paraffins, aromatic hydrocarbons also appear, which according to the characteristic IR bands are present in larger quantities in fraction 3.

In fractions 4-7 the bands of aromatic CH bonds are again weaker, but the skeletal vibrations become stronger and broader, indicating that in these fractions condensed ring systems appear.

From the bands of groups containing hetero atoms the following conclusions can be drawn.

The amount of carbonyl groups — present again mainly in the form of esters — increases with the fraction number, and the complexity of the band also increases, indicating that various types of esters, as well as carboxylic acids and ketones, may be present.

OH and NH groups are present from fraction 5.

In fractions 3-5 the aromatic CH stretching bands are very well observable.

The intensity ratio characteristic of the relative amounts of methyl and methylene groups does not change remarkably.

3.2.5. *The IR spectra of column chromatographic fractions of sample 77/41* (Fig. 12)

The bitumen extract was eluted with a solvent series of 5 members. The spectra of the fractions and the eluents are shown in the figure. Of the possible functional groups listed in the Fig. 8/a the following dominant groups were investigated:

Straight-chain higher hydrocarbons are completely dominating fraction 1. In fractions 2-4 monocyclic aromatic hydrocarbons, and those containing a small number of rings can also be observed to appear ($900-700\text{ cm}^{-1}$). The spectrum of fraction 5 indicates the condensation of rings ($1650-1500\text{ cm}^{-1}$).

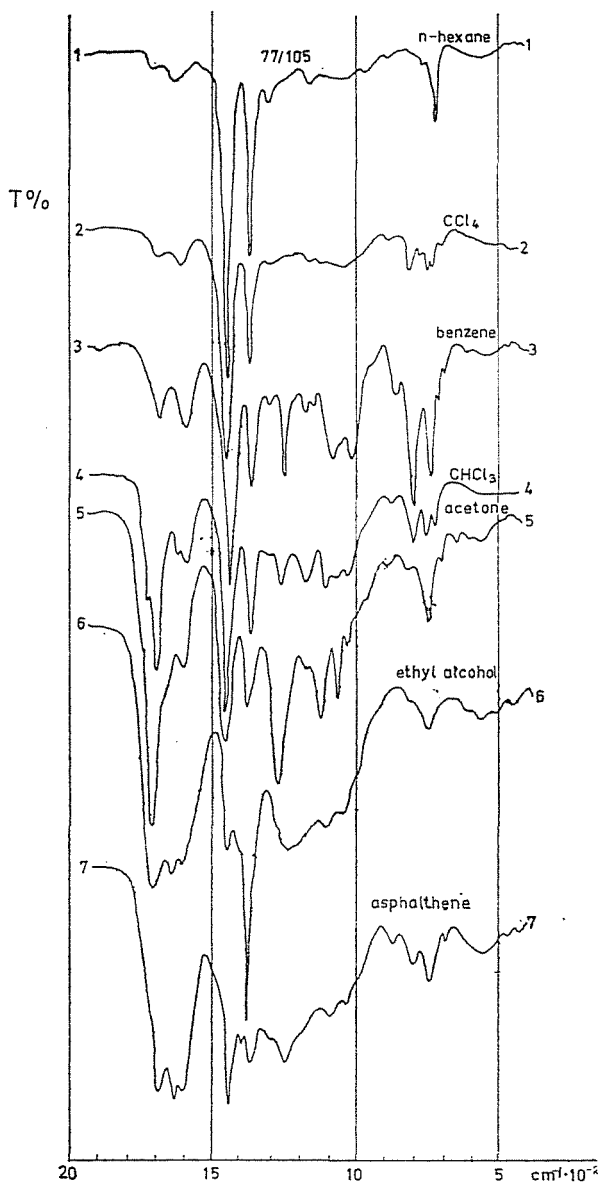


Fig. 11. The IR spectra of column chromatographic fractions from sample 77/105

Cycloparaffins are presumably present in fractions 2–4 (ca. 1000 cm^{-1}).

A splitting, indicating the branching of chains (1380 cm^{-1}), could be observed in all fractions in the form of a shoulder.

The amount of carbonyl groups is not too large in fractions 1–2, it is substantial in fractions 3–4, decreasing again in fraction 5.

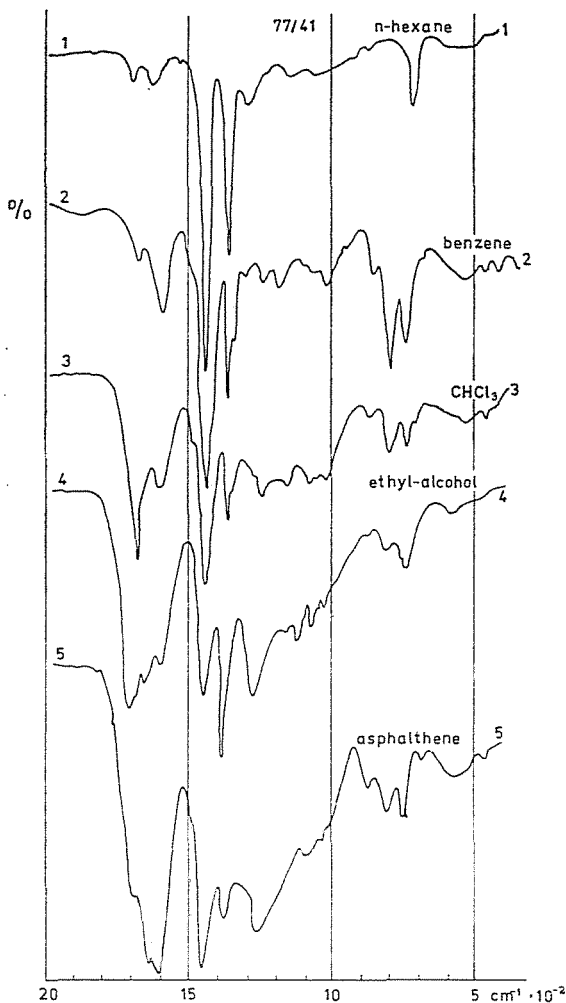


Fig. 12. The IR spectra of column chromatographic fractions from sample 77/41

The spectra of fractions 4–5 show several bands between 1750 and 1600 cm^{-1} , since in addition to esters and other carbonyl compounds amides may also be present. Compounds containing hetero atoms may be present primarily in fractions 4–5. Hydroxy and amino groups are shown only in fractions 3–5 ($3600\text{--}3100\text{ cm}^{-1}$).

In these fractions the ratio of methyl and methylene groups does not vary so considerably than with sample 77/34.

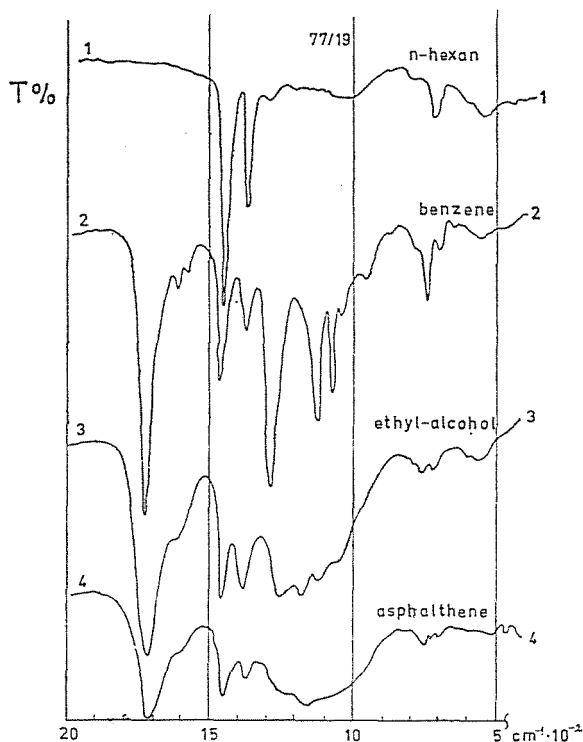


Fig. 13. The IR spectra of column chromatographic fractions from sample 77/19

3.2.6. The IR spectra of column chromatographic fractions of sample 77/19 (Fig. 13)

The bitumen extract, due to its small quantity, was eluted with a solvent series consisting of 4 members. The functional groups presumably present in the fractions are shown in the figure 8/a. Of them, the following ones were investigated:

Higher paraffins form the main bulk of fraction 1. Besides, from fraction 2, hydrocarbons containing aromatic rings appear. The bands of branched and cyclic paraffins are not strong. With fractions 3 and 4 polycyclic and condensed aromatic systems become dominant.

Except for fraction 1, carbonyl groups can be found in all fractions, mostly in the form of esters.

The bands of OH and NH groups are significant in fraction 3 and 4.

Although in the case of this sample less fractions could be investigated, the IR spectra show the same characteristics as a function of the eluent as in the case of the previous samples.

3.2.7. Conclusions

By evaluating the results of IR spectra the examined field can be divided to two parts. The IR spectra of aleurite samples of both parts (A and B) reflect the changes upon the effect of depth and temperature. There are significant differences between the sandstones of the two areas:

“A” area

small amount n-long chain HC
 considerable amount of aromatic, resin constituents
 branched chain HC
 —CO group in different type compounds

↓
no migration

“B” area

considerable amount of n-long chain HC
 very small amount branched chain HC
 little aromatic, resin constituents
 —CO group mainly in ester form

↓
migration

(This fact is also supported by the other geological and geochemical data.

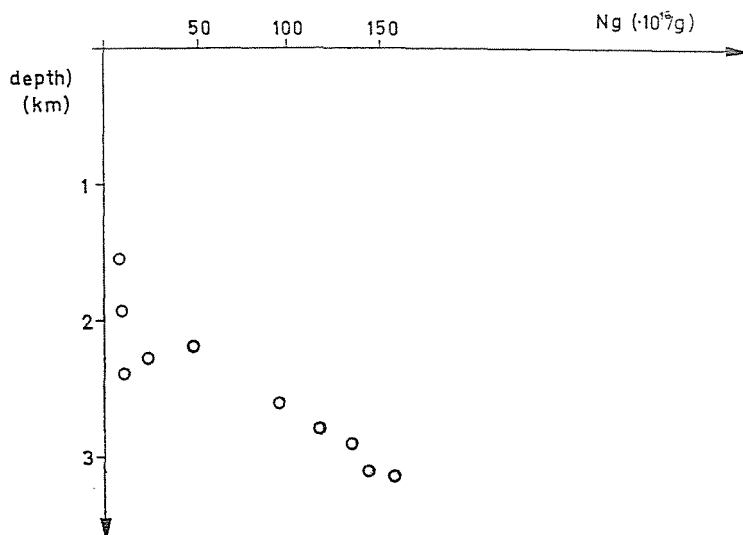


Fig. 14. Variation of N_g value as a function of depth

3.3. Interpretation of the ESR spectrum of asphaltene fraction

Pusey (1973) has reported the ESR investigations of kerogene, used for the determination of the maximum paleotemperature reached by the rocks and of the maturity of organic material. Investigating the ESR spectra of the asphaltenes of sand rocks in a given area, Elofson, Schulz and Hitchon (1977) have tried to elucidate the problems of mother rock and migration.

Asphaltene is similar in structure to kerogene, i.e. it contains a substantial amount of condensed rings, as well as hetero atoms (N, O, S) and paraffin chains, which split from the basic asphaltene molecule upon the effect of increasing temperature. The paraffin fragment stabilizes by taking up a hydrogen, whereas the asphaltene fragment remains in the form of a free radical, owing to a resonance of its unpaired electron with the electrons of the benzene ring.

Fig. 14 shows the ESR parameters of the asphaltenes arising from the area studied by us, as a function of depth. An abrupt change is well observable at the given depth, indicating the start of intense oil formation, or, respectively, a considerable increase in the maturity of organic matter.

Summary

The present paper is dealing with the various kinds of organic solvent extracts, the so-called bitumens, obtained from different depths of a Hungarian neogene basin. Change of quantity and quality with depth of bitumens was examined in the case of 19 rocks.

Organic solvent extracts of 4 rocks were divided by elution technique to fractions on silica gel column. It has been established that the organic constituents present in bitumen, normal and branching hydrocarbons, naphtane, one and polycyclic aromatic compounds substituted in different positions, condensed aromatic systems, as well as compounds containing heteroatoms, can be separated with the applied technique. The type of the rock and depth of finding determine the structure of the various kinds of compounds.

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