

CONTRIBUTIONS TO THE ALKALINE PERMANGANATE OXIDATION OF THE KEROGEN, LIGNITE AND PEAT

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INTRODUCTION

Investigations concerning the oxidation of the kerogen and other organic materials of the sediments play an important role in studying the structure and behaviour of the kerogen and the different organic remnants of sedimentary rocks.

These investigations are directed partly to the identification of soluble products of alkaline permanganate oxidation of organic materials isolated from sediments partly to the determination of the ratio of the different components formed to enable to conclude the structure of the kerogen, at least that of its oxidized part. The non-oxidized part remained, however, have not been investigated in a similarly detailed manner.

PRODUCTS OF THE ALKALINE PERMANGANATE OXIDATION

The oxidation by alkaline permanganate was applied investigating the structure of coals by BONE *et. al.* [1934]. The coals could be oxidized easily and totally, only in the case of anthracite remained a little rest unoxidized. In the series peat — anthracite the presence of benzene carboxylic acids in an increasing amounts besides CO₂, oxalic acid, acetic acid could be stated by the authors.

DOWN and HIMUS [1941] employing the method to the investigation of kerogen stated on the basis of the oxidation products that some of the kerogens are very similar to the coals and in these samples aromatic structure was to be suggested, whereas in kerogens of other origin e. g. in that of the Colorado oil shale and the Estonian oil shale kerogen (kukersite) the aromatic structure was not present or played merely a subordinated role. Among the oxidation products of the first group the non-volatile non-oxalic acids were present only below 1% and they were present similarly in a very small amounts in the oxidation products of the Estonian kerogen, too [ROBINSON *et al.*, 1953; FOMINA and POBUL, 1955]. It has been demonstrated that materials with highly condensed aromatic structure as for example the anthracite produce non-volatile non-oxalic acids (benzene carboxylic acids) in significant amounts, whereas the fatty materials are resistant to the oxidation. This fact alone renders possible some differentiation among the kerogens of different origin.

According to ROBINSON [1969] the Green River kerogen could be oxidized nearly totally to CO₂, oxalic acid and volatile acids demonstrating that it does not contain fatty material or condensed aromatic structures in a remarkable amount. On the contrary, the Middle Dunnet kerogen (Scotland) produced 14% non-volatile

non-oxalic acids pointing to the presence of aromatic structures or at least to the presence of structures able to form aromatic acids during the oxidation. The torbanite from Australia was very resistant to the oxidation owing to its considerable fatty material content.

However, during the oxidation the intermediate products themselves can be oxidized, therefore, to identify the intermediate products the step-oxidation was employed. Many authors dealt with the investigation of the products of the step-oxidation and a series of intermediate products were identified. According to the summary of STEFANOVIČ and VITOROVIČ [1959] among the oxidation products the "regenerated humic acids" [ROBINSON, HEADY, HUBBARD, 1953]; besides the non identified complex acids of higher molecular weight a mixture of dicarboxylic acids ranging from the oxalic acid to the adipic acid [ROBINSON, CUMMINS, STANFIELD, 1956]; volatile monocarboxylic acids, dicarboxylic acids from oxalic to azelaic acids and viscous acids of unknown composition [FOMINA, POBUL, 1955] can be found.

According to STEFANOVIČ and VITOROVIČ the oxidation with potassium permanganate in acetone solution is more suitable being this a more specific oxidizing agent and the oxidation of the kerogen by potassium permanganate occurs at definite points susceptible to oxidative attack [DJURICIC, MURPHY, VITOROVIČ, BIEMANN, 1971].

INVESTIGATION OF NON- OXIDIZED PART

The bulk of investigations of the products obtained by total or step-oxidation was directed mainly to the identification of the products, however, very few data can be found in the literature concerning the non-oxidized part remained after the single steps of oxidation. It may be assumed that besides the study of the oxidation products the investigation of this non-oxidized part may also contribute to the knowledge regarding the structure of kerogen.

The change of the elemental composition of the Estonian oil shale kerogen during its oxidation was reported by FOMINA, POBUL and DEGREVA [1965]. According to them the network of kerogen remained unchanged during the oxidation. This opinion is supported by the fact that the C and H content as well as the amount of the heteroatoms remained essentially unchanged in the oxidation rest after 8—72 hours oxidation even if more than 90 percent of the kerogen transformed into soluble oxidation products. Splitting off saturated structure units would have been revealed by decrease of the hydrogen content. As this decrease could not be stated, according to FOMINA *et al.*, the more kerogen is degraded into soluble oxidation products the more structure units with saturated chains remain.

According to DOWN and HIMUS some of the kerogens contain two types of material, one of them is easily oxidizable by alkaline permanganate, the other one is resistant to this action. According to DJURICIC *et al.*, [1971] the structure of the Green River kerogen consists of a "nucleus" of interconnected long aliphatic methylene bridges to which unbranched and isoprenoid chains are attached and these branching points are susceptible to permanganate oxidation. In this conception the production of mono- or dicarboxylic acids depends upon whether the splitting off occurs at a branching point of a saturated side-chain or at two carbon atoms connected by a methylene bridge.

At any rate, it would be interesting to attempt the characterization of changes taken place in the rest remained undissolved during the step-oxidation. If the structure

of kerogen remains either unchanged or some changes occur as for example the relative increase of ratio of saturated structures or on contrary the splitting off saturated side-chains, lost of some functional groups or fission or recombination of bonds, these changes will presumably be reflected either by IR spectra or by derivatographic examinations.

To approach the solution of this problem Estonian oil shale kerogen, peat and lignite were stepwise oxidized by alkaline permanganate during relatively short time and the rest remained undissolved after the single steps was investigated chemically as well as by derivatographic method and IR-spectroscopy to attempt to characterize the changes taken place during the oxidation.

EXPERIMENTAL PART

Determination of C and H content

The soluble organic material of the samples was extracted by chloroform in a Soxhlet-apparatus, then portions of 0,5—0,5 g was weighed into Erlenmeyer flasks and the oxidation was carried out at 50 °C by alkaline permanganate solution (1% KOH and solid potassium permanganate from 0,1 g increased to 2 g in the successive steps).

The rest of permanganate was eliminated by treatment with sodium sulfite in a weakly acidified solution. After filtration and washing with hot distilled water the rest was dried at 60 °C. The oxidizable organic carbon of these samples was determined by wet method. 0,01 g was weighed in a mixture of 10 ml N K₂Cr₂O₇ and 15 ml Ag₂SO₄—H₂SO₄ solution (25 g Ag₂SO₄ in 1 l concentrated H₂SO₄). The solution was heated for one minute to 150 °C. After cooling the solution was filled up to 200 ml with distilled water and 10 ml 85% phosphoric acid and 0,2 g NaF was given to it and the excess of K₂Cr₂O₇ was titrated by Mohr-salt solution against diphenylamine indicator. Each series requires a blank titration.

$$C_{\text{org}} = \frac{\left(\begin{array}{cc} \text{ml Mohr-solution—ml Mohr-solution} \\ \text{for the blank} \quad \quad \quad \text{for the sample} \end{array} \right) \cdot 0,3}{\text{g sample weighed in}}$$

For the determination of the C_{org} and H one part of the samples was treated by diluted HCl and some drops of diluted hydrogen peroxide. After filtering and washing the samples were dried at 60 °C. These samples served for the C—H analysis by combustion in oxygen as well as for IR investigation and DTA investigations.

The organic C content oxidizable by wet method as well as the total organic C and H content determined by the combustion method in the original samples and the undissolved rests after the single steps of oxidation are shown in Table 1.

Comparing the carbon content obtained by wet method and by combustion in oxygen, respectively, it is conspicuous that the difference between the two values increases by the duration of step-oxidation. The carbon content of the starting Estonian oil shale kerogen determined either by wet oxidation or by combustion method is nearly the same (75,1% and 75,8%), however, after 24 hours oxidation the carbon content oxidizable by wet method amounts to only 6,4%, though the total C_{org} by combustion is 65,8%. A similar situation can be observed also at the peat and lignite, though in the carbon content determined in the starting samples

by wet method and by combustion already a little difference can be stated being the carbon content by wet method some per cent lower than that by combustion. This difference increases by advancing oxidation, e.g. in the case of peat after 2 hours oxidation the carbon content of the rest determined by wet method amounts to 3,2%, whereas the total C_{org} by combustion is 32,3%.

Investigating the H content of the oxidation rests and the starting materials it can be stated in accordance with the observation of FOMINA *et al.* that the decrease of the hydrogen content during the oxidation is very small, in the case of kerogen after the first treatment appears 1% decrease, the H content after the further steps shows nearly no change; the difference in the H content of the single lignite samples is negligible, in the case of peat the decrease in H content after the oxidation steps is somewhat more considerable (in the starting material 6,0% and after 120 minutes oxidation 4,6%).

As to the possible interpretation of these experimental data, the statements of different authors agree that the Estonian oil shale kerogen has a rather aliphatic character and contains very little or no benzenoid structures. The aromatic structures as well as the saturated units are more resistant to the wet oxidation than the unsaturated bonds. In FOMINA's opinion at progressing decomposition of the kerogen during the step oxidation the amount of saturated chain units will increase in the rest. This opinion is supported by the fact mentioned above, by the difference between the total C_{org} by combustion and the C_{org} oxidizable determined by wet method which difference increases by the progressing oxidation.

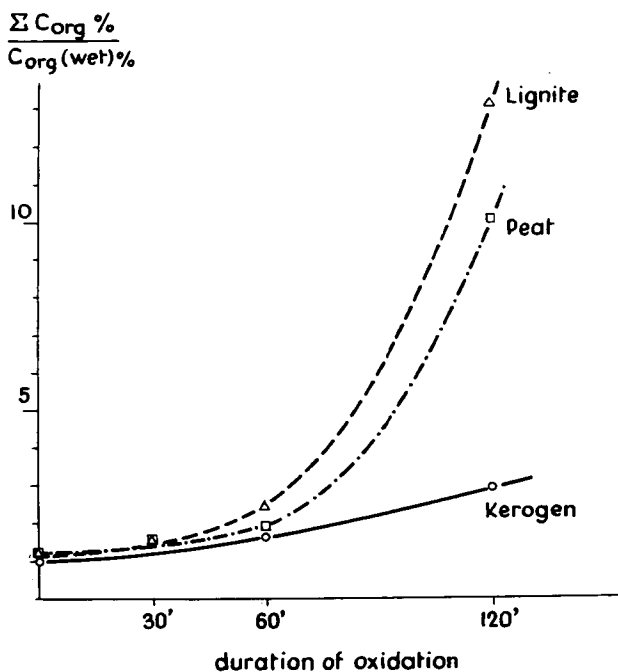


Fig. 1. The change of the quotient of total carbon content determined by combustion and the carbon content oxidizable by wet method in function of the duration of oxidation

The carbon content determined by wet oxidation may represent the carbon in more easily oxidizable bonding that is first of all the unsaturated bonds, whereas the total carbon content determined by combustion in oxygen involves the carbon content of unsaturated, saturated and aromatic structures.

Considering the Fig. 1 and the data of Table 1 it may be stated that in the case of kerogen within the oxidation period applied the quotient of the carbon content of two kinds increases approximately uniformly. It may be interpreted according to FOMINA *et al.* that during the progressive oxidation of the kerogen the amount of the saturated chain units not oxidizable by wet oxidation uniformly increases in the undissolved rest. On the other hand, the change of the quotient is much more significant in the case of peat and lignite and the carbon content oxidizable by wet method amounts to merely 3,2% in the oxidation rest of peat and 1,6% in that of lignite after 120 minutes oxidation, whereas the same value for the kerogen is 23,1%. The total carbon content determined by combustion in the undissolved rest of the samples oxidized for 2 hours, expressed in percentage of the total carbon content of the starting samples: kerogen 88,8%, peat 61,9% and lignite 37,8%, *i.e.* within the given time interval the degradation and transformation of the kerogen into soluble oxidation products is relatively slow, whereas that of the lignite far faster process.

As shown in Table 1 the hydrogen content of the peat samples treated decreases by the duration of oxidation and the amount of carbon content oxidizable by wet method diminishes more and more by progressing oxidation compared to the amount of total C_{org} . A similar tendency can be found also at the lignite samples, however, the hydrogen content of the samples treated remains practically unchanged. The decrease of the total carbon content is much slower than the decrease of the carbon content oxidizable by wet method which may be interpreted by the benzenoid structures originally present and by the relative increase of the amount of aromatic structures partly by the relative increase of the rate of saturation.

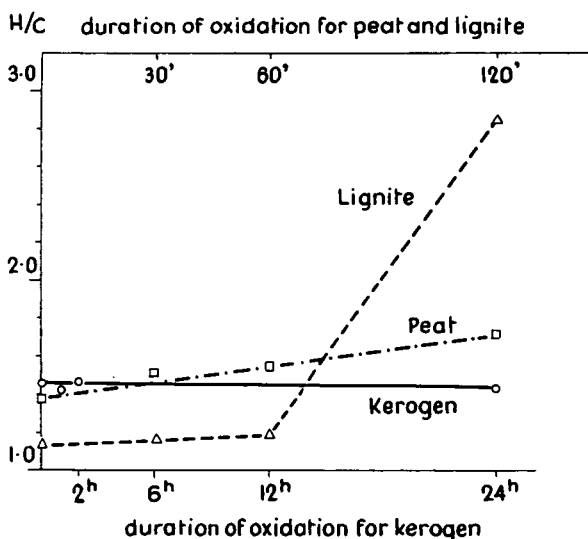


Fig. 2. H/C ratio during the oxidation of kerogen, peat and lignite

As it is shown by *Fig. 2* the H/C atomic ratio is practically unchanged during the 24–hours step-oxidation in the case of kerogen and only a slight increase of the H/C ratio can be stated at the peat samples. Similarly a slight increase of the H/C ratio is exhibited by the lignite samples in the first hour of oxidation, then increases rapidly since the H content remains practically unchanged and at the same time the carbon content decreases significantly.

Infrared spectra of the samples

The IR investigations were carried out by UNICAM SP 200 spectrophotometer. The wavenumbers and estimated intensities of absorption bands observed on the spectra of the starting samples are shown in Table 2–4 and the spectra in *Figs. 3–5*.

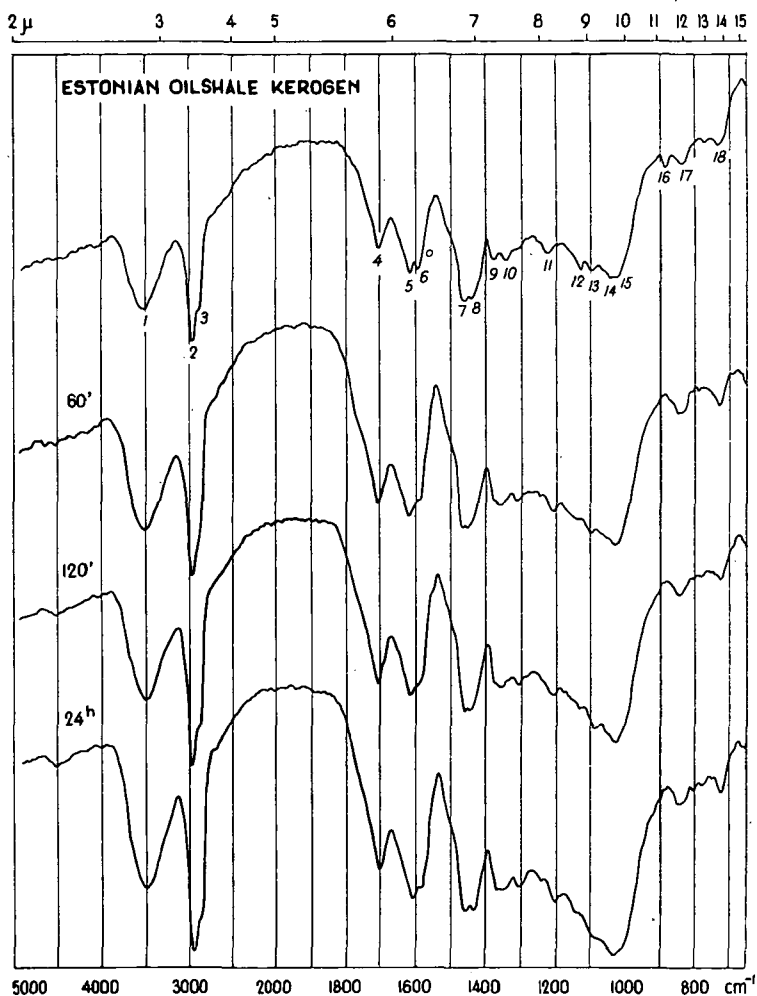


Fig. 3. IR spectra of kerogen samples (the first curve is that of the starting sample, the others those of samples oxidized for periods denoted on the curves)

TABLE 2

Wavenumbers and estimated intensities of absorption bands of IR spectrum of the kerogen

N°	Band positions (cm ⁻¹)		
1.	3500 s (broad)	νOH	
2.	2980 vs	$\nu(=\text{CH})$ $\nu_{\text{as}}\text{CH}_2$ $\nu_{\text{as}}\text{CH}_3$ } $\nu(=\text{CH}_2)$ $\nu(=\text{CH})$ }	aromatic aliphatic olefin
3.	2880 s	$\nu_s\text{CH}_2$ $\nu_s\text{CH}_3$ }	aliphatic
4.	1710 m	$\nu\text{C}=\text{O}$	carboxylic group
5.	1620 s	$\nu\text{C}=\text{C}$ $\nu_{\text{as}}\text{CO}_2$ νCC •	olefin carboxylate anion aromatic
6.	1590 s		
7.	1470 s	νCC $\delta_{\text{as}}\text{CH}_3$	aromatic aliphatic
8.	1440 s	νCC $\delta_{\text{as}}\text{CH}_3$ $\beta_s\text{CH}_2$	aromatic aliphatic aliphatic
9.	1380 w	$\delta_s\text{CH}_3$ νCO_2	aliphatic carboxylate anion
10.	1340 w	$\delta_s\text{CH}_3$	aliphatic
11.	1220 w	$\nu\text{C}_{\text{Ar}}-\text{C}(=\text{O})$	aromatic carboxylic acid
12.	1130 vw	$\nu\text{C}-\text{O}(\text{H})$ $\nu\text{C}-\text{O}-\text{C}$	tertiary and phenolic OH esters with conjugated double bonds
13.	1100 vw		
14.	1040 w		
15.	1020 w		
16.	880 w	$\gamma(=\text{CH})$ $\gamma(=\text{CH}_2)$ }	olefin
17.	830 w		
18.	730 w		

TABLE 3

Wavenumbers and estimated intensities of absorption bands of IR spectrum of the lignite

N°	Band position (cm ⁻¹)		
1.	3450 vs (broad)	νOH	
2.	3000 s	$\nu(=\text{CH})$ $\nu_{\text{as}}\text{CH}_2$ $\nu_{\text{as}}\text{CH}_3$ } $\nu(=\text{CH}_2)$ $\nu(=\text{CH})$ }	aromatic aliphatic olefin
3.	1710 vw	$\nu\text{C}=\text{O}$	carboxylic group
4.	1610 s (broad)	$\nu\text{C}=\text{C}$ $\nu_{\text{as}}\text{CO}_2$ νCC βOH	olefin carboxylate anion aromatic
5.	1520 s	νCC	aromatic
6.	1470 w	νCC $\delta_{\text{as}}\text{CH}_3$	aromatic
7.	1440 vw	$\beta_s\text{CH}_2$ $\delta_{\text{as}}\text{CH}_3$ νCC βOH $\nu\text{C}-\text{O}$	aliphatic aliphatic aromatic combination band of carboxylic acid
8.	1370 vw	$\delta_s\text{CH}_3$ $\nu_s\text{CO}_2$	aliphatic carboxylate anion
9.	1270 m	$\nu\text{C}-\text{O}$ βOH	carboxylic acids
10.	1210 vw	$\nu\text{C}_{\text{Ar}}-\text{C}(=\text{O})$	aromatic carboxylic acid
11.	1140 m	$\nu\text{C}-\text{O}(\text{H})$	tertiary and phenolic OH
12.	1100 w	$\nu\text{C}-\text{O}-\text{C}$	esters conjugated with double bonds
13.	1030 w		
14.	830 m	$\gamma(=\text{CH})$ $\gamma(=\text{CH}_2)$ }	olefin
15.	750 m	$\gamma(=\text{CH})$	aromatic

Considering the IR spectra of the samples investigated and comparing the spectra of samples oxidized for different periods to that of the starting sample, the changes can be summarized as follow:

The IR spectrum of the kerogen exhibits a great number of absorption bands. The spectra of the samples oxidized points to that during the oxidation no significant changes occurred. At least merely the bands 5 and 6 exhibit a slight change in intensity comparing to that of the starting sample. In the spectrum of the starting kerogen sample three weak bands can be established within the interval $1000-1100\text{ cm}^{-1}$ which more and more overlap during the treatment and at last they appear as an intensive, broad band. This may be attributed to the C—O—C vibration of esters conjugated with double bond. In the spectrum of the starting sample the bands characteristic of —OH and —COOH groups are also observed and their intensity

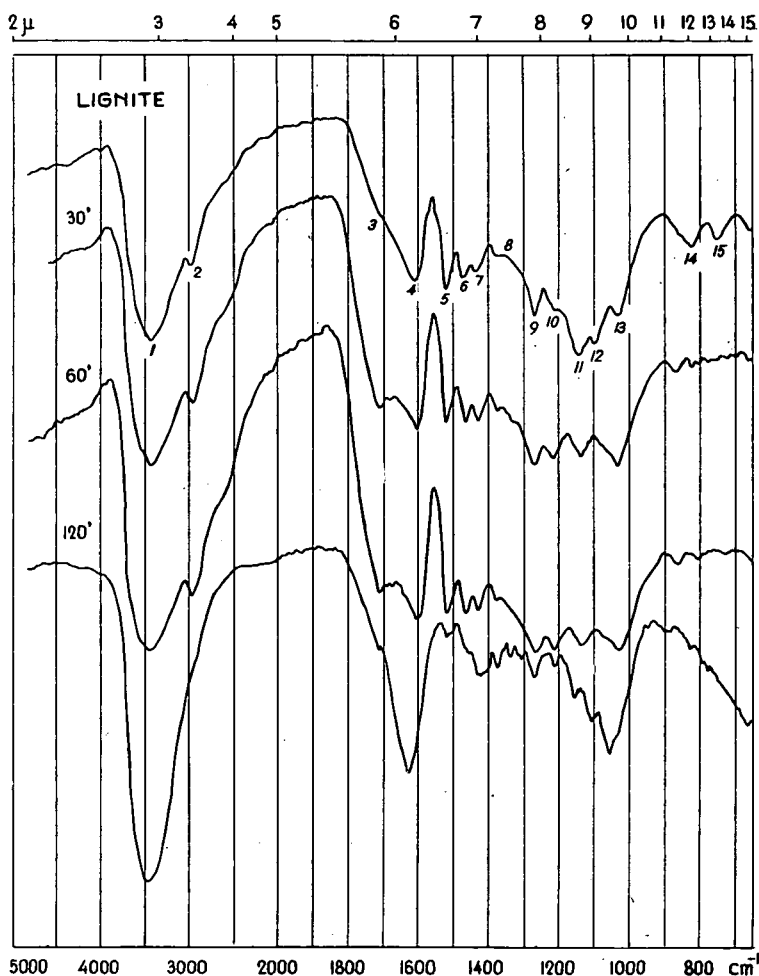


Fig. 4. IR spectra of the lignite samples (the first curve is that of the starting sample, the others those of samples oxidized for periods indicated on the curves)

TABLE 4

Wavenumbers and estimated intensities of absorption bands of IR spectrum of peat

N°	Band positions (cm ⁻¹)		
1.	3450 vs (broad)	νOH	
2.	2980 m	$\nu(=\text{CH})$ $\nu_{\text{as}}\text{CH}_2$ $\nu_{\text{as}}\text{CH}_3$	aromatic } aliphatic } $\nu(=\text{CH})$ $\nu(=\text{CH}_2)$
3.	1720 vw	$\nu\text{C}=\text{O}$	carboxylic group
4.	1640 s (broad)	$\nu\text{C}=\text{C}$ βOH	olefin
5.	1540 vw	$\nu_{\text{as}}\text{CO}_2$	carboxylate anion
6.	1250 m	$\nu\text{C}-\text{O}$ βOH	combination band of carboxylic acids
7.	1150 w	$\nu\text{C}-\text{O}(\text{H})$	tertiary and phenolic OH
8.	1050 s (broad)	$\nu\text{C}-\text{O}-\text{C}$	esters conjugated with double bond

shows no essential change during the treatment. The essentially unchanged character of the spectra of the kerogen samples seems to support the statement of FOMINA *et al.* [1965], the network of the kerogen remains unchanged during the step-oxidation, the H content as well as the H/C ratio exhibit also merely a negligible change during the oxidation, reported in this paper, too.

Comparing the spectra of the starting and oxidized lignite samples a more definite difference can be established. The intensity ratio of bands at 3450 cm⁻¹ and 2980 cm⁻¹ is nearly the same in the first step, however, after 2 hours treatment the band at 2980 cm⁻¹ disappears almost totally and the intensity of the band at 1710 cm⁻¹ exhibits a very slight increase. This band may be attributed to the C=O vibration. A more definite increase in intensity is exhibited by the band at 1610 cm⁻¹ which may be originated either from olefin bond or aromatic structure or from moisture or carboxylate anion. The change between 1000—1100 cm⁻¹ mentioned already at the kerogen spectra can also be observed on the spectra of the lignite samples.

The greatest differences between the spectra of the starting and treated samples are exhibited by the peat samples. The strong increase of the intensity of the band at 2980 cm⁻¹ points to the relative increase of the amount of CH₂ and CH₃ groups.

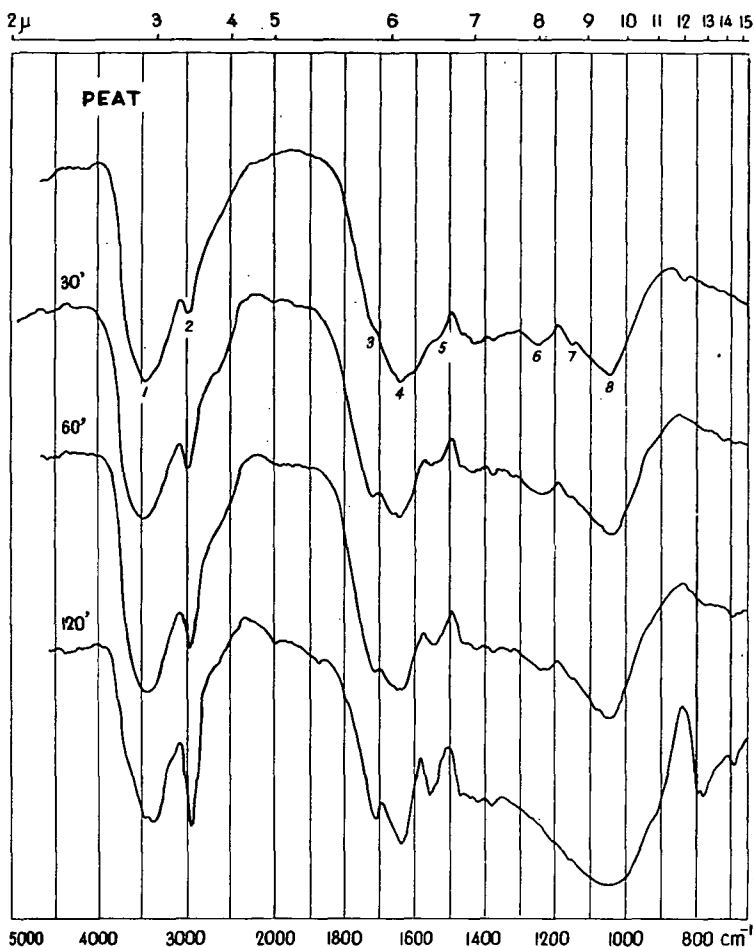


Fig. 5. IR spectra of peat samples (the first curve is that of the starting peat sample, the others those of samples oxidized for periods indicated on the curves)

The intensity ratio of the bands at 3450 cm^{-1} and 2980 cm^{-1} in the starting sample is 4,00 whereas in the spectra of the sample oxidized for two hours is merely 1,05. An increase of the intensities of bands at 1540 cm^{-1} and 1720 cm^{-1} can also be established. The first may be due to the carboxylate anion vibration and the latter due to $\text{C}=\text{O}$ bond pointing to possibly the relative increase of the amount of aromatic carboxylic acids. Amongst the three materials the formation of esters seems to be the most expressed in the case of the peat.

DTA investigations of the samples

The differential thermal analysis of the samples was carried out by ERDEY—PAULIK "Derivatograph". The DTA and DTG curves of the starting and oxidized samples are shown in Figs. 6—8.

It is true that the trend and rate of the thermal decomposition of organic compounds is controlled by the energies of bonds existing in the compound and also it is known that *e. g.* the compounds with alcoholic OH groups or the carboxylic group have a lower thermal stability than *e. g.* the methyl-, methoxy- etc. groups or at higher temperatures the aromatic structures have a greater thermal stability

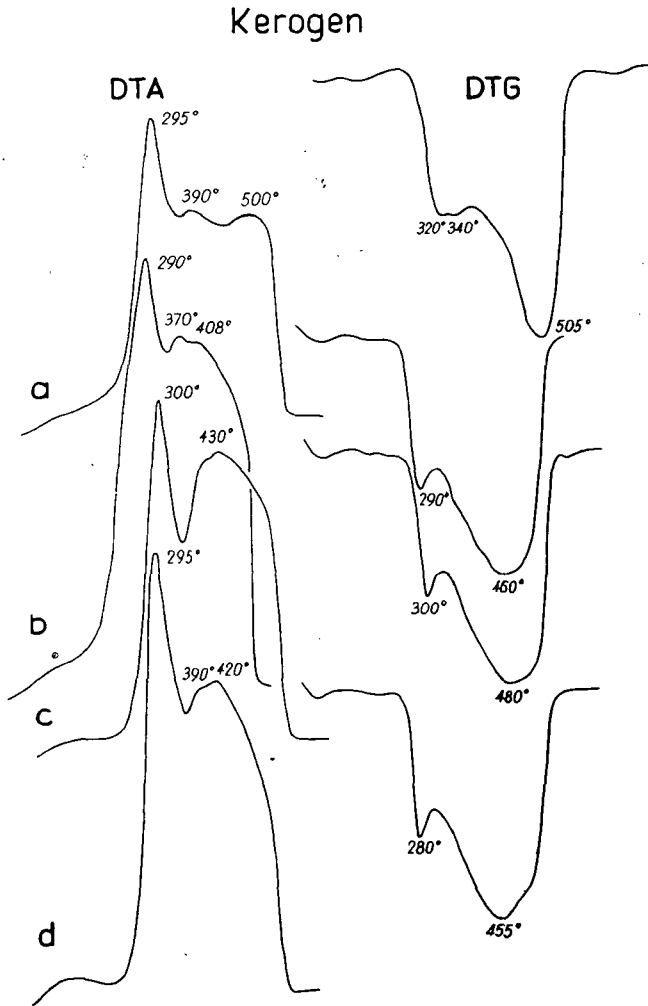


Fig. 6. DTA and DTG curves of the kerogen samples: a) starting sample, b—d) undissolved rest of samples oxidized for 1, 2 and 24 hours

than the aliphatic ones. In spite of all the interpretation of the DTA curves of such complicated organic materials as represented by the investigated ones is a fairly difficult task.

It has to be taken into consideration that during the thermal decomposition a series of reaction products may be formed and the solid material and the volatile

components can react with each other, the degradation products themselves may suffer a further gradual degradation and compounds of greater thermal stability may also be formed by the possible recombination of bonds.

Therefore, it was merely aimed to use the DTA and DTG curves for a qualitative comparison of the starting samples and those of oxidized for different periods to establish the changes taken place in the samples during the step-oxidation.

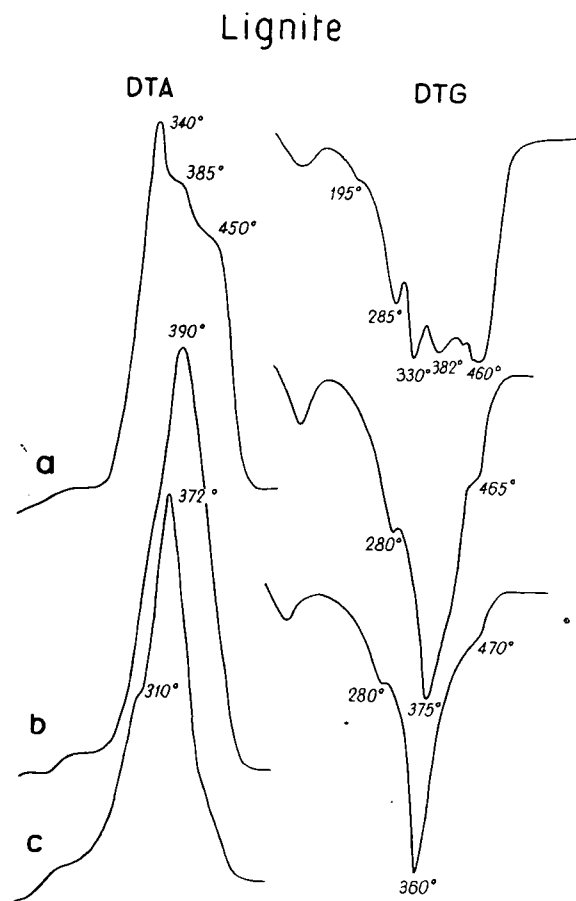


Fig. 7. DTA and DTG curves of the lignite samples: a) starting sample, b—c) undissolved rest of samples oxidized for 30 and 60 minutes, respectively

The DTA and DTG curves of the kerogen samples seems to be in accordance with the statements on the basis of IR spectra inasmuch merely a very little change during the oxidation can be observed. The DTA and DTG curves of the samples oxidized for 1, 2 and 24 hours exhibit nearly the same character, the temperature of the main exothermic DTA peak shows only a very little fluctuation between 290—300 °C and the same is valid for the first DTG peak, it varies between 280—300 °C. It is to mention that the temperature of the first exothermic DTA peak of

the untreated sample is also between 290—300 °C. It may be originated from components remained unchanged during the oxidation by alkaline permanganate, e. g. perhaps by the oxidation of OH and COOH groups as well as the splitting off the methyl- and methylen groups. The vibration of these groups on the IR spectra show namely no remarkable changes in their intensities during the oxidation.

As to the DTA and DTG curves of the lignite samples, considerable differences can be stated among those of the starting samples and those oxidized for 30 and 60 minutes, respectively. The DTA and DTG curves of the starting samples comparing to those of the samples oxidized merely for 30 minutes exhibit already a very definite difference. The DTA and DTG curves of the starting sample show overlappings of more peaks, whereas the curves of the oxidized samples exhibit more simple peaks characteristic of lignin demonstrating that most part of the other components present in the original sample turned into soluble products already at the beginning of the oxidation with alkaline permanganate. The curves of the samples treated are very similar to each other as the IR spectra of samples oxidized for 30 and 60 minutes, respectively, are also very similar.

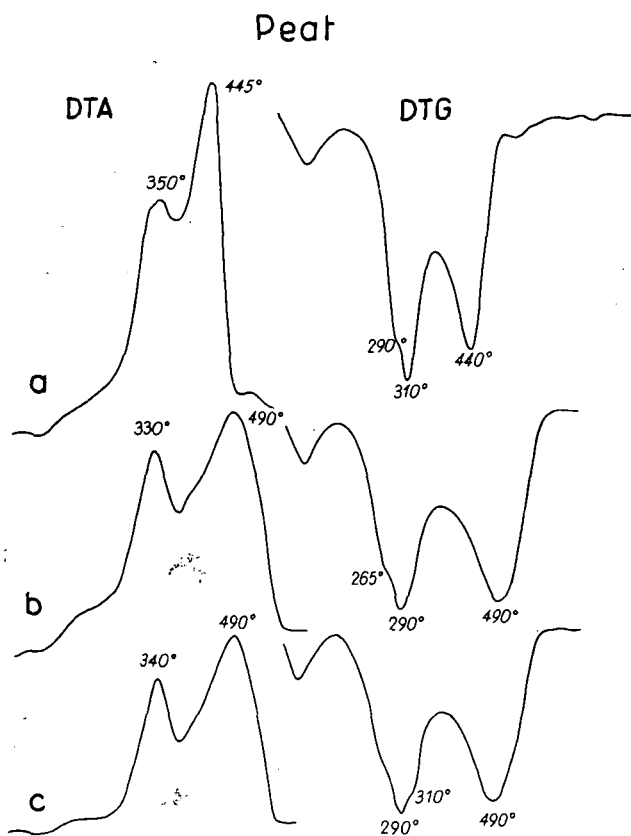


Fig. 8. DTA and DTG curves of the peat samples: a) starting sample, b—c) undissolved rest of the samples oxidized for 30 and 60 minutes, respectively

The DTA and DTG curves of the peat samples are fairly simple. According to F. PAULIK and J. PAULIK [1958] in the first step the thermal decomposition of cellulose and hemicellulose components may be assumed followed by the decomposition of the other components as lignin and/or humic material.

The curves of the samples oxidized for 30 and 60 minutes, respectively, exhibit almost the same character, however, they differ from the curves of the original sample, especially in the temperature of the second peak. It is to mention that the IR spectra of the peat samples oxidized for the time mentioned are also nearly identical but they also show some definite difference compared to that of the starting material.

SUMMARY

Considering the results of this preliminary investigations reported the followings can be established:

1. The statement of FOMINA *et al.* that the structure of the Estonian oil shale kerogen remains essentially unchanged during the step-oxidation by alkaline permanganate and that the constancy of the hydrogen content may be interpreted by the relative increase of saturated units seems to be supported also by the present investigations. The IR spectra and DTA—DTG curves of the starting kerogen sample and those oxidized for 1—2—24 hours exhibited only very small changes and the hydrogen content as well as the atomic H/C ratio showed also negligible variations.

2. The increasing difference between the total C_{org} determined by combustion in oxygen and the carbon content oxidizable by wet method determined in the same samples after the single steps of oxidation may be a qualitative measure of the relative increase of structural units more resistant to oxidation. Plotted the quotient of the $\Sigma C_{org} \%$ and $C_{org(wet)} \%$ against the oxidation period, characteristic curves for the three materials are obtained. This simple way perhaps may be useful in the characterization of insoluble organic materials of sedimentary rocks.

3. The IR spectra and the DTA—DTG curves of the starting samples and those of oxidized for different periods demonstrate that the kerogen samples suffered only a very little change during the oxidation, whereas also a little but better pronounced change can be observed at the lignite and the peat, especially comparing the curves of the samples oxidized to those of the starting samples. At any rate, during the step-oxidation with alkaline permanganate the solid rest remained undissolved suffers a slight change already at the beginning of the oxidation, however, the progress of this alteration is a fairly slow process. The IR spectra of the samples treated for 30 and 60 minutes, respectively, are similar and only a very slight change in intensities of some absorption bands may be established by the progressing oxidation.

4. Investigations of the behaviour of undissolved rests of samples after prolonged step-oxidation by alkaline permanganate are in progress. It seems to be also advisable to carry out the IR investigation of the starting and oxidized samples heat treated at temperatures corresponding to the temperatures stated on the DTA and DTG curves to enable to trace the possible steps of the thermal decomposition of the samples (cleavage of some bonds, recombination of bonds, loss of some functional groups etc.) owing to extend the applicability of the DTA and DTG investigation of such material also for semi-quantitative interpretation.

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