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APPLICATION OF CHROMATOGRAPHIC METHODS IN BIOGEOCHEMICAL INVESTIGATIONS

DETERMINATION OF THE STRUCTURES OF SAPROPELITES BY THERMAL DECOMPOSITION

ILMAR KLESMENT
Institute of Chemistry, Esthonian Academy of Sciences, Tallinn 26 (U.S.S.R.)

SUMMARY

Sapropelite was subjected to standard laboratory low-temperature carbonization and its decomposition products (oil) were analysed by combining various chromatographic techniques. The sample of neutral oil (500 mg) was separated by preparative thin-layer chromatography into groups of compounds —paraffins, olefins, etc. Subsequently, the composition of each group was determined by temperature-programmed gas–liquid chromatography. The presence of fragments of material of biological origin in the structure of the sapropelite was demonstrated, *i.e.* paraffins and ketones of odd carbon number and 1-olefins of even carbon number.

Besides the analysis of the Esthonian oil shale "Kukersite", as an example of the practical use of the method, a total of fifteen sapropelites were investigated, and in most cases the presence of unchanged fatty acid radicals in the structure could be indicated.

INTRODUCTION

Investigations have shown that most of the earth's organic matter does not lie in the biosphere, but in the upper layers of the earth. Part of the organic matter occurs in the form of fuel (coal, peat, petroleum), while the bulk of it is scattered in sedimentary rocks. Several products of biosynthesis are the source material for these carbon compounds. The objectives of biogeochemistry are the determination of the composition of organic matter in the geosphere, its origins, and the living organisms which are its source material.

Marine phytoplankton has been the main producer of organic matter throughout the history of the earth and thus accounts for most fossil matter deposited in sediments, known as sapropelites. The macromolecular organic matter of sapropelites (kerogen) is rich in aliphatic structures, the remains of marine plant and animal lipids. The kerogen is insoluble in common solvents and not amenable to ordinary methods of analysis.

By heating to 500° up to 80% of the organic material of sapropelites is converted into volatile oil. Sapropelites rich in kerogen, known as "oil shales", decompose upon heating to yield large amounts of an oil similar to petroleum in many of its properties. Well known among the oil shales are the Green River oil shale (U.S.A.)[1] and the Esthonian "Kukersite"[2,3].

This paper presents a method for the elucidation of the structure of sapropelites rich in organic material (oil shales) and the results are discussed from the point of view of biogeochemistry.

Relatively high yields of volatile products formed by the thermal decomposition of sapropelites make pyrolysis gas–liquid chromatography (GLC) a promising technique for this purpose. The practical use of the method is limited, however, due to secondary fission taking place at the high temperatures used to cut down the time of reaction.

In this work the standard laboratory low-temperature carbonization method (Fischer assay) was used for thermal decomposition. The oil obtained was separated by preparative thin-layer chromatography (TLC) into groups of compounds, and the composition of each group was determined by GLC.

Many examples have already been published for the use of complex chromatographic methods in the analysis of liquid products from low-temperature carbonization of coal[4–6]. The method described in this paper needs little initial material, is simple to carry out, and has been used over a long period of time for the analysis of many sapropelites.

As an example of the practical use of the method, the analysis of the oil obtained by low-temperature carbonization of the Esthonian oil shale "Kukersite", one of the few oil shales so far utilized industrially[2], was chosen to demonstrate the role of fatty acids in the formation of kerogen.

EXPERIMENTAL

Thermal decomposition

A 25–50 g amount of crushed oil shale (without any concentration of kerogen) was subjected to low-temperature carbonization using the standard Fischer assay apparatus. The oil obtained amounted to 2–10 g. Most of the liquid products emerged in the temperature range 380–450°.

The phenols were extracted from the oil with 10% sodium hydroxide. The dephenolized oil was treated with 20% sulphuric acid to remove the bases.

Preparative thin-layer chromatography

A method developed by Mistryukov[7] was used for separating the oil into groups. Glass plates (24 × 24 cm) covered with a loose 2-mm layer of adsorbent were used. In most experiments the adsorbent was silica gel L (Chemapol, Prague, Czechoslovakia) of 40–100 mesh size. The sample (500 mg) was applied to the plate in the form of a line. Reference compounds (*n*-dodec-1-ene, naphthalene, and *n*-dodecan-2-one) were spotted on to the plate on both sides of the sample line. The adsorbent was covered with another plate to avoid evaporation during elution. The plate was developed with petroleum ether (b.p. 40–60°) by allowing the solvent to run a distance of 20 cm (*ca.* 50 min). The reference compounds were located by means of

iodine vapour (sample area covered) and examination under UV light (254 nm). Fluorescent areas on the plate were marked: alkylbenzenes show a faint fluorescence, whilst polycyclic aromatics display a considerably stronger fluorescence. The borders between distinct groups were marked (Fig. 2a): paraffins, olefins, alkylbenzenes, polycyclic aromatic compounds, and neutral oxygen compounds.

The bands of adsorbent removed were extracted with diethyl ether (20 ml). The solvent was distilled from the samples in round bulbs equipped with a glass tube (20 cm × 4 mm I.D.) to avoid the loss of low-boiling fractions. The loss of fractions boiling over 100° was small, the yield amounting to more than 95%. Weighing was done with a precision of 1 mg.

Gas–liquid chromatography apparatus

A Chrom-4 (Czechoslovakia) gas chromatograph equipped with dual columns and flame ionization detectors was used. The two columns used were 5.5 m × 3 mm I.D. stainless-steel tubes, packed with 3.5% Apiezon L on 45–60 mesh AW Chromosorb G, and 12% Carbowax 20M on 60–80 mesh Celite 545. The polar phase was used for the separation of olefinic and ketonic isomers. Operating conditions were: carrier gas (helium) flow-rate, 30 ml/min; sample size, 1–2 μl; temperature programming rate, 3°/min.

RESULTS

Samples

Esthonian "Kukersite" oil shale contains 30–45% of organic material, from which 66% oil was obtained by laboratory low-temperature carbonization. Approximately 70% of the oil had a b.p. up to 400° and was amenable to GLC analysis. The samples were analysed without preliminary distillation. As the oil contains negligible amounts of nitrogenous compounds, only phenols were extracted before preparative TLC separation. The composition of the oil, according to TLC (Figs. 2a and 4a) was as follows: 7% paraffins, 11% olefins, 6% alkylbenzenes, 16% polycyclic aromatic compounds, 35% neutral oxygen compounds, and 25% phenols (11% monohydric, 14% dihydric).

The gas chromatogram of the total oil is depicted in Fig. 1. Only straight-chain hydrocarbons were present in considerable amounts. The large number of other components present did not form separate peaks. Since straight-chain hydrocarbons are the basic structural elements of all sapropelites, it was possible to obtain some data on their composition from the gas chromatogram of the products resulting from total decomposition. Data on olefin isomers and compounds belonging to other groups were obtained by analysis of TLC fractions.

Composition of paraffins and olefins

Preparative TLC is an effective method for separating olefins, as it involves only a short low-temperature contact with the absorbent, thus preventing isomerization of double bonds. The completeness of separation of paraffins from olefins depends on the boiling range of the sample, the absorption affinity of low-molecular-weight paraffins being close to that of high-molecular-weight olefins. For this reason the paraffin fraction retains up to 5% of olefins, and *vice versa*.

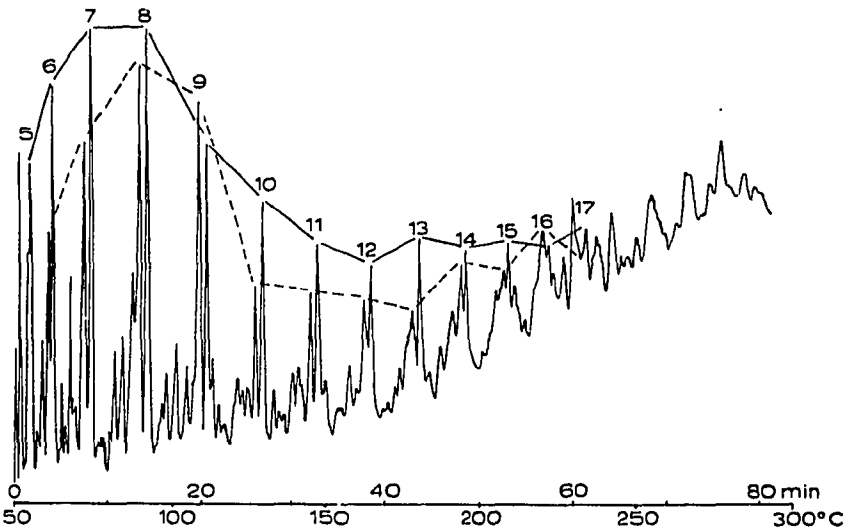

Fig. 1. Chromatogram of whole Esthonian shale semicoking oil on an Apiezon L column. The numbers are the carbon numbers of the straight-chain hydrocarbons corresponding to the peaks. The peaks of straight-chain paraffins are connected by a continuous line, those of straight-chain 1-olefins by a dotted line.

The gas chromatograms of Esthonian shale oil paraffins and olefins are shown in Fig. 2b-I and 2b-II, respectively. They show predominantly a homologous series of straight-chain hydrocarbons, the amount of branched isomers not exceeding 15%. Note the characteristic composition of long-chain compounds: paraffins of odd carbon-number —C_{13}, C_{15}, and C_{17}— are present in relatively higher concentrations, while 1-olefins are represented predominantly by compounds of even carbon number —C_{12}, C_{14}, and C_{16}.

We assume that the paraffin carbon chain length corresponds to the initial length of the aliphatic chains of the macromolecule of kerogen, but olefins contain one carbon atom less, as paraffins are formed by thermal destruction by breaking the first C–C bond connecting the chain with the cyclic nucleus of the macromolecule, whereas olefins are formed by breaking the second bond. In the formation of kerogen the fatty acids of marine plankton (predominantly homologues of even carbon number —C_{14}, C_{16}, and C_{18}) are subjected to decarboxylation, the ester group being replaced by a C–C bond[8].

Most of the aliphatic hydrocarbons obtained by thermal decomposition of kerogen contain from seven to ten carbon atoms. We assume that they were not formed by the fission of longer chains, but correspond to the saturated fragments of unsaturated fatty acids[9] polymerized in the process of fossilization.

Some olefins which contain eleven and more carbon atoms have a double bond in the middle of the chain. These isomers emerge from the GLC column before the corresponding 1-olefins. It is possible that the precursor of such olefins were monoenoic fatty acids, possessing a double bond in the middle of the chain. In the course of thermal decomposition the unsaturation may have been restored to its original place.

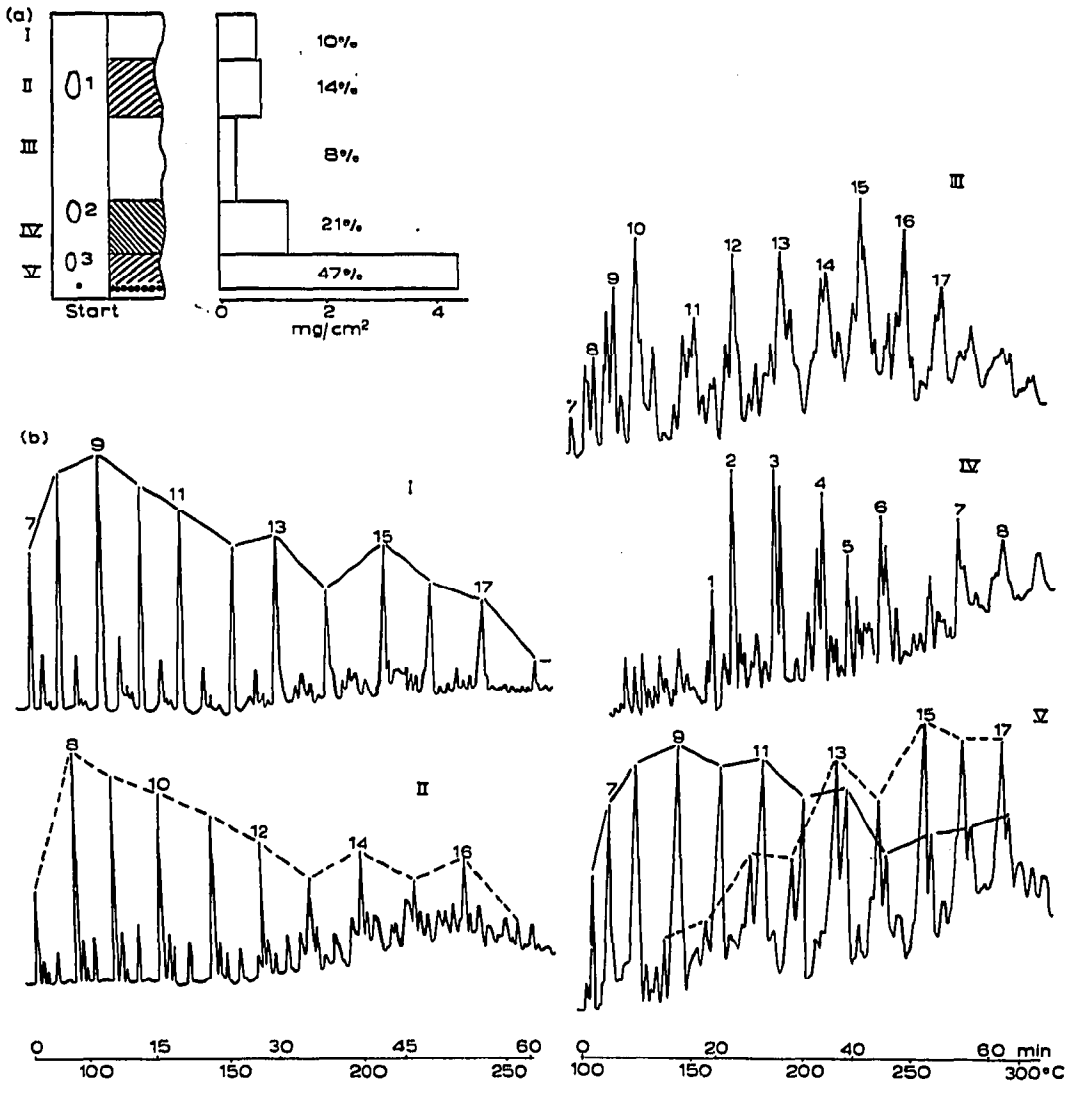

Fig. 2. Division of neutral semicoking oil by preparative TLC and analysis of obtained groups of compounds by GLC. (a) TLC on silica gel showing the quantities and the concentrations of the groups in the adsorbent. Reference compounds: 1 = *n*-dodec-1-ene; 2 = naphthalene; 3 = *n*-undecan-2-one. (b) I. Paraffins —GLC on a Carbowax column. Peaks of straight-chain paraffins are connected by a continuous line, numbers correspond to the carbon number of the paraffins. II. Olefins —GLC on a Carbowax column. Peaks of straight-chain 1-olefins are connected by a dotted line, numbers correspond to the carbon number of the olefins. III. Alkylbenzenes —GLC on an Apiezon L column. Numbers indicate the carbon number of groups of peaks. IV. Polycyclic aromatic compounds —GLC on an Apiezon L column. 1 = Tetralin; 2 = naphthalene; 3 = methylnaphthalenes; 4 = dimethylnaphthalenes; 5 = acenaphthene; 6 = fluorene and methylacenaphthenes; 7 = anthracene and phenanthrene; 8 = methylanthracenes and methylphenanthrenes. V. Neutral oxygen compounds —GLC on an Apiezon L column. Peak numbers indicate the carbon number of the straight-chain ketones. Coinciding 2- and 3-alkanone peaks are connected by a continuous line; the dialkyl ketones that have a carbonyl group in the middle of the chain, or near to it, are connected by a dotted line.

Alkylbenzenes

On the TLC plate between olefins and polycyclic aromatics lies the small but distinct group of alkylbenzenes. It was possible to identify only the compounds in the initial part of the chromatogram (Fig. 2b-III); among these, ortho-isomers predominate: 1,2-dimethylbenzene, 1-methyl-2-ethylbenzene, etc. In the unidentified region, such as in the case of olefins, peak groups are formed which differ by carbon number. The alkylbenzenes possess long side chains and contain up to seventeen carbon atoms. According to our data these structures are the cyclization products of unsaturated fatty acids.

Polycyclic aromatic compounds

The chromatogram of this group is shown in Fig. 2b-IV. Unlike the alkylbenzenes, the polycyclic aromatics possess only short side chains. The native kerogen contains aromatic structures in negligible amounts[10], so it is assumed that aromatization takes place only on pyrolysis. The relationship between source material and polycyclic aromatic compounds has not yet been studied.

Neutral oxygen compounds

Aliphatic ketones are ingredients of all shale semicoking oils.

On the chromatogram of oxygen compounds obtained on a non-polar column (Fig. 2b-V) are pairs of peaks of the same carbon number; to the first peak correspond ketones, the carbonyl group of which is in the middle of the chain or near to it, and to the second peak, 2- and 3-ketones. In order to investigate the isomeric composition of the ketones further, they were once more separated by TLC and analysed on a polar GLC column.

To separate 20–100 mg of the material 20 × 20 cm plates were used, the thickness of alumina being 0.5 mm. The plates were developed with petroleum ether–benzene (1:1). The results of the analysis of Esthonian oil shale ketones are shown in Fig. 3. Near the starting-line remain many high-boiling aromatic oxygen compounds which are not amenable to GLC analysis. Ketones, like paraffins, have up to seventeen carbon atoms in the chain, and are predominantly homologues of odd carbon number. By reaction GLC hydrogenation[11] it was established that the content of unsaturated ketones was negligible. The concentration of 3-ketones was also low.

The position of the carbonyl group depends on the length of the chain; compounds containing up to thirteen carbon atoms are mainly 2-ketones, whereas in a longer chain the carbonyl group is in the middle (dialkyl ketones). The 2-ketones may be formed by thermal fission from dialkyl ketones (β-cleavage). In this case, however, the carbonyl group must have been in a fixed position, which may be concluded from the predominance of 2-ketones of odd carbon number.

Phenols

Only small amounts of phenols are formed by thermal decomposition of most sapropelites, the Esthonian oil shale "Kukersite" being an exception, as its semicoking oil is rich in dihydric phenols, possessing the structure of 5-alkylresorcinols (1,3-dihydroxy-5-alkylbenzenes)[12,13]. Preparative TLC is an excellent method for separating phenols according to the number and position of hydroxyl groups. Most of the analy-

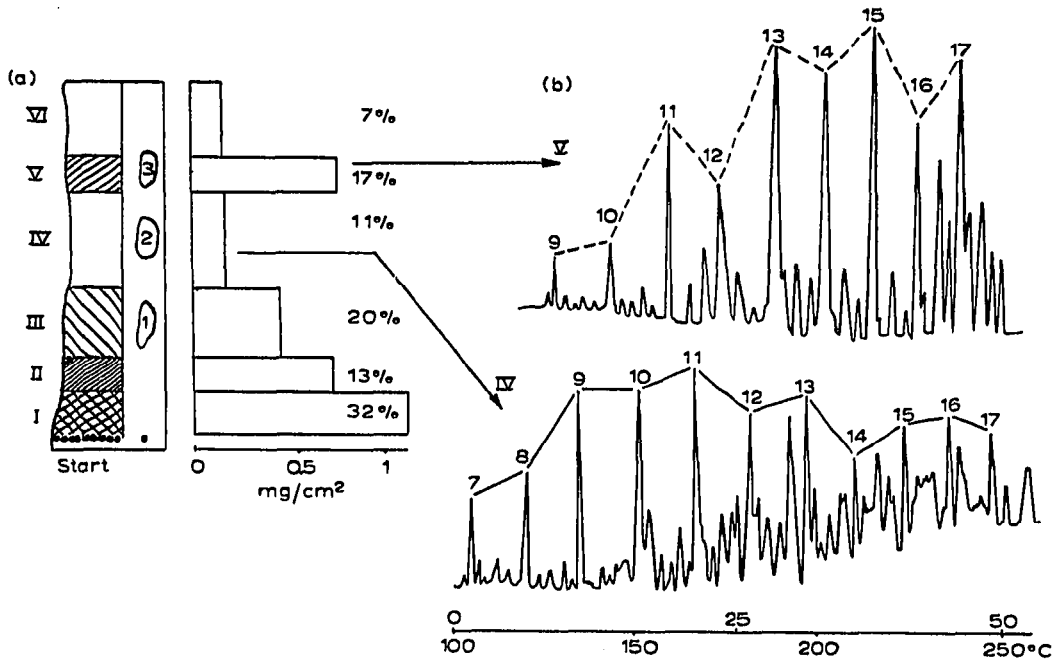

Fig. 3. Separation and analysis of ketones. (a) TLC of neutral oxygen compounds on alumina. Reference compounds: 1 = acetophenone: 2 = *n*-undecan-2-one; 3 = *n*-undecan-6-one. (b) GLC on a Carbowax column. Peak numbers correspond to the carbon number of the *n*-alkyl ketones. IV = 2-alkanone fraction; V = dialkyl ketone fraction.

ses in this work were carried out on silica gel. On alumina even better resolution may be achieved, but the extraction of fractions from the adsorbent is not complete.

The results of analysis of a phenol sample (500 mg) on silica gel, using chloroform–ethyl acetate (4:1) as developing agent, are shown in Fig. 4. The content of dihydric phenols exceeds 50% of the whole acidic group. The main constituents, 5-alkylresorcinols, contain up to ten carbon atoms in the side chains. To some extent they are separated according to the length of the alkyl group.

Isomers which are less readily adsorbed (4-alkylresorcinols) occur in smaller quantities. In the composition of monohydric phenols the same components are present as in the semicoking tars of other sapropelites, but there are in addition two more homologous series that have the same hydrocarbon skeleton type, but differ by the position of the hydroxyl group in the molecule. Long-chain *o*-alkylphenols are weakly adsorbed and readily separated from other isomers. The exact structures of this series of phenols have not yet been established.

The characteristic ingredients of Esthonian shale oil are 5-alkylresorcinols. It was shown in a previous investigation[14] that they can be formed in the process of fossilization from poly-unsaturated fatty acids. These acids are oxidized to polycarbonyl structures which by aldol condensation form cyclic diketones. In the course of thermal decomposition these ketones tautomerize to enolic (resorcinol) forms, which are more stable at high temperatures.

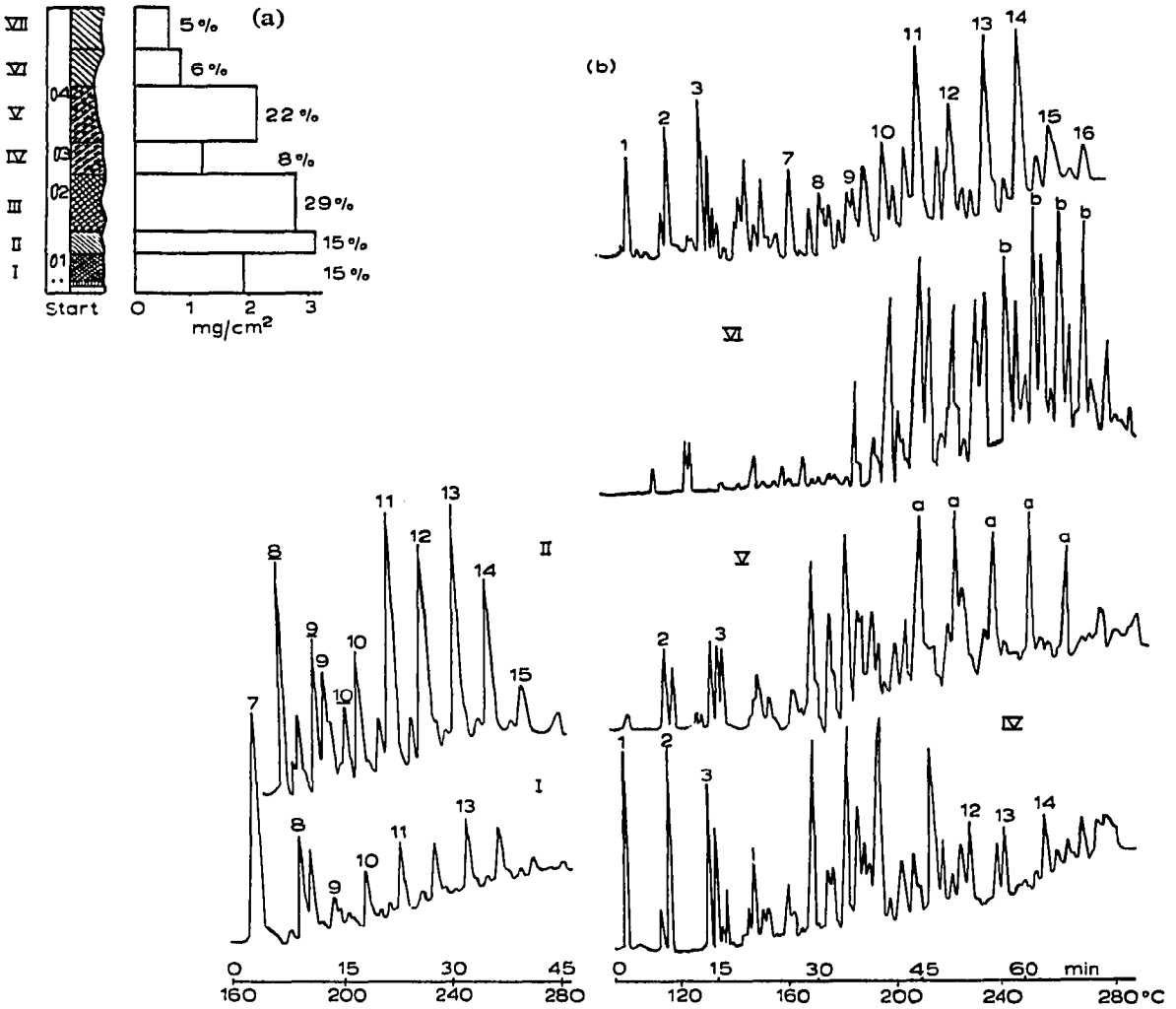

Fig. 4. Separation of semicoking oil phenols by preparative TLC and gas chromatograms of groups of compounds obtained on an Apiezon L column. (a) TLC on silica gel. Reference compounds: 1 = 5-methylresorcinol; 2 = 4-hexylresorcinol; 3 = 1-naphthol; 4 = 2-ethylphenol. (b) Chromatogram of initial phenols. 1 = Phenol; 2 = methylphenols; 3 = dimethylphenols; 7–16 = 5-*n*-alkylresorcinols; 8–10 = 4-*n*-alkylresorcinols. The peak numbers of the resorcinols indicate the number of carbon atoms in the corresponding compounds. The chromatograms show individual composition of corresponding TLC groups. The structure of monohydric phenols belonging to series a and b has not been established.

DISCUSSION

According to the thermal fragmentation products more than 40% of kerogen of "Kukersite" oil shale is a fossilization product of the fatty acids C_{14}, C_{16}, and C_{18}, the main and most stable constituents of lipid material, both modern and ancient. Using the complex chromatographic method the composition of fifteen sapropelites was investigated[8] and the presence of unchanged fragments of material of biological

origin in the structures of most of them was established. These fragments were found in the thermal decomposition products as straight-chain paraffins and ketones of odd carbon number and 1-olefins of even carbon number. Undoubtedly, the predominance of "odd" chains in the structure of kerogen is still considerably higher, in view of the low selectivity of thermal decomposition.

The main advantages of TLC are the rapidity of separation and high degree of resolution, usually considerably superior to that in the case of column chromatography. However, due to the small amounts of sample quantitation is worse.

Once the optimum conditions are established and the techniques of the method familiar, the analysis of a sapropelite may be carried out within a week. In an ordinary solid fuel carbonization oil up to 10,000 components are present[15], but only 500 in measurable amounts[16]. The identification of the main ingredients of a sapropelite semicoking oil is greatly facilitated by their belonging to homologous series.

Though common C_{14}, C_{16}, and C_{18} fatty acids are the main precursors of the aliphatic material of most sapropelites, much of it is constituted by the remains of acids up to C_{32} (ref. 8). Due to different conditions of fossilization no sapropelites exist that possess the same combination of aliphatic structures. The recognizability of biological patterns is not dependent on the age of the sediment, but on the severity of diagenetic processes: the age of "Kukersite" exceeds 450 million years, but its source material has been preserved more completely than that of some sapropelites with an age as short as 50 million years.

By the application of chromatographic methods to the investigation of the thermal decomposition products of sapropelites the structure of kerogen can be determined and data obtained on its biological precursors, formation, and geological past.

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