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CHARACTERIZING CRUDE OILS AND SOLUBLE DISPERSE ORGANIC MATTERS BY HIGH PRESSURE LIQUID CHROMATOGRAPHY

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ABSTRACT

The analysis and the comparative examination of hydrocarbon samples are very important from gcochemical aspects. To determine correlations for rock to rock, rock to disperse organic matter, oil to oil is one of the task of geochemistry.

On the basis of the below introduced and presented method it is possible to analyse quikly significant number of oil samples of relatively small quantities. By so doing comparison and classification of a kind of crudes from different locations and depths can be made. From the experimental results the identity of production site or a migration route may be concluded.

The analysis comprises (i) the samples preparation to HPLC, (ii) the HPLC analysis (iii) the computer processing.

During the analytical process of sample preparation for HPLC the crude oil or the chloroform soluble disperse organic matter were separated on a pre-column packed with silica gel for fractions eluated or non-eluated by *n*-hexane.

The fraction eluated by *n*-hexane containing the *n*-hexane-eluated aromatic components was used for HPLC which are specials and characteristics of different oils so the chromatograms of the crudes and the disperse organic matters are suitable for comparative analysis (finger print).

The computerized comparative analysis involves the determination of the location and heigth of peaks and the cluster analysis. The computer gives a plot of "dendrogram" showing the correlation of different types of crude oils and organic matters.

INTRODUCTION

Using high pressure liquid chromatography (HPLC) many workers investigated the analysis of hydrocarbons.

STEVENSON (1971), SUATONI and SWAB (1975), DARK *et al.*, (1977) determined the group composition of hydrocarbons (saturate, aromatic, heterocyclic aromatic) and obtained valuable informations on the composition, or comparability of oils.

GRIMALT and ALBAIGÉS (1982) pointed out that the polycyclic aromatic hydrocarbons in the crude have structural characteristics which are suitable for identification.

MILAN POPL and co-workers (1978) made a comparative analysis of the rock extracts and arrived at the same conclusions.

The liquid chromatograms of aromatics in the hydrocarbons represent a fingerprint of a given crude therefore are suitable to decide identity, similarity or difference of the samples examined.

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PRINCIPLES OF METHOD

The crude or the disperse organic matter soluble in chloroform was separated in a pre-column packed with silica gel to fractions that can be eluated by normal hexane and that cannot be eluated by *n*-hexane.

The part eluated by *n*-hexane was HPLC analysed. The chromatograms were recorded on a microprocessored data logger and were classified by a computer using cluster analysis technique.

PREPARING SAMPLES FOR HPLC ANALYSIS

The samples examined were crude oils and disperse organic matters soluble in chloroform. In the analitics of disperse organic matters soluble in chloroform (hereinafter bitumens) one of the problems was the small (10 to 20 mg) sample weight. Bitumens are obtained by extracting core samples in a SOXHLET extractor with chloroform, then the chloroform is evaporated in a nitrogen stream.

Max. amount of bitumens compared to the rock is . 25 weight percent, and generally from . 01 to . 07 w%. Only a part of the extracted bitumen samples can be used for chromatographic examinations since the residues can provide — through other analytical methods — further informations that are important from geochemistry's point of view.

It is a well known fact in literature that the liquid chromatographic measuring of crudes and oil-products is preceded by a proper preparation of the samples to be examined. The asphaltenes should be released from the crude since the precipitated asphaltenes damage the HPLC column. The exception is the field of gel chromatography (GPC) where BOMBAUGH and co-workers (1968) demonstrated that chromatograms can also be made from crudes.

Our sample preparation consisted of a simple and relatively quick examination. The oils or bitumens were separated in a glass column 4 mm inside diam. and 120 mm long, through an absorbent Kieselgel 60 of .063 to .2 mm particle composition using normal hexane as solvent, to two fractions: part that can be eluated with normal hexane and part that cannot be.

For the actual HPLC examination fraction eluated with normal hexane was used. The components not eluated with normal hexane were unneeded for the measurements so were left in the column, containing the polarized heterocyclic compounds and the asphaltenes "undesirable" for HPLC measuring. Time for preparatory examination was half an hour.

Preparing the samples took place under identical conditons. Amount of silica gel (Kieselgel 60) was always 2 gs. The silica gel used was activated for an hour at 120 °C by an argonic fluidization. The eluate was the Merck *n*-hexane made for chromatographic purposes and also used for HPLC measuring, and the sample amount was 10 to 20 mg. The sample had been dissolved in normal hexane and was transferred to the column previously wetted with *n*-hexane. The eluation volume was 100 ml, and the eluation rate was 3 ml/min.

It was examined to what extent the amount of hydrocarbons eluated changes with an increase in the volume of the eluate. By using obviously a larger column and a higher amount of sample (.1 to .2 g) it was shown that eluating with 800 ml of *n*-hexane 100 percent of the eluatable amount can be obtained. When increasing the eluation volume no change was observed either in the shape of HPLC chromato-

grams (amount of heterocyclic aromatics) or in the sample weight obtained after evaporating the normal hexane. Separation from this same sample was repeated using an amount of 20 mgs and an eluation volume of 100 mls. The two chromatograms were completely identical.

HPLC ANALYSIS

The chromatograph countained the following units: pump, type WATERS 6000A, a sample injector, type WATERS U6K, detector PERKIN ELMER LC—55, recorder type MICROGRAPH BD—5 and a column 250 mm long and 4.6 mm inside diameter, packed with 5 μ Lichrosorb Si—60.

The solvent was Merck *n*-hexane manufactured for liquid chromatographic purposes, with a water content below. 005 percent.

The *n*-hexane was protected from the moisture content of the air using a calcium chloride tube.

The measuring conditions were as follows: flow rate of the eluate was 2.2 ml/min, pressure drop was 700 psi, paper speed was 10 mm/min, sensitivity was 2.0 mV. The detector was operated at a wavelength of 254 nm in the UV range. Measuring time was 10 minutes.

For the HPLC measurement a hydrocarbon blend obtained during sample preparation and eluated with *n*-hexane was used. This fraction contained the saturated and normal hexane-eluated aromatic components of the oil or bitumen examined (the heterocyclic aromatics cannot be eluated from the pre-column in case of 100 ml eluation volume).

The UV detector is insensitive to saturated hydrocarbons at the 254 nm wavelenght, but the light absorbtion by the aromatics is very high, thus a chromatogram of the suitable quality can be made also of a small concentration (10 mg/100 ml) solution *(Fig. 1a)*.

Chromatograms (finger-prints) for identical types of oils are the same *(Fig. 1a* and *1b)* since they consist of aromatic components of the same composition. On the other hand that of different types of oils is significantly different due to differences in the aromatic compositions *(Fig. 1a) (Fig. 1c)*. Chromatograms in *Fig. 1a* and *Fig. 1b are* almost completely identical. Both oils are from the Szilvágy area, Hungary, but from two different wells. Therefore the significant difference of chromatogram in Figure 1c from the two chromatograms above is surprising since this sample is also from Szilvágy.

Based on the chromatograms it is obvious that samples marked Szilvágy 41 and Szilvágy 33 *(Fig. 1a* and *1b)* are crudes of the same type and age, while sample Szilvágy 24 is totally different from them *(Fig. 1c)*.

Chromatograms in *Fig. 1c* and *1d* also suggest the same origin, but in this case two oil wells at some kilometer distance from each other are involved (the Szilvágy 24 and Barabásszeg 15).

Chromatograms of chloroform-soluble disperse organic matters (most important samples of geochemical survey) also allow the above comparison to be made. Bitumens from Bulgaria were used for the examination.

From chromatograms in *Fig. 2a, 2b,* and *2c* similarity and difference of the bitumens can easily be observed.

To check selectivity of the HPLC column and to process chromatograms using a computer a calibration blend containing aromatics was made. Composition of the calibration blend in the order of eluation was: benzene, naphthalene, phenantrene,

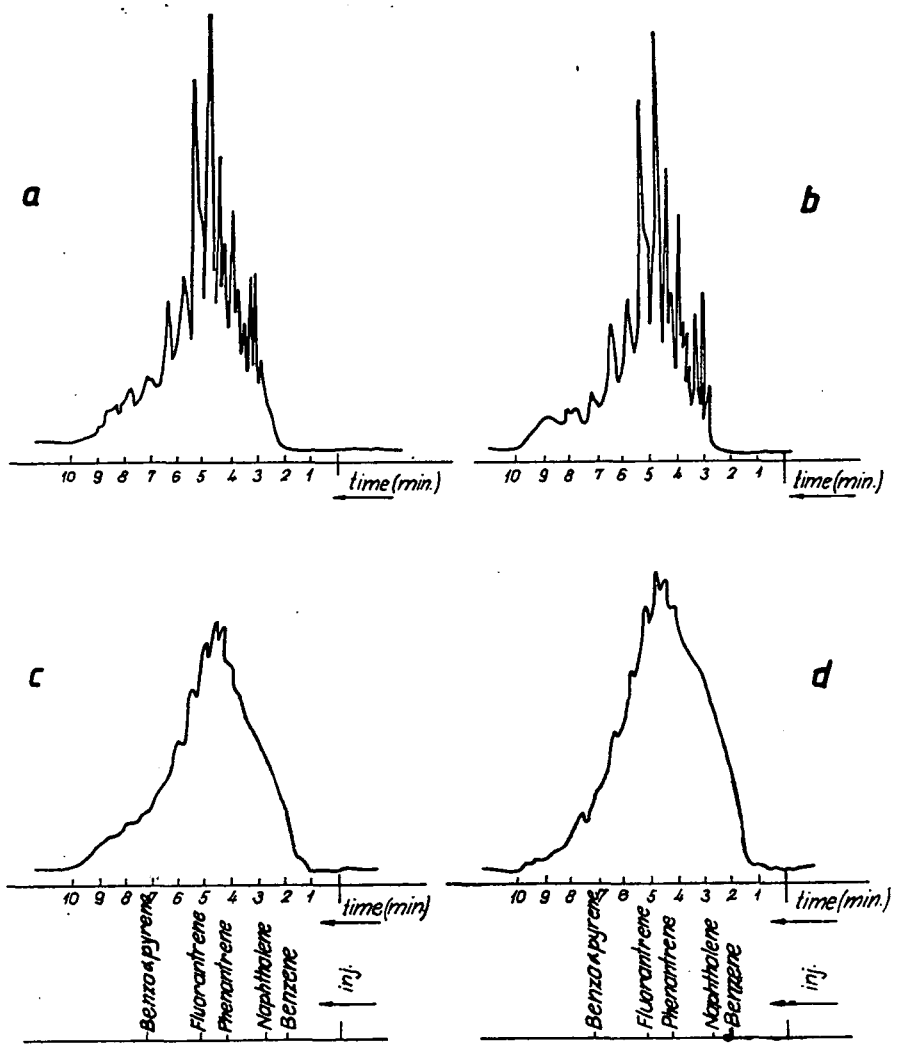

Fig. 1. Chromatograms of oil samples a: Chromatogram of oil sample marked Szilvágy-41 b: Chromatogram of oil sample marked Szilvágy-33 c: Chromatogram of oil sample marked Szilvágy-24 d: Chromatogram of oil sample marked Barabásszeg-15

fluoranthene and benzo-alpha-pyrene *(Fig. 3)*. The HPLC method was adsorption (liquid to solid) chromatography. The column was packed with porous silica gel. This system is very sensitive to traces of water and strong adsorbent substances (e.g. heterocyclic aromatics, resins, asphaltenes). In case these compounds are fed to the column, its selectivity decreases, the shape of the chromatograms changes and thus a comparison between the chromatograms cannot be made.

Therefore after every 10 sample measurements the column was checked using the above mentioned blend for calibration, and correction of errors due to possible

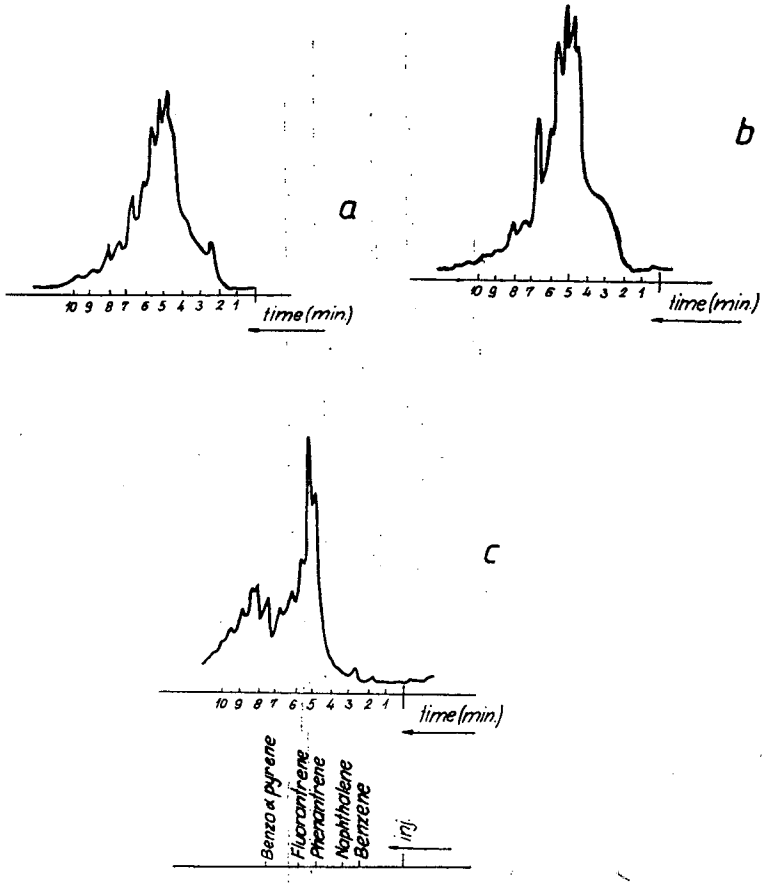

Fig. 2. Chromatograms of bitumen samples. a: Chromatogram of bitumen marked P—427 b: Chromatogram of bitumen marked P—428 c: Chromatogram of bitumen marked M—705

shifts in retention time allowed by means of the computer program. Occasionally hydrocarbon samples were injected into the column together with the calibration blend and thus identifying location of peaks became more reliable *(Fig. 4)*.

Based on chromatograms of the calibrating blend the qualitative examination of the samples was also allowed namely whether the di-, tri- or polycyclic aromatics are dominant in a given hydrocarbon.

COMPUTERIZED COMPARATIVE ANALYSIS OF CHROMATOGRAMS

The computerized processing involved input of the chromatograms into the computer, pre-processing the data, determining location and high of peaks and eventually making the cluster analysis.

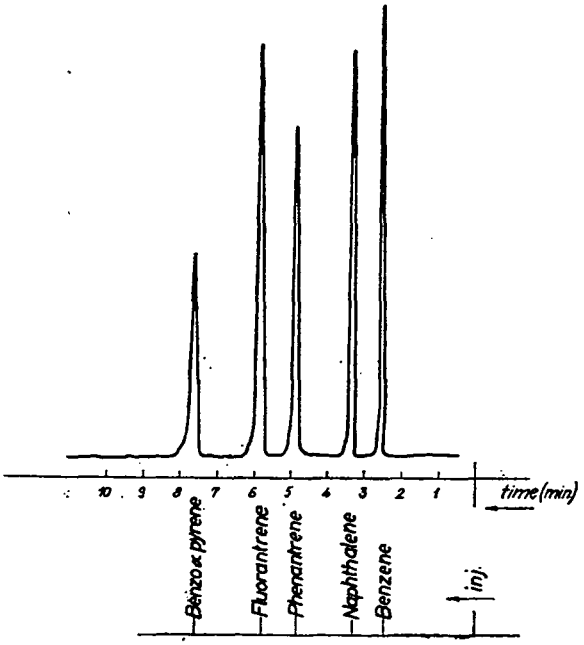

Fig. 3. Chromatogram of calibrating blend

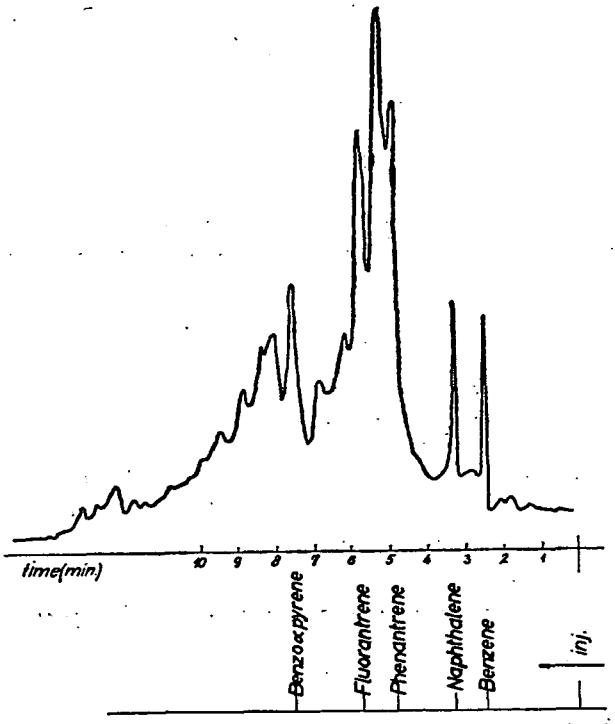

Fig. 4. Chromatogram of bitumen marked M—705 plus calibrating blend

Recording the chromatographic data took place using a casette data logger supported by an i8080 micro processor. The 10 minute measuring time was associated with a .1 sampling time thus a single chromatogram was represented by 6000 points. Data were loaded into the background storage of Computer TPA 1140 by means of the RS232C interface for the data logger.

The high number of points representing the chromatographic data and the noise interfering the data (partly generated during measuring and partly digital noise originated from the caracteristics of the data recorder and computer) required a preliminary data processing. During pre-processing the chromatograms were transformed to the same scale, were smoothed then the number of representing points were reduced to one fith *(Fig. 5)*.

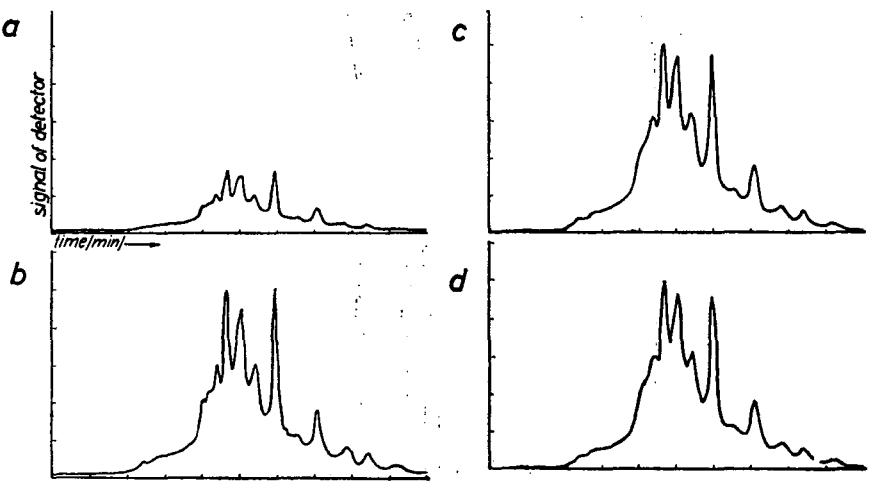

Fig. 5. Chromatogram pre-processing. a: Chromatogram input to machine b: Chromatogram transformed c; Chromatogram smoothed d: Chromatogram reduced

To determine the location of peaks two independent criteria were used in the program system. First, as per the definition in the classical analysis a peak was assumed at every point where the first derivate changes from positive to negative. Secondly, the spot with a minimal negative curve between two inflection points was considered as a peak *(Fig. 6)*. Using this second criterion near peaks not separated can be found, however the technique is very sensitive to noise and the points obtained must be selected. Identifying the peaks was made comparing the expected retention times obtained by processing the chromatogram of the calibrating blend, to the retention time of a given peak. The program corrected the expected retention times through knowing the spot of the newly found peaks. Basis for further processing was formed by the vectors derived from the values of peaks. These so called basic vectors were groupped by cluster analysis.

A primary task was to define the distance between the basic vectors. Out of the established distance concepts the Euclidean distance and the distance formed from

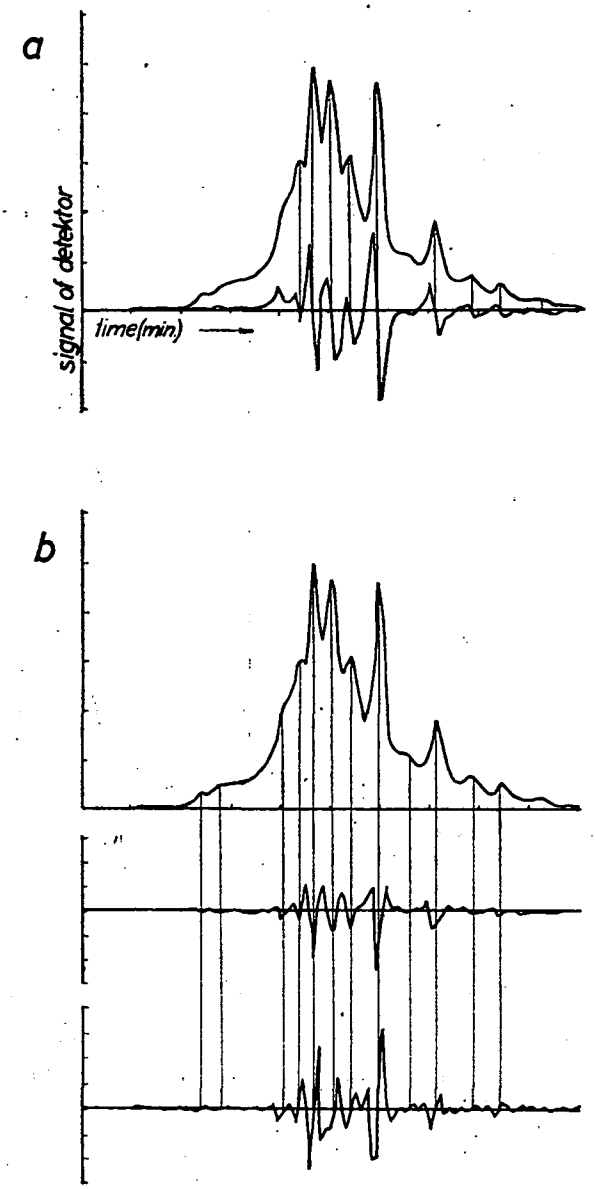

Fig. 6: Determining location of chromatographic peaks. a: As per first criterion first derivate. b: As per second criterion second derivate, third derivate

the correlation proved to be useful. The first one excelled through its simplicity and fastness, the later through its good coincidence with the everyday concept of similarity.

$$D_E(\bar{X}, \bar{Y}) = \sqrt{\sum_{i=1}^{N} (X_i - Y_i)^2}$$

$$D_r(\bar{X}, \bar{Y}) = \frac{1}{r(\bar{X}, \bar{Y}) + 1} - 0{,}5$$

$$r(\bar{X}, \bar{Y}) = \frac{\sum_{i=1}^{N} \left(X_i - \frac{1}{N} \sum_{j=1}^{N} X_j\right)\left(Y_i - \frac{1}{N} \sum_{j=1}^{N} Y_j\right)}{\sqrt{\sum_{i=1}^{N} \left(X_i - \frac{1}{N} \sum_{j=1}^{N} X_j\right)^2 \sum_{i=1}^{N} \left(Y_i - \frac{1}{N} \sum_{j=1}^{N} Y_j\right)^2}}$$

X, Y	basic vectors
Xi, Yi	components of basic vectors
N	dimension of basic vectors
D_E	Euclidean distance
D_r	generalized distance formed from the correlation
r	correlation coefficient from experience

Out of the possible algorhythms for clustering two were carried out.

1. The first one is a Kruskal algorhythm described by ANDERBERG (1973) which is a realization of the smallest spanning tree method. The clusters obtained by this technique correspond to the classes obtained by the nearest neighbour technique. Basic vectors "A" and "B" belong to the same group when there exist a finite series of the basic vectors the first element of which is "A" and the last one is "B", and the distance of any two neighbouring basic vectors is below a given threshold. According to DUDA and HART (1973) this technique is advantageous if the basic vectors form well distinquished groups. It is disadvantageous in case the basic vectors to be groupped can be attached to loosely connected chains *(Fig. 7)*.

2. The second one is the method of the furthest neighbour. Basic vector "A" belong to a given group alpha if its distance from all basic vectors in the group is below a given threshold. This technique is disadvantageous if the groups of basic vectors are of different size. With loosely connected chains they are out up so that elements groupped to a class show great similarity (7.8). This classification is worth carrying out as an addition to the previous one. If the two results obtained are different, detecting the reasons requires a detailed analysis. It is debatable whether the chains obtained by the first method represent a real progressing series, or only the samples difficult to group and interpolated between groups formed by the second method cause the formation of chains mentioned.

MEASURING RESULTS AND CONCLUSIONS

The computer recorded the results of analysis on a "dendrogram". In *(Fig. 8)* "dendrogram" of a given geological area's oils are shown, while in Fig 9 that of the Bulgarian disperse organic matters. The length of the horizontal lines up to the vertical ones indicates the similarity of the hydrocarbons.

In *(Fig. 8)* it can be seen that the computer distinguishes two main groups.

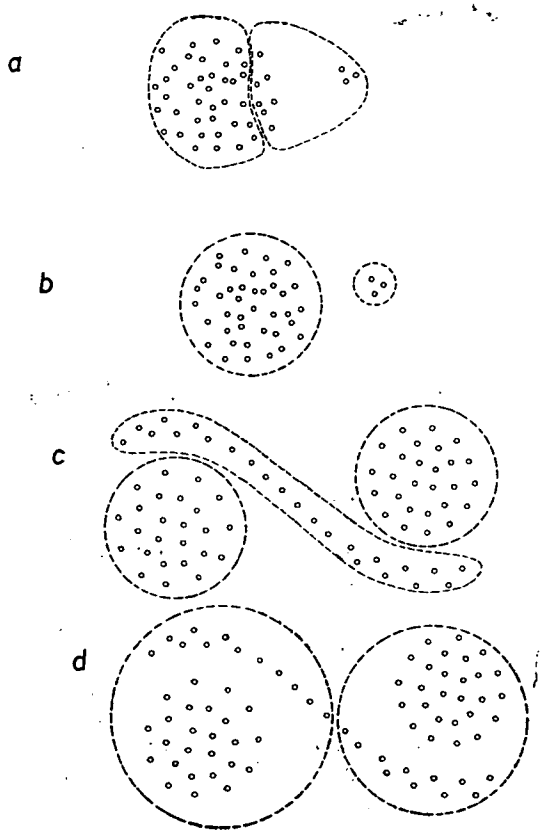

Fig. 7. Cluster analysis for basic vectors of two dimensions. a: Furthest neighbour method — disadvantageous. b: Nearest neighbour method for well distinquished groups — advantageous. c: Nearest neighbour method for loosely connected chains. d: Furthest neighbour method for loosely connected chains.

The first group is terminated at the sample marked Pusztaapáti 4, while the second one starts with sample Szilvágy 24. Further separation of the samples within the groups is shown in *Fig. 8.*

It is obvious that for example within the same group oil marked Szilvágy 41 is much more similar to Szilvágy 33 than sample marked Szentgyörgyvölgy 1 to Csesztreg 1. However oil Csesztreg I. does not belong to any group.

In "dendrogram" of Bulgarian bitumens *(Fig. 9)* a similar grouping can be observed.

The method is fast, requires a low demand for sample and can be rutinly applied in the fields of geochemical survey (great number of samples to be analysed) and in all fields where the objective is to identity hydrocarbons or their derivatives (e.g. detecting sources of trace amounts of oily contaminations).

The computerized evaluation allows establishing a data bank by means of which identification of oil samples with an unknown origin is also possible.

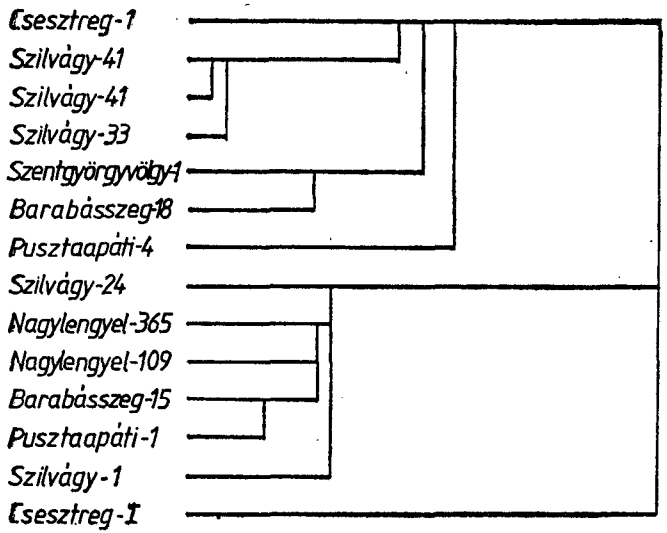

Fig. 8. Result of cluster analysis for oils

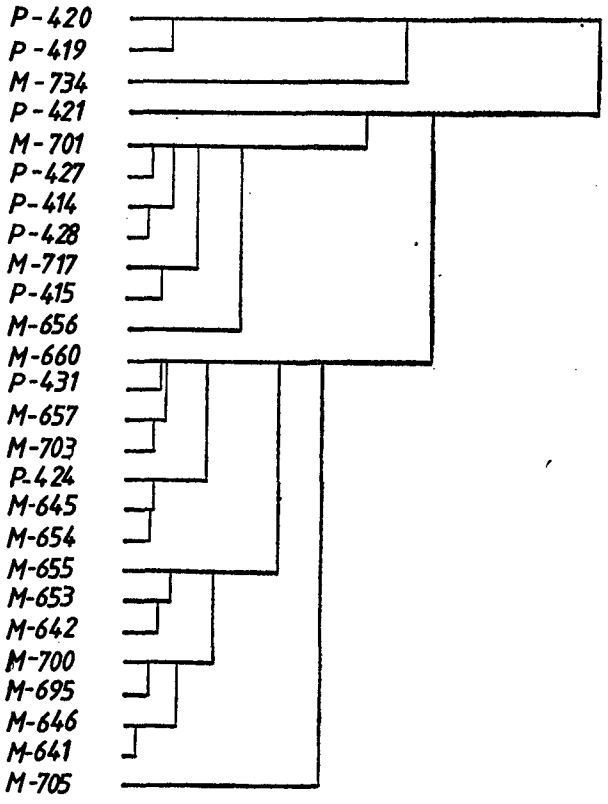

Fig. 9. Result of cluster analysis for bitumens.

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