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## CHROMATOGRAPHIC INVESTIGATIONS OF ORGANIC MATTER FROM ROCK SAMPLES

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### SUMMARY

Core samples of Szirák No. 2 hole were investigated by different chromatographic methods. Mechanical and chloroform extraction were applied to recover the organic matter from rocks. After the mechanical extraction the hydrocarbon gases were analysed by gas chromatographic headspace analysis, and the chloroform extracts were separated on a silica gel column. The saturated hydrocarbon fractions were studied by gas chromatography on a capillary column. Conclusions were drawn about the type and the maturity of the organic matter. Headspace analysis was found to be a good, rapid, and sensitive method for the investigation of hydrocarbon gases from rocks.

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### INTRODUCTION

Hydrocarbons (HCs) have prominent role as energy sources all over the world. The process of HC formation and migration can be traced by the study of the organic matter from rocks. The origin, the type and the maturity of organic matter can be studied by chromatographic investigation of gases and extractable organic matter from rocks. Study of the extractable organic matter made it necessary to develop a rapid, sensitive, routine method for the determination of HC gases from rock samples in order to cut down the number of time-consuming extractions. Headspace analysis of HC gases was found to be suitable.

There have been several studies dealing with the analysis of the light HC content of rocks. Extraction procedures mobilize the compounds continuously from the rock and collect them in a cold trap. Mobilization can be carried out by combined heating and grinding either under reduced pressure or with the aid of an auxiliary gas<sup>1-4</sup>. Another method of determination of light HCs in the range C<sub>2</sub>-C<sub>9</sub> combines extraction by hydrogen stripping with capillary gas chromatography in a closed gas-flow system<sup>5</sup>. These methods are difficult, slow and not suitable for detecting methane from rocks. Therefore the modified headspace analysis of Snowdon and McCrossan<sup>6</sup> was applied to determine the HC gas content in the range C<sub>1</sub>-C<sub>2</sub> from rocks.

The samples were covered with saturated NaCl solution instead of water to prevent the solution of HC gases and the activity of bacteria. To desorb the HC gases

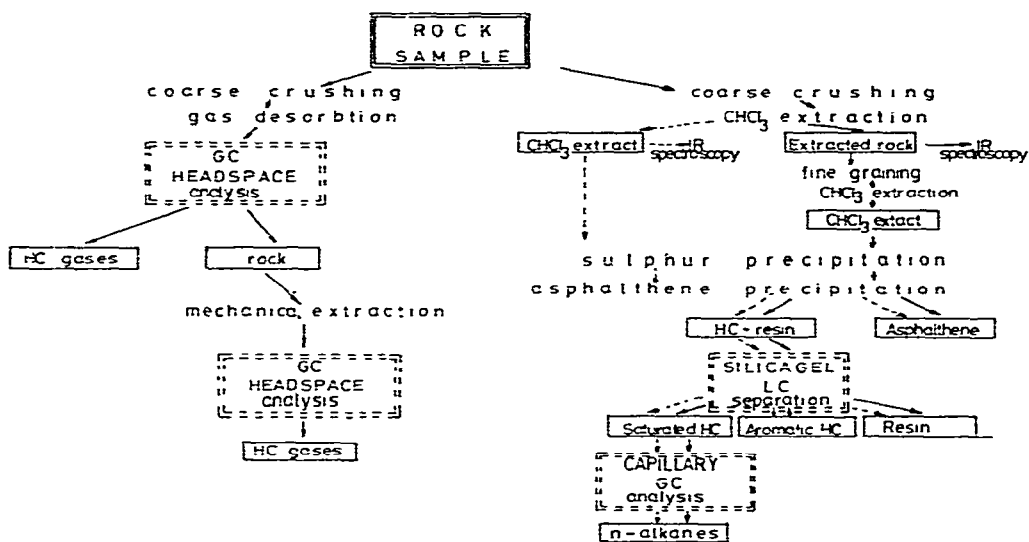


Fig. 1. Separation flow diagram and analytical methods.

from the open pores the samples were heated. The HC gases from both coarse and fine-grained samples were investigated showing the gases in open and closed pores.

## EXPERIMENTAL

The flow sheet of the detailed chromatographic investigation of rock samples is shown in Fig. 1.

### Headspace analysis

Core samples (200–300 g) were taken at the hole site, crushed to 1–2 cm particle size and closed into glass provided with a silicon rubber septum. The samples were covered with saturated NaCl solution (headspace volume 200 ml). The gases were desorbed at 60°C and were analysed in a Chrom 41 type gas chromatograph with a flame ionization detector. Having analysed the HC gases in open pores the samples were put into a stainless-steel blender jar and covered with saturated NaCl solution. The HC gases were extracted in Fritsch-type ball mill. One of the most important factors is the time for crushing. In both experiments 500- $\mu$ l of headspace gas was injected into the gas chromatograph using a gas-tight syringe. The analysis was made on a packed column with Spherosil X-OB-75 (3.2 m  $\times$  3.5 mm I.D.) at 50°C. Methane, ethane, propane, *n*-butane and isobutane were analysed; pentane and other compounds were flushed out of the column at the programmed temperature. Response factors were applied for each peak.

### Liquid chromatographic separation

Asphaltenes were precipitated from the chloroform extracts with a large excess of petrol ether (40–70°C). Asphaltene-free extracts were separated on a silica gel column by the elution technique. Eluents were: petrol ether (40–70°C) for the satu-

rated HC fraction; benzene for the aromatic HC fraction; benzene-methanol (1:1) for the resin fraction.

*Gas chromatography with capillary column*

The saturated HC fraction was analysed on a Chrom 41 type gas chromatograph with capillary column (20 m × 0.25 mm I.D.) coated with OV-1 stationary phase. The temperature was programmed at 5°C/min in the range 100–250°C. The injector was filled with 3 cm of GC column packing (3% Dexsil 300 on 80–100 Chromosorb W AW) to prevent the discrimination of high-boiling compounds<sup>7</sup>. The *n*-alkane peaks were identified by addition of *n*-alkane standards, and response factors were applied.

RESULTS AND DISCUSSION

Direct headspace analysis is a sensitive method (1 μl of propane per kilogram of rock) for determining the HC gas content of rocks. The reproducibility of the method is ± 12%.

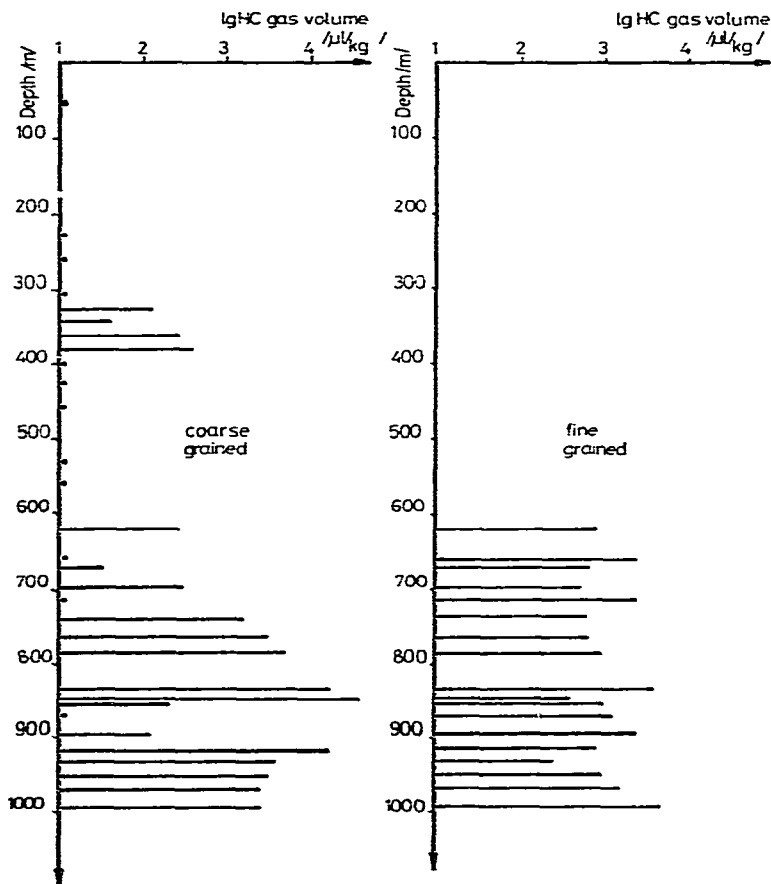


Fig. 2. Headspace analysis of mechanically extracted hydrocarbon gases.

The HC gas content in open and closed pores can be seen in Fig. 2. The highest HC gas content in open pores was found in the samples taken from the 750–1000 m interval. During drilling gas bubble was observed in drilling mud in the same depth interval.

There is a significant difference in wet gas composition between coarse and fine-grained samples. Differences can be found between sands and clays in their wet gas content (Fig. 3).

The genetic type of organic matter is autochthon, according to the isobutane/*n*-butane ratio.

Four different chromatograms representing the hole section are shown in Fig. 4. There are two humps on the chromatograms, the first is assigned to *n*-C<sub>23</sub>, which is the so-called naphthene hump (complex mixture of branched and cyclic alkanes) and the second between *n*-C<sub>26</sub> and *n*-C<sub>31</sub> is the sterane–triterpane hump, which contains many unresolved peaks<sup>9,10</sup>.

The organic matter is in an immature stage according to the high resin content

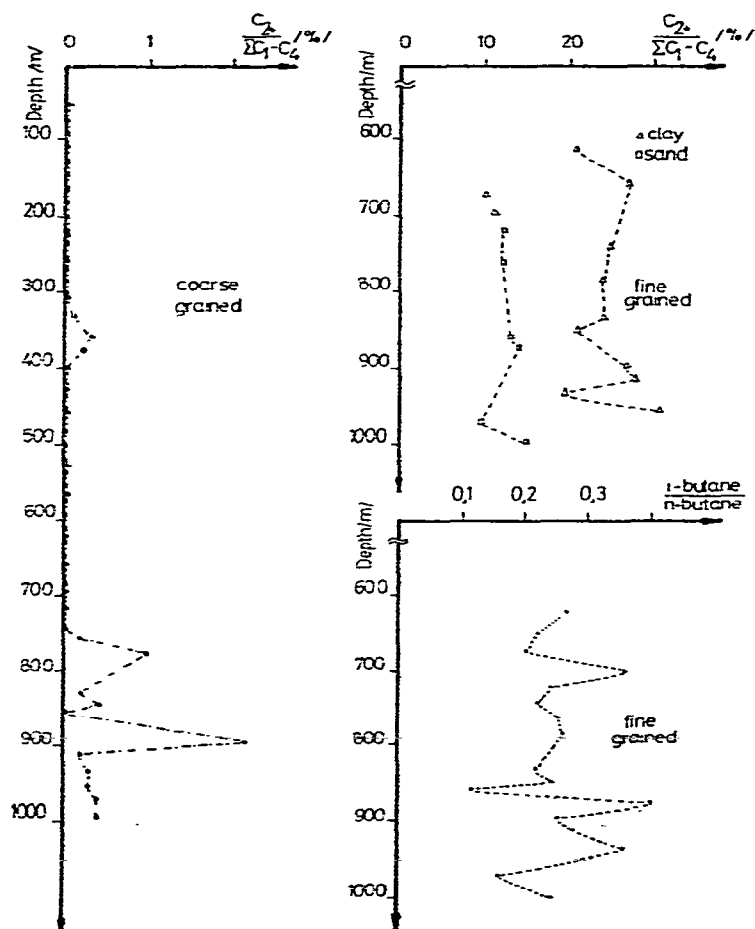


Fig. 3. Wet gas percentage as a function of depth.

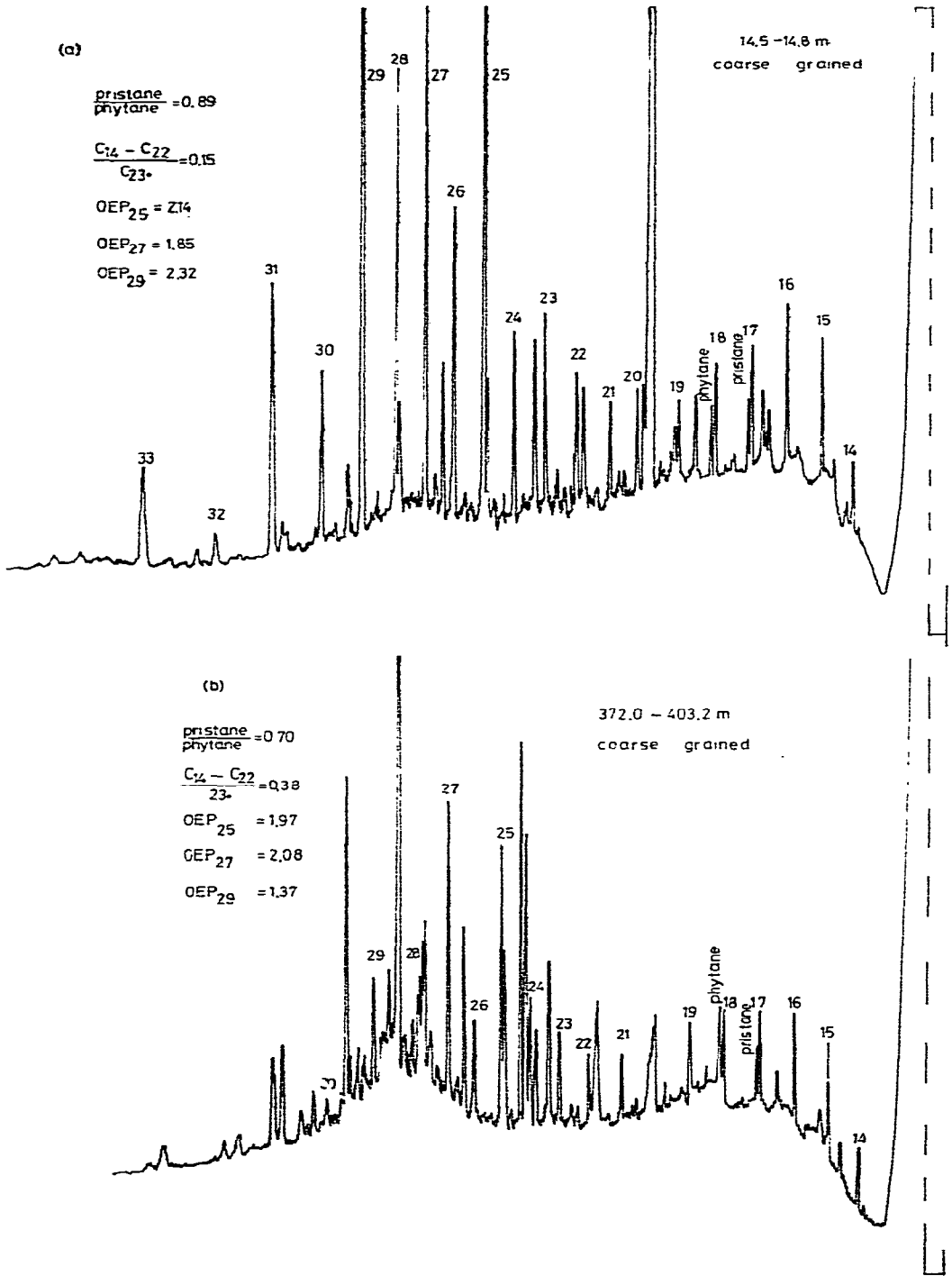


Fig. 4.

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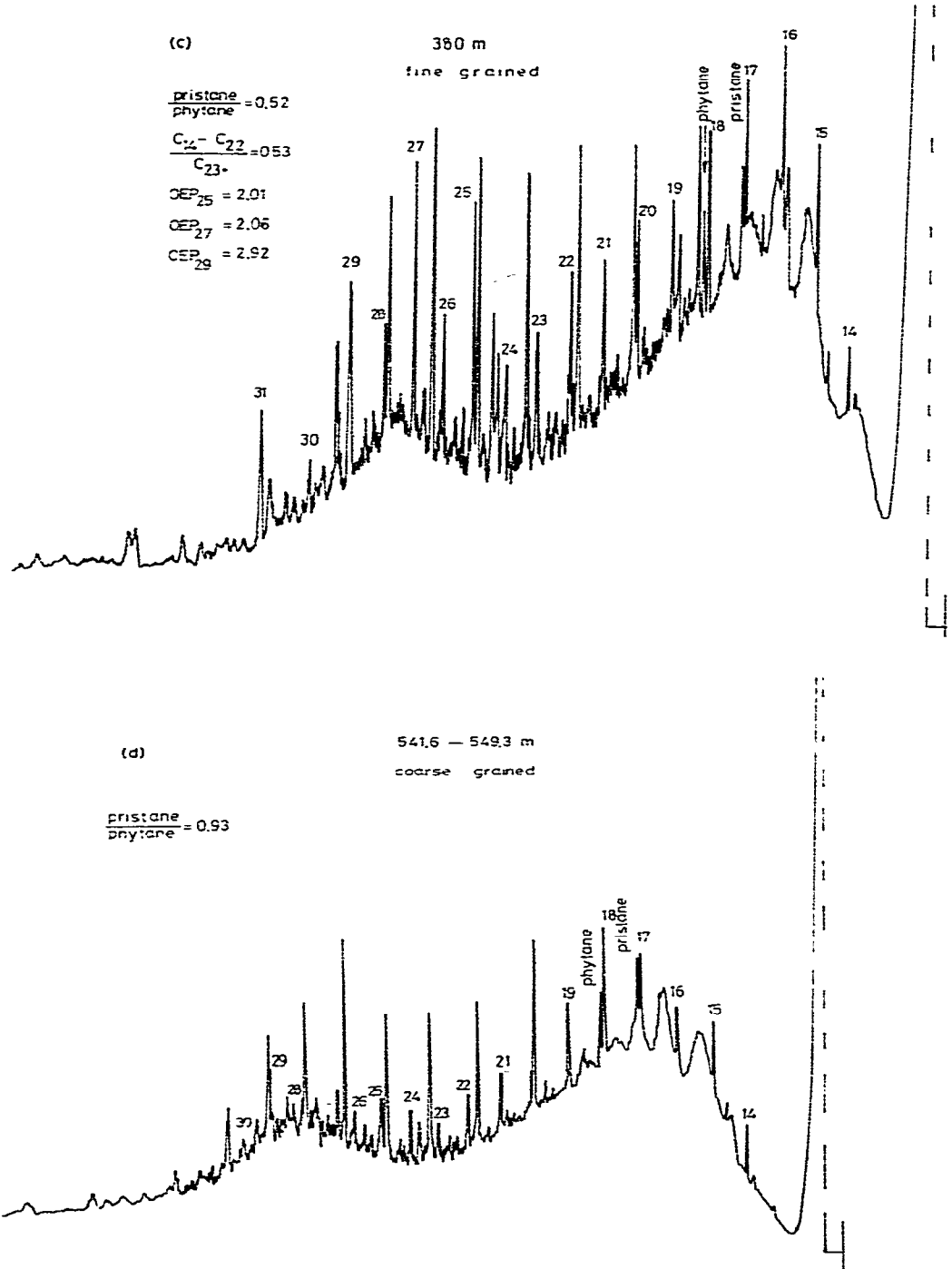


Fig. 4. Capillary gas chromatograms of saturated HC fractions of chloroform extracts from rock samples.

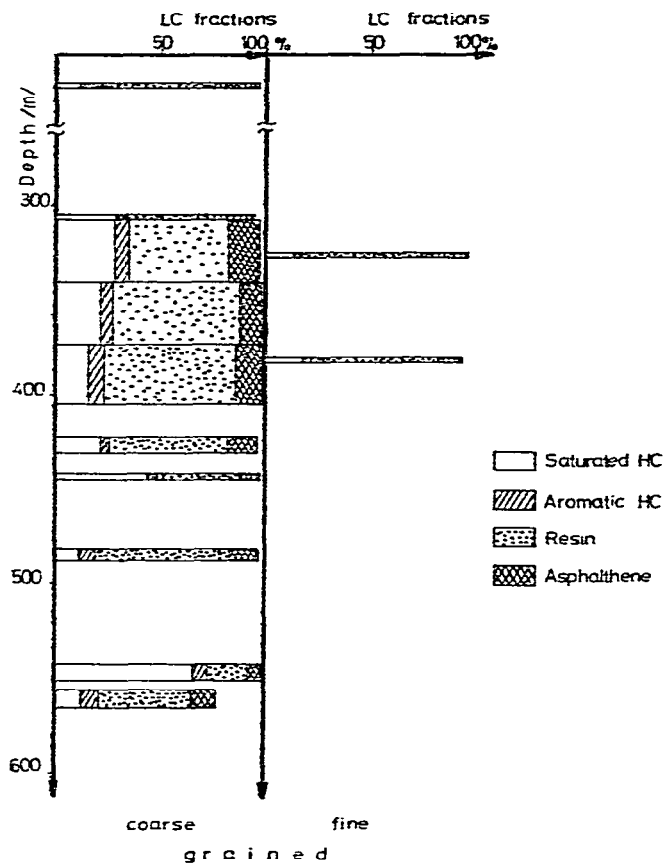


Fig. 5. Group composition of chloroform extracts from rock samples.

(40–70%, Fig. 5), the low wet gas content<sup>11</sup> (10–30%), the presence of naphthene and sterane–triterpane humps, the abundance of unidentified peaks between *n*-alkane peaks in gas chromatograms, and the relatively high OEP values:

$$OEP = \left( \frac{c_n + 6C_{n+2} + C_{n+4}}{4(C_{n+1} + C_{n+3})} \right) (-1)^{n-1}$$

The type of original organic matter buried during sedimentation is mixed, but the terrestrial contribution is much greater than the aquatic. (Maxima are between *n*-C<sub>25</sub> and *n*-C<sub>31</sub> in the *n*-alkane spectra, the low (*n*-C<sub>14</sub> – *n*-C<sub>22</sub>)/*n*-C<sub>23+</sub> ratio.)

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