# EXAMINATION OF FACTORS EFFECTING THE RESULTS OF HIGH TEMPERATURE PYROLYSIS STUDIES USED TO CHARACTERIZE NON-SOLUBLE DISPERSE ORGANIC MATERIAL IN SEDIMENTARY ROCKS. CRITICAL EVALUATION OF GRANSCH AND EISMA'S METHOD

István Koncz

## SUMMARY

Pyrolysis examinations used to study disperse organic matter are review and evaluated here. The information content and use of CR/CT rations obtained by Gransch and Eisma's method in connection with hydrocarbon prospecting problems are analysed here. Due to difficulties during the geochemical interpretation of CR/CT values obtained according to Gransch and Eisma the method had to be reevaluated critically. The effects of pyrolysis temperature upon the CR/CT rations are analysed on natural and artificial rock samples. The reasons underlying the decrease of CR/CT ratios at pyrolysis temperatures above 700 °C are examined.

## INTRODUCTION

By now it is generally recognized that known fossil hydrocarbon reserves originate from the organic (bio-organic) material content of the sedimentary rocks [1, 2]. The greatest part of known hydrocarbon reserves comes from the thermal decomposition of organic material in sedimentary rocks while burried [3].

The best part of organic material in sedimentary rocks is in dispersed form. Concentrated (non-dispers) organic material in sedimentary rocks i.e. coal is mostly of humic type and forms the least fraction of the total organic material present, in the continental sector of the stratisphere. Rocks with lower organic carbon contents contain dispersed material. Sapropelic organic material is their major component. Methane and other higher homologes are formed in significant amounts from sapropelic organic material. Methane is the major component formed from humic type organic material.

Based on the qualitative and quantitative distribution of the organic material in sedimentary rocks the greatest part of hydrocarbons can be concluded to originate from dispers organic material.

Analysis of recent sediments demonstrate that their dispersed organic material content is generally insoluble in organic solvents. During the burial process of sedimentary rocks the non-soluble part of the dispersed organic material undergoes thermal decomposition yielding components more and more soluble in organic solvents or present in gaseous form. During this stage both the composition and the properties of the non-soluble fractions are altered.

In order to predict the outcome of hydrocarbon prospecting it is insufficient to explore the geological structures which potentially allow for hydrocarbon formation. Scientifically founded hydrocarbon prospecting is impossible without information relating to the amount of hydrocarbons formed in promising, potentially hydrocarbon-bearing formations.

Theoretically there are two possibilities to determine hydrocarbon prospecting perspectives and the amount of hydrocarbons formed: direct determination of the hydrocarbons formed, and indirect prediction, i.e. estimation of hydrocarbon quantities from the quality of the non-soluble organic material. Since hydrocarbons are mobile in the crust of Earth direct determination of their quantities frequently yield erroneous results. Depending on their mobility and volatility the error can be negative or, if hydrocarbons of allochton origin are encountered, positive. Quality estimates based on the quality (identity) of the non-soluble organic material are free from mobility-linked uncertainties.

Since analytical techniques make feasible only the description of the current status none of the methods can do without the reconstruction of the initial conditions and the intermediary transformations which is based on so-called geochemical analogies.

To our best knowledge the amount of hydrocarbons formed depends on the amount, type and maturity, i.e. the extent of thermal decomposition of the organic material present.

Due to analytical constraints the organic (non-carbonate) carbon content, $C_{org}$ of the sedimentary rocks is used to characterize the amount of organic material present. In order to express the effects of the type and degree of transformation of the organic material it is advisable to express the amount of decomposition products relative to a carbon unit. Accordingly, at the beginning of decomposition formation (i.e. at initial conditions) the amount of organic carbon content is unity.

The amount of hydrocarbon formed, relative to carbon unit, depends on the type and the degree of transformation of the dispersed organic material. The type of organic material (i.e. humic, sapropelic or intermediary), as an initial condition, is determined by the conditions prevalent at the time of deposition formation. The degree of transformation, i.e. the extent of thermal decomposition depends on both time and temperature.

PYROLYSIS TESTS. AN OVERVIEW

Hydrocarbon formation processes can be modelled in the laboratory by so-called pyrolysis tests by heating the rock sample in an inert atmosphere. In order to achieve the extent of transformation completed under true geological conditions temperatures much higher than naturally found during hydrocarbon formation have to be applied.

The type and amount of decomposition products formed during further transformations of the organic material present in the rock sample can be directly obtained by pyrolysis tests. Also, decomposition products of slightly transformed organic materials can indicate the type of the organic material originally present. No information regarding the amount of decomposition products already formed in the rock sample can be obtained from the pyrolysis tests. However, by combining the results of pyrolysis tests and the reconstructed mechanism of geochemical transformations the amount of decomposition products can be estimated.

Pyrolysis tests are widely used for the characterization of the dispersed organic material in oil shales, coals and sedimentary rocks. Pyrolysis tests, quite abundant as testified by the References list, differ both in the sample, parameters and components tested as well as in the test conditions. So many variants of the pyrolysis test are known that their exhaustive evaluation, or even a detailed listing is beyond the scope of this paper.

As regards the material tested there are pyrolysis tests using organic material islaoted from [4], and not-isolated-from the inorganic matrix [5, 6]. Isolation from the inorganic matrix is a time consuming and never-complete process, frequently accompanied by alterations in the chemical structure of the organic material. On the other hand during pyrolysis of the organic material not separated from the inorganic matrix decomposition products originating but from the organic material are formed. Also, products due to interactions of the organic and inorganic material appear frequently. According to a few methods only the carbonates are removed from the inorganic matrix such as, e.g. in the methods based on the determination of the total organic carbon content. The total organic material [7] or its part not soluble in organic solvents [5] (i.e. the sample after extraction) is used for the pyrolysis tests.

· As regards test conditions pyrolysis tests differ both in the duration, temperature and pressure (atmospheric or vacuum) of pyrolysis. Furthermore, tests were described with stepwise [8] or continous [9] temperature increases.

As regards the parameters and components tested pyrolysis tests differ whether the decomposition products [10, 11, 12, 13], the residual material [5] or both are tested.

Time and apparatus requirements of various pyrolysis tests differ significantly, consequently the information content of the results obtained is also widely different. A fast, and simple (as regards hardware) version of a laboratory pyrolysis unit was developed by GRANSCH and EISMA [5, 14]. Also, it can be easily automated.

### THE METHOD OF GRANSCH AND EISMA

The rock sample used in the method described by GRANSCH and EISMA is carbonate free and contains no soluble organic material. Dispersed organic material is not separated completely from the inorganic matrix. However, carbonates should be removed because their presence contributes a positive error to the method based on the determination of the organic carbon content. After the removal of carbonates with hydrochloric acid, part of the original pyrite content, non-hydrochloric soluble metal oxides, silicates (mostly clay minerals) and silicium dioxide is left over as inorganic matrix. In order to eliminate the uncertainties caused by the mobilization of the decomposition products the method of GRANSCH and EISMA was used for the determination of non-soluble dispersed organic material.

Tests were carried out as follows: the carbon content (CT) of a carbonate-free and extracted, finely ground rock sample was determined by the so-called PREGL—DUMAS method. Another portion of the sample was pyrolyzed in purified nitrogen stream at 900 °C for 1.5 hr. The carbon content of the sample after pyrolysis (CR) was once again determined by the PREGL—DUMAS method.

GRANSCH and EISMA used the relative amount of non-volatile carbon (CR/CT) to characterize the non-soluble organic content of the sample. Volatile (pyrolysable) carbon content was calculated as

$$1 - \frac{CT}{CR}$$

Some authors call the CR/CT ratio the *diagenetic coefficient* or the *degree of diagenesis* [15,16].

Neither the diagenetic coefficient, nor the katagenetic coefficient terms are fortunate because the result obtained needs not to be assigned to any specific stage of organic material transformation. In fact, any such assignment is highly misleading.

The pyrolysis temperature, 900 °C used by Gransch and Eisma is the stand-ardized pyrolysis temperature used for the characterization of the *"fixed organic carbon content"* of coals. In this test the weight loss of a finely ground coal sample in inert gas atmosphere at 900 °C is measured (naturally, corrections are made for the moisture and ash contents of the sample). With coal samples weight losses due to heat decomposition of the inorganic matrix are negligable or can be accounted for by correction. Since the best part of any sedimentary rock sample is inorganic, weight losses characterize not only the organic material but also the inorganic matrix. Therefore, Gransch and Eisma modified the fixed carbon test method by measuring the pyrolysis-induced-weight-loss of the organic carbon content.

They note [5] that "Determination of the CR/CT ratio is an empirical approach. The values might be influenced by the inorganic material present." Effects of the inorganic matrix were investigated in clay-enriched mixtures of relatively high organic carbon content, 1—9% w/w. Slight increase could be attributed to the inorganic matrix. Based on the identical or similar CR/CT values of the valuable and covering layers slight changes were attributed to the presence of inorganic matrix. Thus, they concluded that "CR/CT ratios reflect characteristics strictly connected with the non-soluble organic material." CR/CT ratio characterizes the over-all non-soluble organic material present. Therefore, its value depends on both the type of the non-soluble organic material and the degree of its transformation. It is in contrast with such parameters as color and shape of pollen, reflection of vitrinites which depend only on the degree of transformation.

Consequently, CR/CT ratios can be used for the determination of the degree of transformation only when the non-soluble organic material is of the same type. On the other band, if the degree of transformation of the non-soluble organic mate-rial determined by other methods is the same, differences in the CR/CT ratios can be used to determine the type of organic material. Results of pyrolysis tests carried out with humic coal samples indicate that irrespective of the degree of transforma-tion CR/CT ratios below 0.6 indicate the presence of organic material suitable for hydrocarbon formation (more sapropelic). When the CR/CT ratio is higher than 0.6 other methods have to be used to determine the degree of transformation in order to distinguish between organic materials suitable and not suitable for hydrocarbon generation.

Gransch and Eisma compared their pyrolysis test results with the results of other methods and found good agreement, identical tendencies and conclusions. With concentrated dispersed organic material, i.e. peat, lignite and humic coals the CR/CT ratios correlated well with the fixed carbon content values. They conluded that similarily to the fixed organic carbon content the CR/CT ratio is also unsuitable for the determination of the degree of transformation with volatile rich, slightly transformed bituminous and other coals. Also, humic coals display CR/CT ratios above 0.6 even at low degrees of transformation (in early stages of diagenesis). CR/CT ratios of West Venezuelan sediments display good correlation with the maxi-mum depth of burial, ratios increase with depth. This correlation proves that with similar organic material CR/CT ratios increasing proportionally to depth indicate that the deeper the sediment (i.e. the higher the temperature) the higher the degree of transformation. The relationship of CR/CT ratios and the relative amount of extractable organic material (i.e. ratio of extracted and total carbon content) was also tested in samples obtained at approximately identical depths, i.e. which were of approximately identical as regards the degree of transformation. It was found that at high extracted/total carbon ratios the CR/CT ratios were high and *vice versa*.

This relationship indicates that with identical degrees of transformation lower CR/CT ratios indicate the presence of organic material more suitable for hydrocarbon generation. Similar conclusions were reached by comparing the H/C atom ratios and CR/CT ratios of various organic materials with low degrees of transformation. The higher the H/C ratio (i.e. hydrogen rich, more sapropelic organic material, more suitable for hydrocarbon generation) the lower the CR/CT ratios and *vice versa* (i.e. humic materials).

### CRITICAL EVALUATION OF THE GRANSCH—EISMA-METHOD

Some 500 samples from the Hungarian part of the Pannonian Basin were tested by the method of GRANSCH and EISMA. Measured CR/CT values were compared with the results of other methods (i.e. vitrinite reflection, selective oxidation) for a limited number of samples [16]. Except for a few samples the results correlated excellently. CR/CT ratios obtained on samples of Bulgarian sedimentary rocks could also be interpreted [18]. Kaolinite-coal composite samples of 6—8% organic carbon content prepared from coals of known degree of transformation obtained from the Perniski and Donec basins were tested by Bulgarian scientists and measured CR/CT values were compared with the volatile contents and vitrinite reflexion [19]. Results agreed vell. CR/CT ratios measured by the method of GRANSCH and EISMA could be used to follow the transformation of the disperse organic material and formed the basis of the reaction kinetic description of hydrocarbon formation [16, 17, 20, 21].

However, problems encountered occasionally during the interpretation of CR/CT ratios measured with sediment samples from the Pannonian Basin necessitated the reevaluation and critical analysis of the method of GRANSCH and EISMA. In most rock samples obtained from depths of 2.5 km and temperatures of 130—140 °C CR/CT values were above 0.6. However, significantly lower values were obtained occasionally and on the basis of extracted/total carbon ratios these samples could not be considered more sapropelic. To explore more these contradictions the effects of pyrolysis temperature upon the CR/CT values were tested with a natural clay-marl rock sample of average carbon content (CT=0.556%) and a coal-quartz mixture of 0.355% organic carbon content in a temperature range of 760—980°. Results are shown in Table 1 and *Fig. 1*. In order to eliminate the effects of various CR/CT ratios percent changes of the CR/CT ratio at identical pyrolysis temperatures
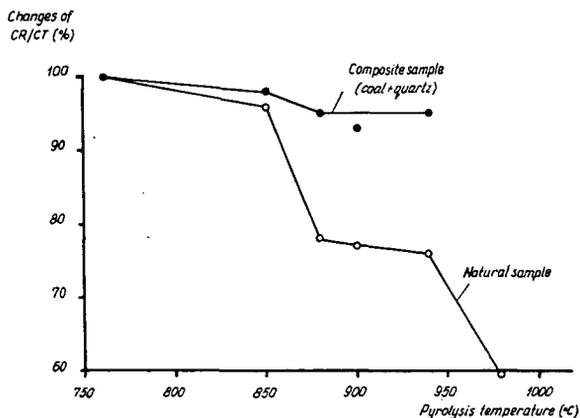


*Fig. 1.* Changes of the CR/CT ratio with the pyrolysis temperature

are shown. The CR/CT ratio measured at 760° is taken 100% and CR/CT ratios measured at higher temperatures are expressed with respect to this value. (Naturally, the question whether higher CR/CT ratios obtained at lower pyrolysis temperatures were due to temperature effects or merely to inadequately short pyrolysis times, had to be answered. Therefore, CR/CT values were obtained in the 400—900° temperature range with pyrolysis times above 90 min. CR/CT values obtained in 90; 120; 150 and 1440 min pyrolysis tests were identical within experimental error. Thus, higher CR/CT values at lower pyrolysis temperatures were caused by lower temperature).

It can be seen that in the case of the composite sample decrease of the CR/CT ratio with increasing temperature is not significant (7% up to 900°) but is considerable with the natural sample (23% up to 900°).

Effects of the pyrolysis temperature upon the CR/CT ratios in natural samples were studied in higher temperature ranges (350—950°). The results, percentage changes of the CR/CT ratio are shown in *Fig. 2* and Table 2. The CR/CT ratio measured at 350 °C was taken 100% and other values expressed in percent relative to this figure. It can be seen that the amount of carbon lost with the pyrolysis products $(1-CR/CT)$ is negligible, i.e. CR/CT is close to unity. The greatest part o carbon is lost in the 400—500 °C range. Carbon is lost in this range mostly as hydrocarbon [6, 10]. There is almost no carbon loss in the 500—700 °C range. However, further carbon is lost from 800—900 °C upwards. The relative amount of pyrolysable carbon at 700 °C $(1-CR/CT$ or volatile carbon) can be considered the hydrocarbon generating potential of the sedimentary rock.

Effects of pyrolysis temperature in a narrower temperature range (500—900 °C) were also studied with a large number of samples. Results are shown in Table 3 as percent changes of the CR/CT ratio taking the CR/CT ratio at 500 °C hundred percent. 500 °C was selected as initial pyrolysis temperature because previous experiments proved (Table 2) that the majority of volatile hydrocarbons is lost up to 500 °C. Up to 700 °C the decrease of the CR/CT ratio remained within the experimental error (4%), then at 800 °C it became slightly higher while at 900 °C it became significant (10—27%) and varied greatly from sample to sample. The extent of the decrease could not be correlated with the depth where the samples tested were taken from. The CR/CT ratio at 700 °C is also shown in Table 3, along with the CR/CT at 900 °C, as it is a parameter related to the amount of carbon lost by pyrolysis. The difference between CR/CT values at 700° and 900 °C $(\Delta CR/CT)$ are also shown in
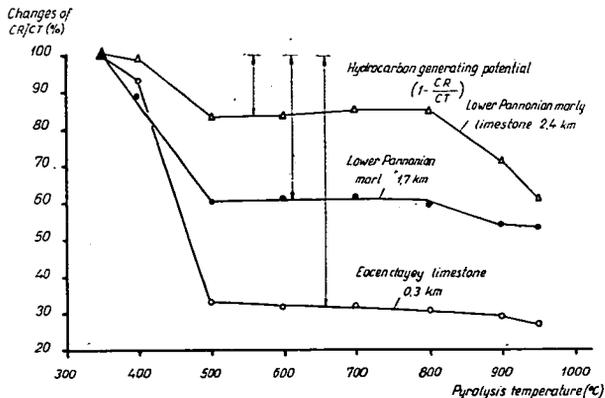


*Fig. 2.* Changes of the CR/CT ratio with the pyrolysis temperature

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TABLE 1

*Relative changes (%) of the CR/CT values with the pyrolysis temperature (CR/CT=100% at 760 °C) with natural (clay-marl) and composite (coal+quartz) samples*

| Sample | CT % | Pyrolysis temperature, °C | | | | | | CR/CT | |
|---|---|---|---|---|---|---|---|---|---|
| | | 760 | 850 | 880 | 900 | 940 | 980 | 760 °C | 900 °C |
| Clay-marl | 0.556 | 100% | 96% | 78% | 77% | 76% | 59% | 0.914 | 0.707 |
| Coal+quartz | 0.355 | 100% | 98% | 95% | 93% | 95% | — | 0.820 | 0.763 |

TABLE 2

*Relative changes (%) of the CR/CT values of sedimentary rocks with the pyrolysis temperature (CR/CT=100% at 350 °C)*

| Sample characteristics | | | | Pyrolysis temperature, °C | | | | | | | | CR/CT | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Age | Rock | Depth (km) | CT % | 350 | 400 | 500 | 600 | 700 | 800 | 900 | 950 | 350 °C | 500—800 °C |
| Eocen | clayey limestine | 0.3 | 31.01 | 100 | 93 | 33 | 32 | 32 | 30 | 29 | 27 | 0.975 | 0.294—0.320 |
| Lower Pannonian | marl | 1.7 | 2.66 | 100 | 89 | 60 | 61 | 61 | 59 | 54 | 53 | 1.000 | 0.589—0.614 |
| Lower Pannonian | marly limestone | 2.4 | 1.32 | 100 | 99 | 83 | 83 | 85 | 85 | 71 | 61 | 0.946 | 0.784—0.808 |

TABLE 3

*Relative changes ( % ) of the CR/CT values of sedimentary rocks with the pyrolysis temperature*
*( CR/CT=100% at 500 °C)*

| Sample characteristics | | | | Pyrolysis temperature, °C | | | | CR/CT | | ΔCR/CT* |
|---|---|---|---|---|---|---|---|---|---|---|
| Age | Rock | Depth (km) | CT % | 500 | 700 | 800 | 900 | 700 °C | 900 °C | |
| Eocen | clayey limestone | 0.3 | 31.01 | 100 | 98 | 92 | 88 | 0.313 | 0.282 | 0.031 |
| Lower Pannonian | marl | 1.7 | 2.66 | 100 | 100 | 97 | 90 | 0.611 | 0.544 | 0.067 |
| Sarmatian | marl | 2.3 | 3.38 | 100 | 97 | 90 | 73 | 0.605 | 0.458 | 0.138 |
| Lower Pannonian | marly limestone | 2.4 | 1.32 | 100 | 100 | 100 | 85 | 0.808 | 0.670 | 0.138 |
| Lower Pannonian | clayey marl | 2.7 | 0.60 | 100 | 99 | 91 | 82 | 0.868 | 0.714 | 0.154 |
| Lower Pannonian | clayey marl | 2.7 | 0.63 | 100 | 100 | 94 | 81 | 0.881 | 0.708 | 0.176 |
| Lower Pannonian | aleurolite | 3.0 | 0.56 | 100 | 100 | 90 | 75 | 0.818 | 0.613 | 0.205 |
| Helvetian | clayey marl | 3.7 | 1.25 | 100 | 98 | 90 | 84 | 0.924 | 0.799 | 0.125 |
| Range of decrease (%) | | | | | 0—3 | 0—10 | 10—27 | | | |

* ΔCR/CT=(CR/CT) 700 °C—(CR/CT) 900 °C

the Table. This difference as a function of depth changes as expected. Both CR/CT ratios at 700 and 900 °C increase with depth, the relative amount of pyrolysable carbon decreases, the degree of transformation increases, the hydrocarbon generating potential of the organic material is increasingly depleted.

Further test were carried out to learn the cause of the second thermal decomposition from 800 °C onwards, following the first thermal decomposition yielding mostly hydrocarbons, and which is practically completed by 500 °C. The second thermal decomposition step increases the relative amount of pyrolysable carbon and significantly decreases the CR/CT ratio.

Samples pre-pyrolysed at 700 °C were subjected to further pyrolysis at 800° and 900 °C and the amount of carbon monoxide swept out by the purified, oxygen-free nitrogen carrier was analysed similarly to the oxygen determinations [22]. The only difference was that in the latter case the glowing carbon filling was substituted by the sample investigated. The amount of carbon monoxide relased at 800° and 900 °C was expressed as pure carbon and compared with the "carbon-loss" relative to the pyrolysis at 700 °C. It was found that the amount of carbon lost as carbon monoxide increased with the temperature and its value agreed well with the "carbon-loss" due to pyrolysis at 800 and 900 °C temperatures. No volatile carbon lost as carbon monoxide could be detected above the experimental error with composite (coal+quartz) samples, in agreement with the results of pyrolysis tests.

We could conclude that "carbon-loss" at higher pyrolysis temperatures (800 and 900 °C), i.e. thermal decomposition accompanied by the decrease of the CR/CT ratio was caused by the interaction of inorganic and organic material in the sample and the oxygen content of the organic material. It is known that if the pyrolysis products of an organic material are transmitted through a carbon bed heated to 1100 °C temperature those containing oxygen form quantitatively carbon monoxide. (This process is made use of when the oxygen content of organic materials is determined.) In the presence of platinum catalyst conversion to carbon monoxide takes place at lower (900 °C) temperatures. Naturally, the reaction takes place without catalyst even at lower temperature if there is oxygen present in the organic material or if there are oxygen releasing components (such as oxides of metals of changing valency) in the inorganic material of the sample. Sedimentary rock samples prepared for pyrolysis tests may contain such oxides non-soluble in hydrochloric acid (e.g. $Cr_2O_3$, etc.). Tests carried out with coals and organic material isolated from sedimentary rocks proved that the oxygen content of the organic material is significant at low degrees of transformation and it decreases rapidly with increasing degree of transformation due to thermal decomposition resulting in water-and-carbon-dioxide-formation. Thus, the oxygen content of the organic material might enhance the decrease of the CR/CT ratio only with organic materials of low degree of transformation. However, carbon left over by pyrolysis at 700 °C might partially react with the metal oxides present in the catalytical environment provided by the clay minerals resulting in the formation of carbon monoxide and dioxide. Carbon dioxide is further reduced to carbon monoxide by any carbon present according to the BOUDOUARD reaction.

This assumption was to be proved by adding oxidizing metal oxides ($Fe_2O_3$; $V_2O_5$, $PbCrO_4$) to the samples. Magnesium oxide was used as control since its presence could not increase the degree of oxidation. Composite samples were prepared from quartz and carbon black ignited in nitrogen flow. Results are summarized in Table 4 along with the CR/CT values of the samples containing no additives. Changes of the CR/CT ratio caused by admixed metal oxides are expressed with respect to

TABLE 4

*Relative changes ( %) of the CR/CT ratios of composite and
natural samples with metal oxide admixing
( CR/CT = 100 % at 700° and 900 °C, without additives)*

| Type of sample | CT (%) | Pyrolysis temp. °C | CR/CT without additive | Added metal oxide | | | |
|---|---|---|---|---|---|---|---|
| | | | | $Fe_2O_3$ | $V_2O_5$ | $PbCrO_4$ | MgO |
| Composite | | | | | | | |
| (carbon black + quartz) | 1.380 | 900 | 1.000 | 86 | 84 | 66 | 100 |
| Natural | 2.068 | 900 | 0.605 | 77 | 85 | 58 | 95 |
| (sedimentary rock) | | 700 | 0.697 | 100 | 100 | 86 | 100 |
| Natural | 0.972 | 900 | 0.602 | 87 | 80 | 67 | 100 |
| (sedimentary rock) | | 700 | 0.869 | 95 | 95 | 93 | 94 |

the CR/CT ratio of the sample containing no admixed metal oxide. It can be seen
that non-oxidizing quartz had no effect upon the CR/CT ratio with oxygen-free
carbon black. (CR/CT obtained at 900 °C temperature was 1.000.) Oxidizing metal
oxides added to the samples decreased the CR/CT ratio. As expected theoretically,
non-oxidizing MgO had no effect on the CR/CT ratio. With natural rock samples
there was only one case when the presence of oxidizing metal oxide decreased the
CR/CT ratio at 700 °C beyond the experimental error. At 900 °C, however, signi-
ficantly decreased CR/CT ratios were obtained in all cases. (Practically the same
results were obtained when the amount of oxidizing metal oxides present was halved.)
    These tests proved that inorganic materials, the major components of rock
samples play a significant role in determining the decreased CR/CT ratios of samples
pyrolysed at 900 °C.

## CONCLUSIONS

    Pyrolysis test can be used to model hydrocarbon formation taking place in
sedimentary rocks. Results of the pyrolysis tests can be used to determine the degree
of transformation of a given type of disperse organic material.
    Pyrolysis tests were carried out according to GRANSCH and EISMA resulting
in the relative amount of non-soluble organic carbon not pyrolysed at 900 °C
(CR/CT ratio).
    In order to explore the origin of certain problems encountered during the
geochemical interpretation of the CR/CT ratios measured at 900 °C their method
of determination was evaluated critically. The effects of pyrolysis temperature on
the CR/CT ratios were studied. Results of the pyrolysis tests carried out with natu-
ral and composite samples can be summarized as follows:
    1. The relative amount of non-pyrolysable organic carbon (CR/CT ratio)
decreases rather rapidly up to 500 °C, depending on the type of organic material
and the degree of transformation. The ratio is almost constant in the 500—700 °C
range but decreases further, or remains constant, above 700 °C.
    2. Decreased CR/CT ratios above 700 °C are due to the interaction of the
organic and inorganic part of the sample and/or the oxygen content of the organic
material present.
    3. The value of the CR/CT ratio measured at 700 °C depends on the type of
the organic material and the degree of its transformation.

4. The value of the CR/CT ratio measured at 900 °C depends, apart from the type of the organic material and the degree of its transformation, on the interactions of the organic and inorganic parts of the sample and/or the effects of the oxygen content of the inorganic parts — secondary effects which have no influence under the conditions of natural hydrocarbon formation.

5. Interaction of the organic and inorganic material might be due to oxides of metals of changing valency non-or only partly soluble in hydrochloric acids. At pyrolysis temperatures above 700 °C these metal oxides promote carbon monoxide formation from part of the organic carbon present. If the organic material contains oxygen it can lead alone to carbon monoxide formation above 700 °C.

6. Secondary effects can be characterised by the difference of CR/CT ratios measured at 700 and 900 °C ($\Delta$CR/CT).

## ACKNOWLEDGEMENTS

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Dr. I. KONCZ
Dept. of Chemistry,
Industrial Laboratory for Oil and
Gas Research (OGIL),
Nagykanizsa, H-8800, Hungary