

# CONTRIBUTIONS TO THE INTERPRETATION OF SOLUBLE ORGANIC MATERIALS OF SEDIMENTARY ROCKS\*\*

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## INTRODUCTION

The study of the types and peculiarities of the insoluble organic material as well as that of the organic material soluble in organic solvents plays an important role in geochemical investigations in connection with hydrocarbon prospection.

The investigation of the soluble organic material, the determination of the ratio of the quantity of the soluble and insoluble organic material is closely connected with the problem of migration, with differentiation between the primary and secondary character of the soluble organic material. In the relating literature one can find a diversity of opinions.

Still less the study of the insoluble dispersed organic material in the sedimentary rocks, the determination of its character, type, grade of diagenesis as well as of its reduction capacity has a paramount importance. The determination of the parameters mentioned theoretically renders possible to draw essential conclusions concerning the role of the insoluble organic matter in question in the generation of hydrocarbons. In the related literature, however, very controversial ideas may be found. One of them over-emphasizes perhaps the importance of the source rock concept though there is no method rendering possible the distinct and unequivocal determination of the source rock character of the beds whereas according to other opinions, represented by COLOMBO and others, under special conditions any sedimentary bed can contribute to a smaller or greater extent to the generation of hydrocarbons which can accumulate in the reservoir rocks.

In the present paper it is not an aim to give a critical evaluation of the related literature rather some ideas and questions, respectively, will be raised sometimes increasing only the number of question open so far, however, such questions may also contribute to the solution of the problems.

The sedimentary rock samples investigated are originated from the Upper Pannonian, Lower Pannonian and Miocene layers of the south part of the Great Hungarian Plain.

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QUESTIONS CONCERNING THE INTERPRETATION OF THE  
SOLUBLE ORGANIC MATERIAL CONTENT

The Bitumen A content of the samples was extracted by chloroform in a SOXHLET apparatus, and after having removed the solvent, the amount of Bitumen A was weighed. The extraction thereafter was continued with benzene: acetone: methanol (70:15:15). After exhaustive extraction and removing the solvent the amount of the extract (BAM extract  $\approx$  Bitumen C) was weighed.

The total organic carbon content of the samples was determined by ignition on oxygen stream. From these values the bitumen coefficient was calculated using the formula

$$\frac{\text{Bitumen A} \cdot 100}{C_{\text{org}}}$$

The lowest, the mean and the highest values of data mentioned above are comprised in Table 1 denoting also the depth interval of the single borings wherefrom the samples were originated.

In Table 2, however, the samples are grouped according to their age and the mean values of data related to the samples of the same age are shown.

It is to be noted that of the samples of borings Fe-3—13 three showed a fairly extreme chloroform bitumen concentration. One sample was taken from the Upper Pannonian (Bitumen A=0.1928%) and the other two were from the Lower Pannonian layers (Bitumen A amounts to 0.5488% and 0.5730%, respectively). The samples are medium-grained and fine grained sandstones.

As it is seen the elimination of the samples with higher Bitumen A content at the calculation of the mean values influences only the calculation of the mean value

TABLE 1

*The lowest, mean and highest values of some parameters measured in the  
samples investigated grouped by the borings*

№ of borings	Number of samples	Depth m	Bitumen A %	BAM extr. %	$C_{\text{org}}$ %	Bitumen coeff.
M-2	31	2000—4800	0.0079	0.0051	0.05	2.93
			<u>0.0360</u>	<u>0.0228</u>	<u>0.28</u>	<u>14.62</u>
			0.0660	0.0563	0.68	34.60
Fe-K-1	9	1450—2060	0.0099	0.0120	0.12	2.91
			<u>0.0274</u>	<u>0.0304</u>	<u>0.42</u>	<u>8.41</u>
			0.0530	0.0533	1.20	24.75
Fe-3-13	21	1700—2450	0.0221	0.0170	0.03	5.32
			<u>0.0951</u>	<u>0.0352</u>	<u>0.30</u>	<u>43.77</u>
			<u>(0.0380*)</u>	<u>(0.0336*)</u>		<u>(27.59*)</u>
			0.5730	0.0868	0.93	177.00

\* mean values without taking into account three extreme values

of the Bitumen A concentration, however, at the calculation of the mean value of the BAM extract it causes only very slight differences. It seems that in the three samples mentioned the fairly considerable increase of the chloroform bitumen compared to its mean value is not accompanied by the increase of the amount of the BAM extract, even in two samples the value of the latter is lower than that of the other samples from the same area.

The highest mean value both for the Bitumen A and BAM extracts and therefore for the total soluble organic material could be stated in samples of borings Fe-3—13, however, the mean concentration of the BAM extract remained always below that of the chloroform bitumen. In the samples of boring M-2 the mean value of the BAM extract is lower than that of the chloroform bitumen, however, both values are lower than measured in the samples of borings Fe-3—13. In the samples of boring Fe—K—1 an inverse relation could be established, the mean BAM extract concentration exceeds that of the chloroform bitumen and of the borings the samples of Fe—K—1 show the relatively highest mean organic carbon content and the lowest bitumen coefficient.

Considering the ratio of the amounts of chloroform bitumen and BAM extract, respectively, of the samples taken from the three area mentioned it seems to be advantageous to consider TISSOT's [1969, 1971] order of ideas and statements. According to him the amount of organic compounds of higher molecular weight containing also many hetero-atoms decreases by the depth owing to formation of lighter compounds without or poor in hetero-atoms.

According to TISSOT during the hydrocarbon generation first the formation of the heavier compounds with hetero-atoms takes place from the kerogen. These compounds would correspond to the compounds of the BAM extract and the formation of the lighter components (chloroform bitumen) will take place on account of them.

The mechanism assumed was also experimentally proved. The samples of Toarcian sediments of the Parisian Basin were extracted by chloroform, thus in the samples merely the BAM components and the kerogen remained. Heating the samples under temperature and pressure corresponding to the conditions established in the sedimentary basin investigated, formation of chloroform bitumen could be stated preceding a shortlived formation of a new amount of BAM components. Thus, the compounds of the BAM extract would represent an important step of evolution between the kerogen and the components of the petroleum.

Starting from the concept outlined above the question would arise what connections may be observed among the chloroform bitumen, the BAM extract and the total organic carbon content in the samples of sedimentary rocks from the south part of the Great Hungarian Plain.

The connections according to TISSOT can hardly be stated on the basis of the data of Table 1, however, the decrease of the amount of the BAM extract by the depth is faintly observable in the section of single borings. It is to mention that the knowledge of the ratio of the single fractions of the BAM extract and their change by the depth, respectively, would have given rather meaningful informations.

Grouping, however, the data according to the depth of burial i. e. according to the age of the samples and the mean values of the parameters mentioned are calculated for the Upper Pannonian, Lower Pannonian and Miocene samples, some connections can be established.

Investigating the mean values of parameters by grouping the samples according to their stage and epoch, respectively, it may be stated that the amount of the BAM extract, as well as, the  $C_{org}$  decreases from the Upper Pannonian to the older Miocene

TABLE 2

Mean values of chloroform bitumen, BAM extract, organic carbon content as well as the bitumen coefficient of the samples in function of their stage

Stage Epoch	Number of samples	Bitumen A %	BAM extr. %	C <sub>org</sub> %	Bitumen coeff.
Upper Pannonian	15	0.0417 0.0309*	0.0413 0.0391*	0.36 0.37*	14.08 9.50*
Lower Pannonian	36	0.0607 0.0390**	0.0314 0.0316**	0.315 0.313**	25.37 19.55**
Miocene	10	0.0272	0.0189	0.28	12.56

\* mean values without one and two extreme values

i. e. by the depth, moreover, this connection between the change of the amount of the BAM extract and the organic carbon is nearly linear as shown in *Fig. 1*.

Naturally, the change shown in *Fig. 1* is not a monotonous one bed by bed, rather a tendency obtained by grouping and averaging the samples according to their ages can be stated.

The chloroform bitumen content of the samples does not show similar connections with the total C<sub>org</sub> and the depth, respectively. Its mean value in the samples of Upper Pannonian practically is nearly the same as the mean of the amount of the BAM extract, in the samples of the Lower Pannonian its mean value exceeds that of the BAM extract (to a fairly great extent taking into account the samples with extreme chloroform bitumen content, too) and in the Miocene samples also exceeds slightly the mean value of the BAM extract.

Leaving the three samples with extreme chloroform bitumen content out of consideration, it gives merely negligible differences in the calculation of the mean value of the BAM extract and the total C<sub>org</sub>, however, in the case of chloroform bitumen, especially in samples from Lower Pannonian, more considerable differences can be established (Table 2).

As shown in *Fig. 1*, besides a nearly linear correlation between the mean values of the BAM extract and C<sub>org</sub> also the decrease of the amount of these constituents by depth is accompanied by increasing temperature measured in the M—2 borehole.

BRENNEMAN and SMITH (1958) in their paper cited by NAGY and COLOMBO [1967] stated that between the crude oil and the organic extract of its alleged source rocks no unique property could be observed which would be considered as a linkage between crude oil — source rock pairs.

In connection with this statement taking into consideration the correlation shown in Table 2 and *Fig. 1*, respectively, perhaps it may be concluded that within the beds there exists presumably a genetically closer connection between the insoluble organic matter and the compounds of the BAM extract with higher molecular weight than between the insoluble organic material and the chloroform bitumen extractable from the same samples. The lighter components of the chloroform bitumen have a greater migration ability than the heavier compounds of the BAM extract, with higher molecular weight. Thus, a greater or smaller portion of the chloroform bitu-

men in the different beds can be taken as migrated there and so this portion has really no genetic connection with the insoluble organic material of the bed in question. On the other hand, it may be assumed that rather the heavier compounds of the BAM extract formed from the insoluble organic material remained — at least a portion of them which did not turned into lighter compounds — in the bed where they formed, together with the rest of the insoluble organic material.

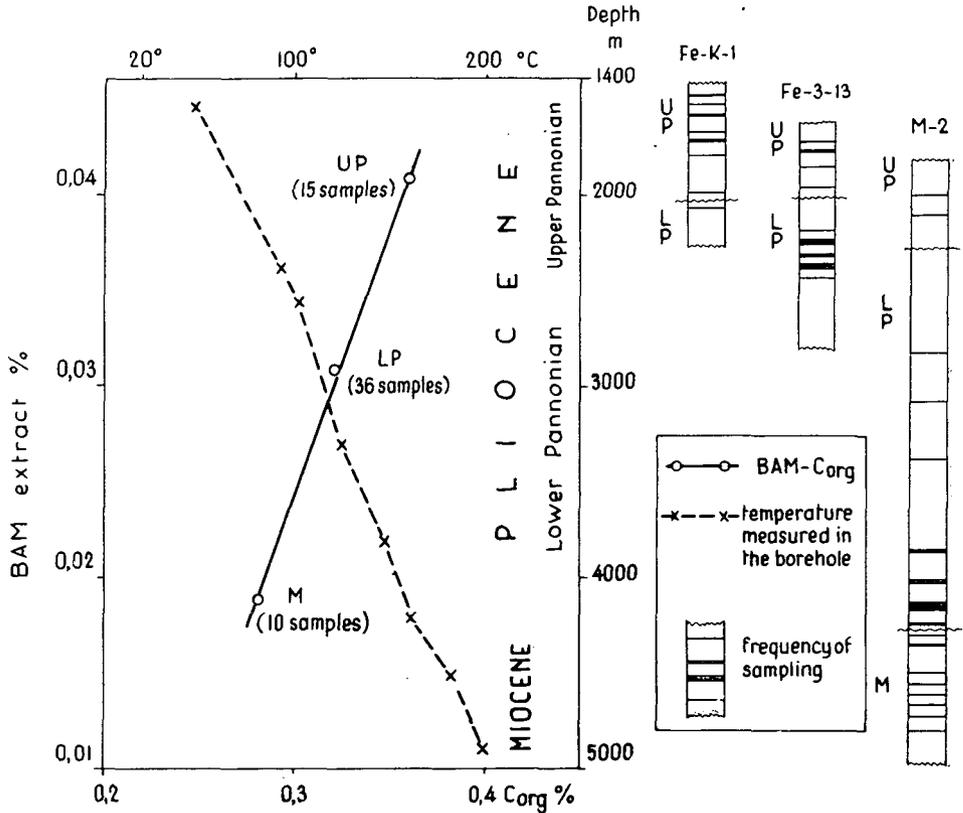


Fig. 1. Connection of mean values of the BAM extract and organic carbon grouping the samples and averaging the values according to the age (depth) of the samples investigated

According to PHILIPPI [1957] cited by NAGY and COLOMBO [1967] the source-quality of sediments would be estimated by the amount of residual hydrocarbons generated per unit weight of dry rock. Merely it is very difficult to prove that the "residual" hydrocarbon is really indigenous to the bed investigated and not migrate there after the sedimentation.

In the literature many references, statements concerning the differentiation of primary and secondary bitumen can be found. One of the parameters for delimitation of primary and secondary bitumen is the so-called bitumen coefficient. It renders, however, only qualitatively probable whether primary or secondary bitumen is in question but the distinct delimitation of the two depends on many local factors as was explained by SIMANEK [1968].

It seems that many open questions still exist and will remain in connection with the bitumen coefficient especially with its interpretation. Some authors calculate with the formula  $\frac{\text{Bitumen A} \cdot 100}{C_{\text{org}}}$  others calculate instead of  $C_{\text{org}}$  with the organic material in the denominator. The amount of the organic material is calculated from the  $C_{\text{org}}$  content determined by ignition in oxygen stream and multiplying this value with an "organic factor". But what may be taken as a correct „organic factor". Factor 1.33 was used by VYCEV and MATEEVA [1968] for recalculation of  $C_{\text{org}}$  into the organic material, in other papers different factors can be found depending on the age and rank of coalification. The factor is 1.22 in the case of metamorphic shales and 1.75 in the case of recent sediments. It seems that it is more advantageous to use in the denominator the  $C_{\text{org}}$  per cent if on the basis of detailed C—H-analysis of isolated organic material the organic factor suitable for real calculation is not known.

A further problem mentioned also in PHILIPPI's paper referred to what bitumen coefficient can be assumed as dividing value between primary and secondary bitumen. According to RODIONOVA (cited by LEGMANN *et al.*) the border is at 5 in the case of terrigenous rocks and 15 in that of carbonate rocks. According to other authors (LEHMANN *et al.*, 1968] in the case of very low organic material content it is more advantageous to use the diagram constructed by WASSOJEVITCH. Using this diagram it renders the presence of primary bitumen probable also at lower  $C_{\text{org}}$  content (below 0.6%) and relatively higher bitumen coefficient. At such values using the delimitation according to RODIONOVA the bitumen might be considered as secondary. It seems that the problem propounded by PHILIPPI has not yet reached a reassuring solution.

Further, if the bitumen coefficient is the expression of the degree of transformation of the insoluble organic material into hydrocarbons, the question may arise, why merely the chloroform bitumen content is taken into consideration although the amount of the BAM extract is also not negligible containing sometimes considerable amount of paraffine-hydrocarbon fraction, too. Would not be more convenient to take into consideration the paraffine-hydrocarbon fractions both of the chloroform bitumen and the BAM extract.

In the lack of sufficient data an exact delimitation of the primary and secondary bitumen in the samples of the area investigated cannot be given, however, the experiences so far are stimulating on putting up some ideas.

Of the samples investigated those from the Lower Pannonian beds have the highest chloroform bitumen content in average and they showed the highest bitumen coefficient, too. Grouping the data according to the boreholes, the highest mean values for chloroform bitumen and bitumen coefficient were determined in the samples of the boreholes Fe-3—13.

In 58 per cent of the samples of borehole M-2 the bitumen coefficient is lower than 15, in samples of borehole Fe-K—1 88 per cent of the samples whereas of the samples of boreholes Fe-3—13 47.5 per cent has a bitumen coefficient below 15. At the same time in 43 per cent of the samples from the latter boreholes rather high bitumen coefficient values — above 40 — can be found not shown by the samples from the other boreholes.

Grouping the samples from the boreholes Fe-3—13 according to their lithological character into groups of sandstones and marls, claymarls, respectively, and calculating the average values for the different parameters, the data of Table 3 are obtained.

The sandstones corresponding to their reservoir capacity contain considerably more chloroform bitumen than the marls and claymarls, however, at the same time hardly any differences can be found between the amounts of the BAM extract determined both in sandstones and marls, claymarls and between chloroform bitumen and BAM extract content of claymarls, marls. The former idea is coming up again, the components of the BAM extract of at least a portion of them may be in a closer genetic connection with the insoluble organic material present and may be rather considered of primary character. On the contrary, a considerable part of the chloroform bitumen would be perhaps primary in the marls, claymarls and it is dominantly secondary in the sandstones.

TABLE 3

*Mean values of chloroform bitumen, BAM extract, C<sub>org</sub> content and bitumen coefficient in the sandstones and marls, claymarls from boreholes Fe-3-13*

	Sandstone	Marl, claymarl
Chloroform bitumen	0.1588	0.0312
BAM extract	0.0336	0.0372
C <sub>org</sub>	0.25	0.36
Bitumen coefficient	85.55	10.29

The fact that in the migration first of all the component corresponding to the chloroform bitumen and within it first the lighter compounds participate is supported also by data of Table 4, showing the ratio of different fractions of chloroform bitumen and the BAM extract of some samples from the boreholes. Fe-3—13.

TABLE 4

*Ratio of fractions of chloroform bitumen and BAM extract of samples from boreholes Fe-3-13*

Fraction (solvent)	Chloroform bitumen	Chloroform bitumen of extreme value	BAM extract
I (n-hexane)	41—58	80—90	8—28
II (benzene)	16—26	5—7	11—40
III (benzene-ethanol)	23—41	3—9	32—74

(Fraction I contains mainly the paraffine-hydrocarbons, fraction II mostly the aromatic compounds, fraction III contains the so-called acidic resins)

As it can be seen among the fractions of the chloroform bitumen extracted from three sandstone samples having a very high chloroform bitumen content, and therefore considering undoubtedly this bitumen as secondary by migration into these reservoir rocks, fraction I is predominant and the amount of the other two fractions is very low. In the other samples where fraction I is high but not so dominant, the proportion of the other two fractions is also more considerable. Among the fractions of the BAM extract from the same samples the lowest is the proportion of fraction

I and fraction II containing aromatic compounds and even more fraction III corresponding to the acidic resins plays a dominant role.

It may be assumed on the basis of the facts and ideas outlined above that at the delimitation of primary and secondary bitumen more importance should be attributed to the BAM extract besides the chloroform bitumen as well as to the comparison of their fractions separated by column chromatography.

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