

DETERMINATION OF THE METHOXY-GROUP CONTENT OF INSOLUBLE ORGANIC SUBSTANCES OF SEDIMENTS

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INTRODUCTION

A major part of geochemical investigations carried out in connection with hydrocarbon occurrences aimed to decide whether the sediment is either a source rock of hydrocarbons or perhaps it is merely a reservoir-rock where the hydrocarbons accumulated by migration.

However, so far investigations of the identification of source-rocks have not yielded exact results. [MACOVEI, 1928; TRASK, 1932; TRASK and PATNODE, 1942; PHILIPPI, 1957; BRENNEMAN and SMITH, 1958; KALIFEH and LOUIS, 1961; BREGER and BROWN, 1962; HEDBERG, 1964; BRAY and EVANS, 1965. — cited by NAGY, B. and U. COLOMBO, 1967.]

Relying upon results obtained through experiments of investigators referred to, COLOMBO [1967] stated that practically it is impossible to draw a well defined line between hypothetical source-rocks and no-source ones. This statement means that all sedimentary rocks more or less contribute to the generation of hydrocarbons, which at last are accumulated in the reservoir rocks.

To decide to what extent had the organic matter coming from a given area contributed to the formation of hydrocarbons found there, very important data may be yielded by a complex study of kerogen, the insoluble organic material of sediments.

FORSMAN and HUNT [1958] differentiate three types of kerogens isolated from sediments coming from different localities. They classify coaly-, non-coaly oil shale- and coaly oil shale-types.

Coaly-type kerogens are very markedly similar to substances found in peat, lignite and other coals; they mostly consist of lignin-like compounds. These kerogens can be regarded as built up of macromolecules consisting of condensed aromatic rings, wherein the rings are connected by ether-, alkoxi- and sulphuric bridges, respectively. Hydroxyl-, methoxy- and sometimes esterified carboxyl-groups may be connected with the aromatic core.

Non-coaly oil shale kerogens are characterized by straight-chain structures, with little cycloparaffin and an aromatic ring with one core, connected with a functional group with less oxygen content.

Coaly oil shale kerogens, as regarding their properties represent a transition between kerogens classified in the former two types.

It has been pointed out that from the point of view of the formation of hydrocarbons sediments containing non-coaly oil shale kerogens are the most important.

A number of experiments have been carried out to classify kerogens of sediments of different hydrocarbon occurrences according to the former classification.

These experiments had as a primary aim to isolate from the rocks, to determine the composition and to clear up the structure of kerogens.

Besides the above mentioned studies some important data could be obtained by determining the periferical functional groups, what is a well-known method in the case of different carbons. However, literature contains relatively few data on kerogen. [SEMENOV *et al.* 1955; VAN KREVELEN and SCHUYER, 1957; AARNA and LIPPMAN, 1957. — cited by A. S. FOMINA *et al.*, 1965.]

Especially important data may be got by the determination of the methoxy-group content, since from this deductions can be made on the type of the kerogen isolated from the sediment, its being of coaly-type or non-coaly oil shale type, and whether it might have played a role in the formation of hydrocarbons. [FORSMAN, 1963.]

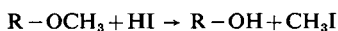
Having this problem cleared up may help in marking the direction of possible migration, discovering further hydrocarbon occurrences.

The subject of the present study is how to make applicable the determination of the methoxy-group content, a generally used method, for the study of insoluble organic-carbon content of sediments.

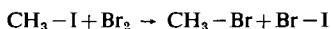
EXPERIMENTAL PART

For the analytical determination of the periferic methoxy-group content of kerogen essentially we have used a modified version of the hydrogen iodide acid method described by ZEISEL [1885].

The essence of ZEISEL's method can be summarized as follows: periferic methoxy-groups react with hydrogen iodide forming methyl-iodide:



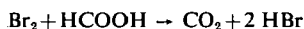
Methyl-iodide formed in an equivalent to the methoxy-groups amount has a lower boiling point thus it easily can be expelled from the system by heating. The formed methyl-iodide vapours are adsorbed by bromine dissolved in glacial acetic sodium acetate:



Bromine-iodide is formed, which, affected by excess bromine in aqueous media is oxidized to iodic acid



Excess bromine can be reduced by formic acid what is indicated by the solution losing its colour:



Finally iodine formed in an amount equivalent to iodic acid can be determined with iodometry.

In order to make ZEISEL's method suitable for the determination of the methoxy-group content of insoluble organic substances of sediments, several modifications are necessary both regarding the apparatus and various steps of the method. *E. g.* in contrast to the description in the literature of introducing hydroiodide acid, it is better to add it dropwise through a funnel while cooling the reaction vessel to avoid the loss of methyl-iodide owing to a very rapid reaction; because of the slow gas stream the aqueous suspension of red phosphorus as a washing agent did not prove

to be suitable, therefore a 1:1 mixture of 5% sodium thiosulphate and 5% cadmium sulphate solutions was used taking much care that the temperature of the washing agent did not rise markedly otherwise the formation of sulphur from the decomposition of sodium thiosulphate would hardly affect the determination, etc.

To perform the determination the following apparatus was used (*Fig. 1*).

The dissolution of 30—50 mg kerogen of <60 nm grain size measured in the reaction vessel was done by adding 0,5 g crystalline phenol, 0,2 g red phosphorus

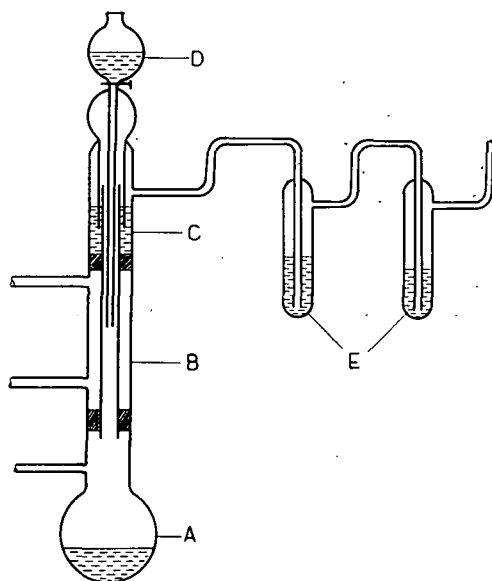


Fig. 1. An apparatus for the determination of the methoxy-group. A — reaction vessel; B — cooler; C — washer; D — funnel; E — absorption bulb

and 1 ml acetic acid anhydride, or propionic acid anhydride, under nitrogen atmosphere, then while cooling the reaction vessel, 5 ml hydrogen iodide, freshly distilled from red phosphorus was added dropwise from the funnel. Having this completed, the reaction vessel was heated to 140—150 °C by putting it in glycerin bath and maintaining this temperature for about two hours, the periferic methoxy-groups were transformed into methyl-iodide. The formed methyl-iodide vapours were led through a cooler — which is advisable to be heated only in the first third of the time of reaction — in 1:1 mixture of 5% sodium thiosulphate and cadmium sulphate or the aqueous suspension of red phosphorus, and adsorbed in 10% sodium-acetate containing 10—12 drops of bromine, distributed in a one third-two thirds ratio in two parts of the adsorbing vessel. After the completion of the reaction the content of the adsorbing vessel is washed into an Erlenmeyer flask with a ground cork, a few drops of formic acid added to make the excess bromine react then, by adding 10 ml 2 N sulphuric acid and 0,5 g KI, after five minutes the iodine obtained is titrated with 0,1 sodium thiosulphate. The same process is used with the blank as well.

RESULTS AND DISCUSSION

To control the reproducibility and applicability of the method, as well as for the purposes outlined in the introduction, the methoxy-group content of non-coaly oil shale type kerogen, enriched from shale of brown coal and kukersite from Estonia, respectively, studied by other researchers as well was determined, then experiments were carried out with insoluble organic-carbon substances isolated from rocks deriving from the area investigated by us.

Values found in the literature compared with those measured and calculated by us are summarized in Table 1.

Although our aim was to develop a method suitable for an exact determination of the methoxy-group content of insoluble organic-carbon substances of kerogen and its sediments, respectively, on the basis of the obtained data we think that by the determination of the methoxy-group content of insoluble organic-carbon substances of kerogens of non-coaly oil shale type, coming from different localities and of sediments coming from our research area, some deductions can be made upon the properties of the latter samples. Deductions are to be made as well on the character of behaviour of the studied samples, which type can they be ascribed to, and accordingly, could they play a role in the formation of hydrocarbons, namely, the sediment studied is a mother rock or only a reservoir of the hydrocarbons found.

TABLE I

Sample	Age	Locality	C W. %	-OCH ₃ W. %		Notice
				Literary	Measured	
Lignin	—	—	68,18*	17,61*	—	*Calculated
Brown-coal	Pleistocene	Ecséd	54,4*	7,35*	7,25 7,32 7,38	*KEDVES and SIPOS [1967]
	Pleistocene	Gyöngyös- visonta	59,3*	8,75*	8,82 8,85 8,76	
	Miocene	Herend	56,9*	8,44*	8,48 8,56 8,50	
Kukersite- kerogen	Ordovician	Estonian SSR	66,65*	0,2*	0,21 0,30 0,25	*SEMENOV et al. [1955]
Isolated organic matter	Upper- Pannonian	Makó-7 S-100	31,52 73,57*	—	0,65 0,59 0,55	*Calculated on zero ash content
	Lower- Pannonian	Makó-2 S-111	22,35 64,04*	—	0,60 0,64	
	Lower- Pannonian	Makó-2 S-112	25,47 65,77*	—	0,48 0,52	

When determining by pyrolysis the degree of diagenesis of the insoluble organic content of the sediments, according to GRANSCH and EISMA [1966], in the case of the same type of organic matter, from the C_R/C_T quotient we can deduce on the degree of diagenesis; in the case of the same degree of diagenesis, on the type of the organic matter.

We think that the determination of the function groups and of those that of the methoxy-group may give further impact for the determination of the type of the organic matter.

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