

CONTRIBUTIONS TO THE ISOLATION OF THE KEROGEN IN HUNGARIAN OIL SHALES

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ABSTRACT

Concentration of kerogen of the Hungarian alginites can be carried out by separation in organic solvents. This method is very quick, it does not need a lot of work and the solvent can be removed without residue. Applying other physical method, e. g. separation in calcium chloride solution the amount of the kerogen concentrate is larger but its organic carbon content smaller than using chloroform for separation. The quality of the organic phase is better if solvents of lower specific gravity are used. As the other physical separation methods, this one has also the disadvantage that the kerogen of samples of low organic content can not be separated. Acidic treatment of the samples of high carbonate and relatively low organic carbon content promotes the separation by physical method.

INTRODUCTION

The kerogen is in organic solvents insoluble part of the organic material of the sediments. In order to study its structure, first of all it has to be separated from the soluble organic material and mineral components. The soluble part is extracted in different organic solvents (chloroform, acetone, benzene, methanol and/or their mixture). To separate mineral components is much more difficult than to remove soluble organic material. Some sediments are argillaceous, others calcareous and/or contain pyrite or quartz. On removing these minerals it needs various methods.

Requirements for isolation methods [FORSMAN, 1963]:

1. No chemical alteration of the kerogen should take place in the process.
2. The method should yield sufficient pure material for elemental analysis and degradation studies.
3. Fractionation of the kerogen should be avoided, that is the kerogen concentrate obtained should be representative of the starting material.

The methods used for isolating kerogen are physical or chemical ones.

Physical methods

Differential wettability method

This procedure was used first by QUASS [1939, cited by Eglinton and Murphy, 1969], who isolated kerogen of Australian torbanites. Later this technique has been employed and modified by various authors. According to ROBINSON [1969] "method is based upon the principles of differential wetting of the organic kerogen and the inorganic mineral by two immiscible liquids such as oil and water. The organic kerogen is wet by the organic liquid phase and the mineral is wet by the water phase resulting in the kerogen being retained in the oil phase and the mineral being released into the water phase". The advantage of this method is that the isolated kerogen remains

chemically unaltered. The disadvantage is that it takes a long time and in numerous cases only a small part of the minerals can be removed.

Flotation method

The flotation method are based upon the differences in the specific gravity of the kerogen and the minerals. The separation is taken place in a liquid of specific gravity which is between that of the kerogen and the minerals. The specific gravity of the mineral components usually changes from 2 to 5.

The specific gravity of Green River Formation kerogen 1,07. FORSMAN and HUNT [1958] also published data on the specific gravity of some kerogens, but these data have been corrected for mineral content, which consists chiefly of pyrite and insoluble fluorides. By them the corrected specific gravity of the Green River kerogen 1,22—1,38.

Aqueous calcium chloride solutions are often used in the flotation techniques. [cited by EGLINTON and MURPHY, 1969].

HUBBARD *et al.* [1952], carried out the separation with a mixtures of carbon tetrachloride and benzene (specific gravity between 1,15—1,40). The kerogen rock were extracted with benzene and carbonates were removed. The material was centrifuged in the mixture of specific gravity — mentioned above — which first was 1,40, second 1,20 and third 1,15. By repeated flotation the yield of the kerogen can be increased only in a small degree, but the ash content will be less than 10 per cent.

Generally the advantage of the flotation technique is that the kerogen does not altered chemically, however, on the other hand, it gives a high ash content. The method can be used only in cases of rocks relatively rich in kerogen.

Chemical method

The chemical method has in general the advantage that the kerogen obtained is purer and has a lower ash content, however, the mineral components can not perfectly be removed.

Its disadvantage is, however, it takes a long time, consists of successive steps, and each step have to be repeated, and the structure and composition of the original kerogen will be attacked by the chemicals used.

At first, the carbonates are decomposed usually by hydrochloric acid. Hydrochloric acid is suitable because such a way the calcium can be removed as well. In the next steps silicates and quartz are removed by hydrogen fluoride, but the presence of the calcium disturbs this treatment, due to formation of insoluble calcium fluoride [FORSMAN and HUNT, 1958]. After removing the fluorides the residue is treated first with ammonium hydroxide, then with hydrochloric acid and hydrogen fluoride, respectively. This process is repeated some times [LÜCK, 1969].

Pyrite can be removed by a reduction with zinc and hydrochloric acid [FORSMAN and HUNT, 1958], or with LiAlH_4 used by other authors.

According to HIMUS [1950] "There is no universally satisfactory method for the determination of the composition of kerogens in a kerogen rock, every sample must be the subject of special investigation". DANCY and GIEDROYC [1950] similarly states that "no method generally applicable for removal of mineral matter from oil shales can be described, and variations must be made to suit individual samples". [See BREGER, 1963].

EXPERIMENTAL PART

Examination of the insoluble organic material is necessary for study the genesis of the newly discovered Hungarian oil shales. Therefore organic material of sufficient quantity and of low ash content has to be isolated. Some of the available samples can be separated by physical method, but another part having lower organic carbon content can be isolated only by chemical method.

Since the structure of kerogen does not suffer alteration at all during physical technique, it was important to develop a quick and simple physical method to obtain insoluble organic material in sufficient quantity for investigation.

Comparing the physical and the chemical method some differences can be established in the organic materials obtained by these two different ways (Table 1).

TABLE I

Specific gravity, ash, organic and inorganic carbon content of the kerogen isolated by chemical and physical method

	Kerogen isolated by physical method	Kerogen isolated by chemical method
Specific gravity	1,16	1,04
C _{org} %	66,9	69,2
C _{inorg} %	0,6	0,0
Ash %	7,2	1,2

Although the kerogen isolated by chemical method seems to be purer — lower ash and inorganic carbon content — still this method destroys the structure of the kerogen. It is demonstrated by the infrared spectra of the kerogens (*Fig. 1*).

As it can be seen on the *Fig. 1*, the spectrum of the kerogen isolated physically has more bands, than that of the kerogen isolated chemically. For example band between 3600—3100 cm⁻¹ (νOH band), and some bands in the region between 1800—1000 cm⁻¹ are missing in spectrum of kerogen isolated chemically.

The mineral components of the Hungarian oil shales from neighbourhood of Pula detected by X-ray diffractometry, are calcite, dolomite, aragonite, clay minerals, quartz and feldspar, olivine, pyrite (J. MEZŐSI's personal communication). The specific gravity of these minerals is between 2—5.

The specific gravity of kerogen isolated from different oil shales by different methods is between 1,07—1,51 [FORSMAN and HUNT, 1958; BREGER, 1963].

The specific gravity of the kerogen isolated from Hungarian oil shales by chemical method is 1,03—1,05.

On the basis of the differences in the specific gravity the organic and inorganic components can be separated in liquid phases having a specific gravity of 1,1 to 1,9.

Organic solvents appear to be more suitable for separation because they wet

these materials perfectly. Aqueous solutions do not wet organic compounds so that the problem of wettability arises.

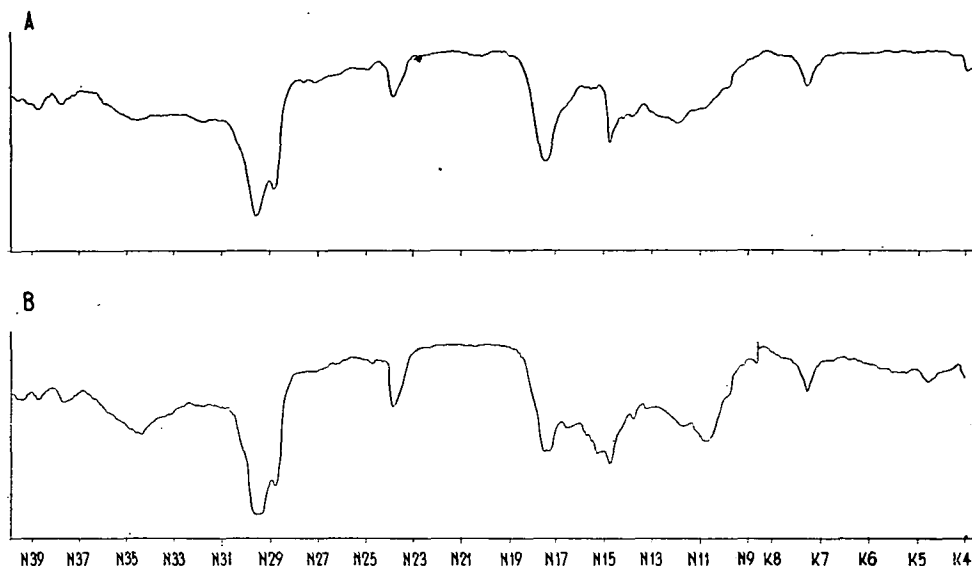


Fig. 1. Infrared spectra of the upper phase of the sample 4.

A = isolated by chemical method

B = isolated by physical method

Considering problems mentioned above chloroform (sp. gr. 1,5) and mixture of chloroform and methanol (sp. gr. 1,15 to 1,35) were used for separation.

Four samples were chosen from Hungarian oil shales (Table 2).

TABLE 2

Depth, organic and inorganic carbon content of the samples

Sample N ^o	Depth (m)	Original sample		Sample extracted	
		C _{inorg} %	C _{org} %	C _{inorg} %	C _{org} %
1	14,5—15,0	1,8	32,6	2,3	26,3
2	16,0—16,5	1,2	45,7	1,2	40,5
3	19,5—20,0	5,9	9,8	5,9	6,6
4	25,0—25,5	3,2	30,1	3,4	27,0

Three of them have high organic carbon content (> 30 per cent) and one has a relatively low organic carbon content (< 10 per cent). The inorganic carbon content changes from 1,2 to 5,9 per cent.

The separation was carried out with original samples as well as with samples extracted by chloroform and mixture of benzene-acetone-methanol, respectively.

The air dried core samples were first ground in ball mill (grain size < 60 μm), and after extraction the samples were dried at 60 °C.

1,5 g of the sample was suspended in 20 ml solvent in a tube, and when the suspension have been separated into two phases, the upper phase was removed. Both solid phases were dried at 60 °C.

The same samples were also separated in aqueous solution of CaCl₂ (sp. gr. 1,20). Flotation was made by MRS BERTALAN on the basis of the method of FOMINA *et al.* The results of the two different methods have been compared, as follows.

Two phases were gained in organic solvents, and three phases in CaCl₂ solution.

The quantity, the organic and the inorganic carbon content of each phase and the ash content of upper phase was determined. Results are given in Table 3.

TABLE 3

Values of some parameters of the upper and lower phases separated by different physical method

		Separation in chloroform		Separation in aqueous calcium chloride solution		
		Upper phase	Lower phase	Upper	Middle phase	Lower
Sample 1						
Quantity	%	34,2	65,8	2,6	18,0	79,4
C _{org}	%	56,7	16,7	65,7	41,9	22,6
C _{inorg}	%	0,6	3,0	0,0	1,4	2,7
Ash	%	18,2		8,6		
Sample 2						
Quantity	%	58,6	41,4	12,1	61,4	26,5
C _{org}	%	59,3	18,6	71,0	48,2	21,7
C _{inorg}	%	0,3	3,5	0,1	0,8	2,0
Ash	%	16,3		8,6		
Sample 3						
Quantity	%	6,0	94,0	1,5	5,2	93,3
C _{org}	%	66,3	5,2	70,9	40,3	11,4
C _{inorg}	%	0,5	7,1	0,2	3,2	6,4
Ash	%	15,1		8,1		
Sample 4						
Quantity	%	31,0	69,0	8,6	32,0	59,4
C _{org}	%	65,5	12,6	70,4	43,2	18,9
C _{inorg}	%	0,7	4,5	0,3	2,4	4,1
Ash	%	14,0		7,4		

As it can be seen on the Table 3, the amount of the organic phases separated in chloroform is larger, than the organic phases gained in CaCl₂ solution. The quality of kerogen is characterized by ash and organic carbon contents. Considering these values the quality of the organic phases separated in chloroform is not as good, as the first phase, but better than second organic phases gained by CaCl₂ method. However, the lower phase separated in chloroform are more suitable for further mineralogical analysis because of their lower organic matter content. Due to the high organic carbon content the baseline of the X-ray diffractograms displaces, thus, the evaluation of the diffractograms is very difficult. After physical separations, lower phases is suitable to X-raying.

It was supposed that repeated separation of the upper organic phase supplies a concentrate of higher organic carbon and lower ash contents. The separation of the upper phase of the sample 2 was repeated three times. The organic carbon and ash contents are shown in Table 4.

TABLE 4

Ash and organic carbon content of the upper phases of the sample 2 separated by different physical method

		Separation in chloroform	Repeated separation in chloroform	Separation in aqueous CaCl ₂ solution
C _{org}	%	59,3	71,3	71,0
Ash	%	16,3	8,4	8,6

The organic carbon content is increased, the ash content is decreased, so, their values are the same, as that of the upper phase floated in CaCl₂ solution.

Isolation by means of organic solvents is a very quick method and these solvent are removed by drying at 60 °C. In this way even the repeated separations require less work, than the method using CaCl₂ solution.

It was examined whether the removing of carbonates influences the separation. Carbonates were removed by monochlor-acetic acid. These samples were not extracted previously. The results are given in Table 5.

TABLE 5

Quantity, organic and inorganic carbon content in original samples as well as in samples after removing carbonates

		Separation of the original sample		Separation of the sample free of carbonate	
		Upper phase	Lower	Upper phase	Lower
Sample 1					
Quantity	%	34,2	65,8	42,1	57,9
C _{org}	%	62,2	17,9	61,7	26,5
C _{inorg}	%	0,5	2,8	0,0	0,0
Sample 2					
Quantity	%	55,1	44,9	70,0	30,0
C _{org}	%	65,6	19,3	63,0	29,2
C _{inorg}	%	0,1	2,3	0,0	0,0
Sample 3					
Quantity	%	6,0	94,0	13,8	86,2
C _{org}	%	62,6	7,2	66,1	18,7
C _{inorg}	%	0,5	6,1	0,0	0,0
Sample 4					
Quantity	%	31,9	68,1	55,5	45,0
C _{org}	%	61,5	13,5	59,3	26,8
C _{inorg}	%	0,7	4,3	0,0	0,0

After the acid treatment the amount of upper phases increased, their organic carbon content practically remained the same. Because of the increase of the efficiency of the separation some samples with high carbonate and relatively low organic carbon content become also suitable for physical separation.

Four further samples were examined. The CO₂ content of the samples: 9,5 per cent (sample 5), 8,2 per cent (sample 6), 22,1 per cent (sample 7), 21,5 per cent (sample 8). Their organic carbon content changes between 10,5 and 11,7 per cent. After acidic treatment sample 7 and 8 became separable by physical method, but sample 5 and 6 did not seem suitable for physical separation.

In order to obtain kerogen with higher organic carbon content and lower ash content the samples were separated in the mixture of chloroform and methanol (sp. gr. 1,25). Results are shown in Table 6.

TABLE 6

Values of some parameters of the upper and lower phases separated in organic solvents

Specific gravity of the solvents		Separation in the mixture of chloroform and methanol		Separation in chloroform	
		1,25		1,50	
		Upper phase	Lower	Upper phase	Lower
Sample 1					
Quantity	%	17,2	82,8	34,2	65,8
C _{org}	%	62,2	21,2	56,7	16,7
C _{inorg}	%	0,4	2,7	0,6	3,0
Ash	%	13,2		18,2	
Sample 2					
Quantity	%	50,0	50,0	58,6	41,4
C _{org}	%	65,3	24,0	59,3	18,6
C _{inorg}	%	0,2	1,8	0,3	3,5
Ash	%	10,9		16,3	
Sample 3					
Quantity	%	3,6	96,4	6,0	94,0
C _{org}	%	66,9	6,0	66,3	5,2
C _{inorg}	%	0,4	6,6	0,5	7,1
Ash	%	6,8		15,4	
Sample 4					
Quantity	%	8,2	91,8	31,0	69,0
C _{org}	%	66,9	24,8	65,5	12,6
C _{inorg}	%	0,6	3,6	0,7	4,5
Ash	%	7,2		14,0	

The amount of the organic phase decreased concerning the efficiency of the separation in chloroform. Organic carbon content increased slightly, but ash content significantly decreased.

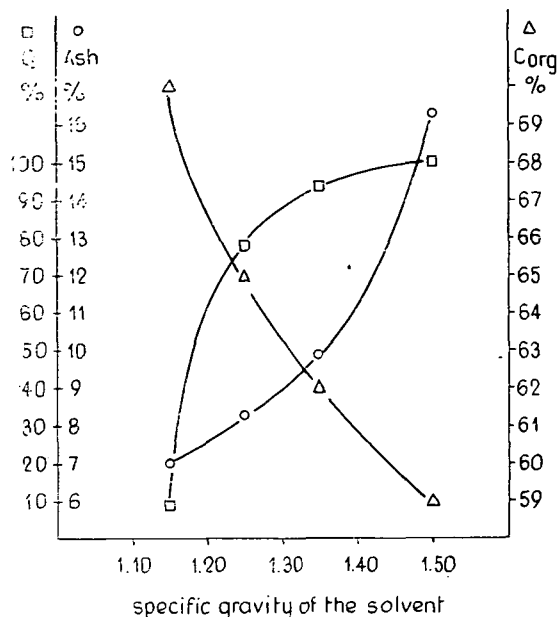


Fig. 2. Quantity, ash and organic carbon content in the function of the specific gravity of the solvent.

On studying the effect of the specific gravity of solvents, the upper phase of the sample 2 was separated in solvents of different specific gravity. (Table 7) Previously 10 g of sample 2 was separated in chloroform. The organic phase obtained in this way was dried at 60 °C. The dried material was suspended in the mixture of chloroform and methanol having specific gravity of 1,35, 1,25 and 1,15, respectively. The amount of the kerogen was decreased, the organic carbon content increased and ash content also decreased by the decreasing specific gravity.

TABLE 7
Values of some parameter in the two phases of samples separated in the mixture of organic solvents having specific gravity

	Specific gravity of the solvents						
	1,50	1,35	1,25	1,25	1,15	1,15	
	Upper phase	Upper phase	Lower phase	Upper phase	Lower phase	Upper phase	Lower phase
Quantity %	100	94,1	5,9	77,8	22,2	9,2	90,8
C _{org} %	59,0	61,8	36,0	65,0	59,7	70,3	65,4
C _{inorg} %	0,3	0,2		0,1		0,1	
Ash %	16,3	9,9		8,3		7,0	

SUMMARY

Kerogen of Hungarian oil shales from neighbourhood of Pula was separated by a physical method. Since the specific gravity of the mineral components is greater than 2 and that of the kerogen less than 1,2, the specific gravity of the liquids suitable for separation is between 1,2 and 2. Organic solvent as well as the mixture of organic solvents were used for they wet the samples well. Further advantage of organic solvent is that they can easily be removed from the solid phases.

Removing of aqueous salt solution is difficult, it can be carried out by repeated washing, and it causes loss in the amount of organic material. In a solvent of comparatively high specific gravity, for example in chloroform (sp. gr. 1,50), the first separation gives kerogen with not so good quality, as in aqueous solution. Repeating the separation of the upper phase in the same solvent, the ash and organic carbon contents become as good as that of the kerogen obtained in CaCl_2 solution.

Separation in the mixture of solvents (sp. gr. 1,25) results in a higher organic carbon and a lower ash content than in the chloroform alone.

One of the disadvantages of the physical technique is the high ash content. Repeated separation gives better results, the ash content decreases.

The advantage of the separation in solvents is the large amount of the organic phase. For some examinations the quality of the material of relatively high ash content is sufficient, as well. However, some analyses need material of high quality. Therefore, samples can be separated in chloroform to obtain a large quantity of organic material then this material can be purified by solvents of lower specific gravity.

According to our experience, acid treatment promotes the separation of the samples of relatively low organic carbon content. This effect appears in the materials of high carbonate content. It is due to the relative increase of the organic carbon content after having removed the carbonates.

REFERENCES

- FORSMAN, J. P. and J. M. HUNT [1958]: Insoluble organic matter (kerogen) in sedimentary rocks. *Geochim. et Cosmochim. Acta* 15, p. 170—182.
- FORSMAN, J. P. [1963]: Geochemistry of kerogen. In: I. A.: Breger Organic Geochemistry, p. 148—182.
- LÜCK, J. [1969]: Die Kerogenanalytik — Verfahren zur Ermittlung des Diagenesegrades der organischen Substanz in Sediment. — *Erdöl-Erdgas Information* 6. p. 34.
- ROBINSON, W. E. [1969]: Isolation procedures for kerogens and associated soluble organic materials. In: G. Eglinton and M. T. I. Murphy: Organic Geochemistry, p. 181—195.

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