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The organic matter type in the shale rock samples assessed by FTIR-ATR analyses

The aim of the paper was to show possibilities of applying the relatively new, and quick FTIR molecular vibrational spectroscopy with Attenuated Total Reflectance – ATR technique – in order to correlate extracted organic matter samples of different types with its infrared spectra. The technique was employed for 22 shale rock samples of the Carpatian Flysch – mainly from Menilite Beds, Istebna Beds and Verovice Beds. They were selected on the basis of their different maturity levels – from immature ones through all stages of the oil window, up to the early gas window phase of generating hydrocarbons. The Rock-Eval analysis and optical microscope techniques (organic petrography and vitrinite reflectance), were the methods chosen to confirm the samples classification assessment, in terms of kerogen typing and samples maturity. The major kerogen types in these source rocks include Type I, II and III. In consequence the measurement and data analysis (like choosing analytical bands and parameterization) for distinguishing between different kerogen types (I-III) should be possible by the proposed FTIR-ATR technique.

Key words: Shale rock analysis, organic matter FTIR analysis with ATR mode, vitrinite reflectance, Rock-Eval and petrographical analysis.

Typ substancji organicznej w łupkach, a jej widma spektroskopowe FTIR-ATR

Artykuł przedstawia możliwości zastosowania relatywnie nowej, szybkiej odmiany spektroskopii w podczerwieni FTIR – w wydaniu z wykorzystaniem techniki ATR (*Attenuated Total Reflectance*) – bazującej na zjawisku tłumionego całkowitego odbicia. Celem jest korelacja próbek kerogenu reprezentujących różne jego typy z ich widmami w podczerwieni. Przebadano 22 próbki skał formacji łupkowych fliszu karpackiego. Były to łupki menilitowe, warstwy istebniańskie oraz wierzowskie, wyselekcjonowane w taki sposób by reprezentować różne stopnie dojrzałości materii organicznej – od niedojrzałych poprzez okno ropne aż do okna gazowego. W celu potwierdzenia ich klasyfikacji przeprowadzono badania pirolizy Rock-Eval, użyto mikroskopowych metod petrograficznych jak analiza refleksyjności witrynitu oraz petrografia składników organicznych. Stwierdzono, iż poszczególne próbki przynależą do kerogenu typu I, ale także II oraz III. Na podstawie przeprowadzonych dotychczas badań oraz doniesień literaturowych stwierdzono, iż rozróżnienie takie było możliwe także z użyciem zaproponowanej w pracy odmiany metod spektroskopii w podczerwieni – FTIR-ATR. Jednak w celu bardziej szczegółowego poznania ograniczeń metody oraz stwierdzenia zakresu jej stosowalności konieczne jest przeprowadzenie badań na większej populacji próbek.

Słowa kluczowe: analizy próbek formacji łupkowych, analizy materii organicznej metodą FTIR-ATR, refleksyjność witrynitu, analizy Rock-Eval.

Introduction

One of the first papers concerning shale rock infrared vibrational spectroscopy analysis was published by Solomon, and Miknis in 1980 [21]. The technique has been used by the group for evaluating the oil yielding potential of raw oil shales. Cronauer, Snyder and Painter, published their research report in 1982 [5] where they analyzed rock mineral matrices together with contained organic matter. The chosen analytical method was transmission mid infrared spectroscopy in

KBr pressed pallets. The technique as well as the Diffused Reflectance method [1, 3, 4, 6, 8, 13, 15, 19, 20] was also applied by many other researchers over the next 30 years. Cronauer and his group [5] signalized the great importance of sample preparation procedure for the quantitative usage of the technique, pointing out the problem of grinding minerals of different hardness and the influence of grain size on the pick intensities especially when a whole rock sample is analyzed. Other analytical problems with quantitative shale rock analysis where also identified. Among them the problem of representativeness of the sample is very important especially in the case of KBr pallets preparation (the procedure is to take about 1mg of the sample for each 300 mg of potassium bromide). In this situation the sample needs to be well homogenized from the representative rock volume to give reliable results. There is also some other difficulties like the problem of particle agglomeration during grinding, water absorption in hygroscopic KBr, weighing errors, reproducbility of sample and dilutant mixing [17].

In the last few years a significant development of infrared analytical techniques has been established and some convenient and effective solutions where introduced into laboratories, like the ATR (Attenuated Total Reflectance) mode with a branch of different analytical crystals (like germanium, silica, zinc selenide and diamond) characterized by their range of hardness values and optical properties [18]. Recently authors have been trying to apply this technique also to the shale rock mineral composition analysis as a quick and robust method and together with some mathematical correction and quantification protocols (like multivariate regression models based on PLS protocols) [17], it was introduced as a reliable quantitative mineral composition analytical technique, useful especially in fast screening analysis. It also might be used in organic matter analysis. In this case there are at least a few ways of data treatment, most of them where prepared for the transmission FTIR mode and needs to be recalibrated and adopted for the ATR mode of analysis.

The advantage of using this type of accessory is minimal or no sample preparation as well, in case of whole rock and extracted kerogen analysis. Dry wet and viscous samples may be analyzed. The procedure of spectrum acquiring is quick and simple (it takes minutes). The sample is put on the diamond crystal and pressed to the surface of the crystal by a pressure rig to the moment until good optical contact is achieved. Optical contact between sample and measuring element is a condition for quality spectrum obtaining. So in case of hard samples (like rocks) grinding is needed. Samples should be fine grinded (best would be fraction below 10 μm or even below 2.5 μm) according to measuring wave length. Of course it is not necessary if soft and viscous samples are acquired.

In the case of organic matter analysis by molecular spectroscopy it has to be done thoroughly and carefully since the complexity of the problem is significant. There is a variety of the macerals which may be composed of each kerogen type [7, 13]. In consequence it does not imply trivial spectra interpretation, due to possibly different organic matter macerals composition in each kerogen type and different evolution paths in the maturation processes [24, 25].

Experimental methods

Several methods have been used in order to analyze and correlate the characteristics of samples, along with FTIR analysis, Rock-Eval technique as well as different microscopic techniques listed below with technical details were employed.

FTIR analysis: For infrared analysis the Thermo Nicolet 6700 FTIR spectrometer equipped with the DLaTGS detector and XT-KBr beam splitter was used. The analysis was performed on a standard ATR Golden Gate extension equipped with single reflectance IIIA diamond crystal and ZnSe lenses. 128 scans were averaged for each background and spectra acquisition.

Rock-Eval analysis: Rock-Eval pyrolysis was performed with the Rock-Eval-6 standard model.

Optical microscopy: For optical microscopic investigations: Nikon Opthiphot, Zeiss Axioplan and Nicon Eclipse were used. Samples were investigated using reflected light on polished samples. Also isolated kerogen in transmitted light as well as in fluorescence mode was investigated. Magnifications from 200 to 500x were used. Vitrinite reflectance (R_o) was measured using the Zeiss Axioplan microscope.

Kerogen extraction: Standard Extraction procedure was performed in order to obtain isolated kerogen samples. By several HCl and HF treatments and H_2O samples washing carbonates and silicates were removed. In the next steps organic matter was separated from heavy minerals using high density liquid (CdJ_2, density 2.2 g/cm^3) leading to organic matter separation. Finally the smallest fraction of 15 μm was sieved from the OM material.

Methodology and results

In many cases, spectra of the kerogen samples analyzed by FTIR method, differ only in minor details like in the case of kerogen type I and II (Figure 1A and Figure 1B and C). Significant difference appears only in the case of the compari-

son of kerogen type I and III (Figure 1A and Figure 2A, B). Fortunately the parameterization of the analyzed spectra
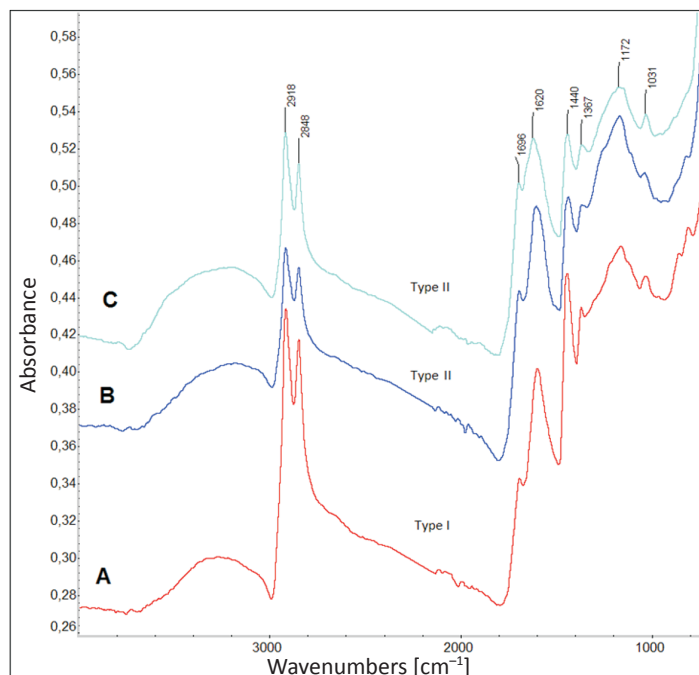

Fig. 1. Kerogen FTIR-ATR spectra: spectrum A – type I kerogen, sample 7868; spectrum B – type II, sample 5517; spectrum C – typ II kerogen, sample 5520 – strong aliphatic groups bands are well visible in high frequency range 2700÷3000 cm⁻¹ with symmetric and asymmetric stretching vibrations of -CH₂, -CH₃
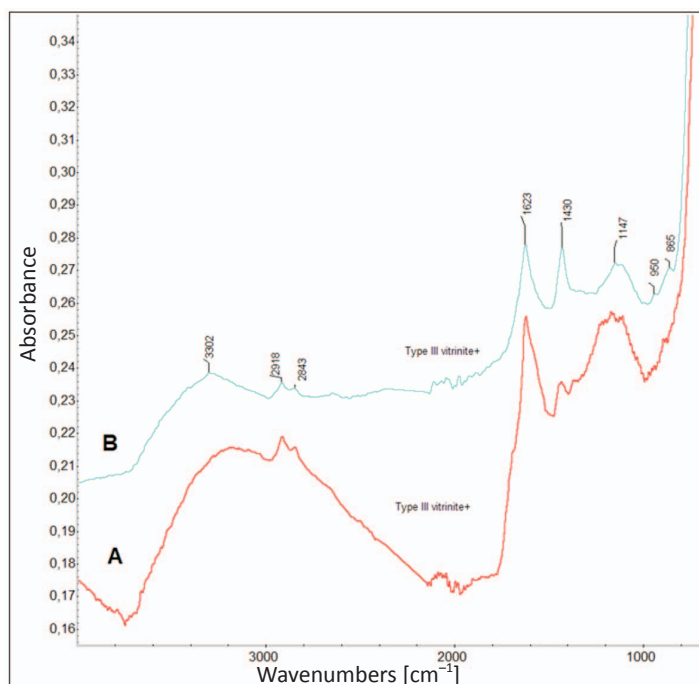

Fig. 2. Kerogen FTIR-ATR spectra: spectrum A – type III kerogen, sample 7872; spectrum B – type III, sample 7864; week aliphatic groups bands are visible in high frequency range 2700÷3000 cm⁻¹ symmetric and asymmetric stretching vibrations of -CH₂, -CH₃

is possible, helpful and in the case of kerogen typing, even necessary. On the other hand it seems that in the case of parameterized spectra, the results are sensitive enough for maceral composition changes, consistent with results obtained from other geochemical analysis, like Rock-Eval Pyrolysis [2, 9, 10].

So in order to analyze the kerogen type for selected samples, various ideas and correlations proposed in the literature were tested for FTIR-ATR analytical technique calibrated also with Rock-Eval analysis results and organic petrology by optical microscopy. Most promising were the Ganz and Kalkreuth factors adaptation [9].

Their idea, of FTIR kerogen type analysis in oil shales was published by the authors in 1987 [9]. They presented the methodology on the basis of 39 selected samples of oil shales, black shales and coals. They proposed the way of data presentation on a graph similar to that of van Krevelen, diagram [25]. The authors used transmission technique with KBr pallets. "A" and "C" factors in papers were proposed to express changes in peak intensities of analytical bands in spectra of the samples of different organic matter origin, upon assumptions about the geochemical changes in organic matter and in particular, about the nature of molecular composition of different kerogen types [23]. The analyses were supported by complementary data from the Rock-Eval pyrolysis. As analytical bands the authors choose, vibrations assigned to stretching vibrations of aliphatic, and carbonyl groups, usually present in organic matter spectra.

In transmission spectra using KBr pallets, this will be: 2860 cm⁻¹ and 2930 cm⁻¹ respectively for methylene CH_2 and methyl CH_3 groups, 1630 cm⁻¹ for stretching vibration of C=C bond in aromatic ring, and 1710 cm⁻¹ for carbonyl C=O groups bonds vibrations.

The A factor is expressed as relative intensities of bands with maxima in 2930 cm⁻¹, 2860 cm⁻¹, 1630 cm⁻¹:

$$A = \frac{\text{Int}(2930 \text{ cm}^{-1}) + \text{Int}(2860 \text{ cm}^{-1})}{\text{Int}(2930 \text{ cm}^{-1}) + \text{Int}(2860 \text{ cm}^{-1}) + \text{Int}(1630 \text{ cm}^{-1})} \quad (1)$$

and C factor is a quotient of the bands intensities: 1710 cm⁻¹ and sum of intensities of 1710 cm⁻¹ and 1630 cm⁻¹:

$$A = \frac{\text{Int}(1710 \text{ cm}^{-1})}{\text{Int}(1710 \text{ cm}^{-1}) + \text{Int}(1630 \text{ cm}^{-1})} \quad (2)$$

Their way of spectra analysis was used in other researches to describe the kerogen type with a combination of the results with thermogravimetric data on kerogen maturation kinetics on the oil shales of Beypazari in Turkey and Maroccan Timahdit shales [2]. Also Guo and Bustin applied it for oil shales assessment in 1998 [11].

FTIR-ATR results

The analytical bands for kerogen measurements by diamond ATR method are shifted into lower frequencies. So detailed bands assignment is necessary in order to perform further calculations. The bands assignments for analyzed spectra are listed in Table 1. The assignments for different analytical methods has also been presented.

was measured. Detailed results of this analysis were published separately in another paper [26] together with samples localizations presented on the map. The example of the analysis is presented in Figure 5 and Table 2. The results were used in order to confirm the composition of organic matter.

Table 1. Bands assignments according to literature and proposed for diamond FTIR-ATR technique

| Type of molecular group	Mastalerz [13], Dutta [7] (*Transmission technique and micro FTIR reflectance*)	Machnikowski [14] (*Diffuse reflectance*)	Proposed in the paper (*ATR technique on the diamond*)
C_{ar}-H	3000÷3100	3050	3030
CH_3 as		2950	2950
CH_2 asym	3000÷2800	2920	2912÷2918 Depending of the maceral composition
CH_3 sym		2870	2850
CH_2 sym			
Esters	1775÷1720	–	–
COOH	1700	1695	
C=O	1672÷1650	1660	1700÷1710
C=C	1600	1600	1598÷1620 Depending of the maceral composition
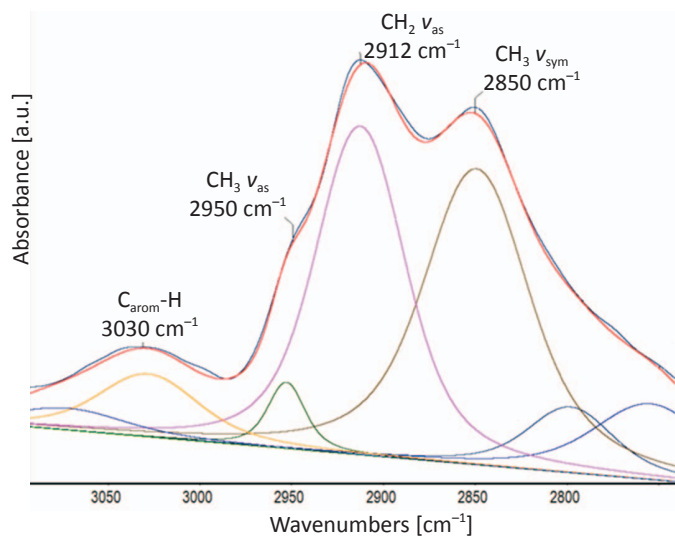
Fig. 3. High frequency bands deconvolution for kerogen spectrum

All spectra were corrected and the bands intensities were determined for each kerogen sample. The manner of bands intensities evaluation is illustrated in Figure 4.

From these values, the A and C parameters were calculated for all examined samples (Table 3, Figure 5 and 7).

All the samples were investigated with the use of microscopic methods (white reflected light, fluorescence mode). Maceral composition was described and vitrinite reflectance

The raw rock samples (mineral matrix together with kerogen) were also analyzed by the FTIR-ATR. The method was used before for mineral matrix analysis and it was published for clay rock samples investigation by Mroczkowska and Kowalska [16]. In the paper FTIR results were calibrated by X-ray diffraction technique.

The approach allowed to roughly distinguish the kerogen type in the samples analyzed by the FTIR-ATR method in some cases even without kerogen extraction. It appeared that it's possible mostly for kerogen types I and II. The assessment of kerogen type III presence in the rock, especially in its mature state is hardly reliable due to the low value of high frequency aliphatic bands in the spectra [22]. As an example of this investigation, spectrum for kerogen and row rocks were presented in Figure 6 and Figure 7.

Factors A and C were calculated and gathered in Table 3 for analysis performed on isolated kerogen samples. The results were also presented on the Figures 8 and 10. The kerogen type II and III on graph 8 was distinguished first on the basis of the Rock-Eval analysis (Figure 9). According to this result kerogen type III was marked by the red dots on Figure 8. It is visible that it's grouped on the bottom of the graph. For exact and reliable evolution paths evaluation in C versus A diagram (by FTIR-ATR technique) the analysis on a larger amount of samples must however be performed.
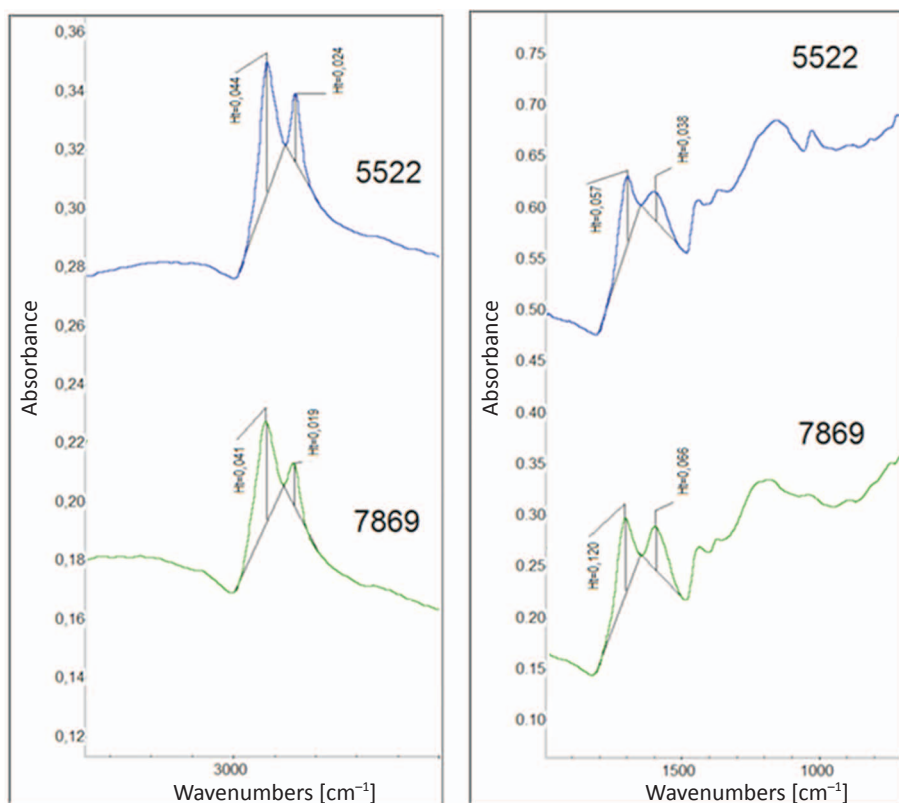
Fig. 4. Manner of bands intensity determination on the example of kerogen FTIR-ATR spectra of the samples: 7869, 5522

On the graph 10 we present the relation between factor A and C'. C' factor was proposed in this paper and for analyzed samples allows also for very good distinguishing between different types of organic matter. Mixed kerogen types were not presented on the graph.

The correlation between aliphatic groups presence (measured by their relative bands intensities) and the hydrogen index values, was also verified and presented in Figure 11. Correlation coefficient (Persons – r) for the results was around 0.84 for the analyzed group of samples, which means that the presence of CH_3 bands and their relative intensities may be valuable indicators for the organic matter type distinguishing, based on hydrogen index (HI) in the case of oil shales. This observation is consistent with previous results by Solomon and Miknis [21],

Table 2. The results of pathological and geochemical analysis for 5522 sample

Sample code	Rock-Eval parameters											Vitrinite reflectance R_o
	T_{max}	S_1	S_2	S_3	PI	PC	RC	TOC	HI	OI	total MINC	
5522	423	0.80	43.02	6.82	0.02	3.96	5.47	9.43	456	72	0.43	0.67

Lithology: menilite beds.
Petrological description: dark grey and dark brown, silicified and noncalcareous, clay reach shale, splitting into parts around 1 cm thick, with rusty signs of weathering.
Dominant kerogen component: algal derived amorphous organic matter (strong fluorescence).
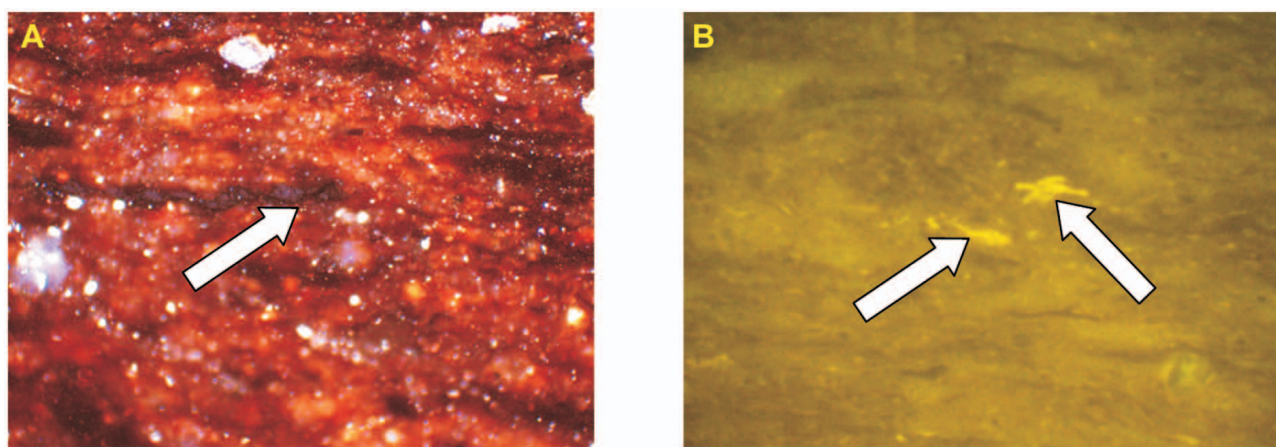Alginite: very common.
Vitrinite: frequent.

Fig. 5. Photomicrograph of sample 5522, A – reflected light – vitrinite is visible (marked by the arrow), B – the same sample in fluorescence mode – algainite is visible (marked by the arrows)

which means that the ATR method also shows reliable results and may be as adequate for this type of semi quantitative analysis as the transmission technique used previously by other authors.
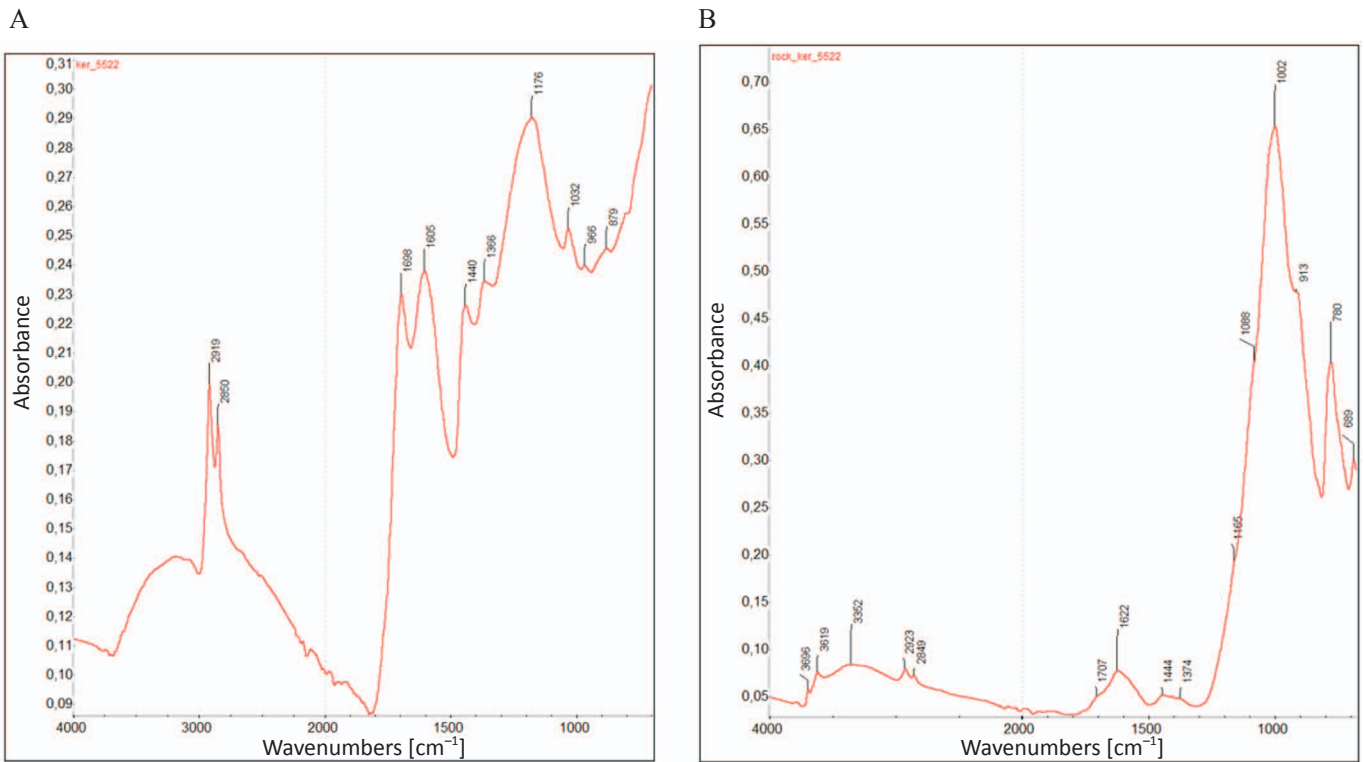
A

B

Fig. 6. FTIR-ATR spectra: A kerogen sample of extracted shale rock sample no 5522,
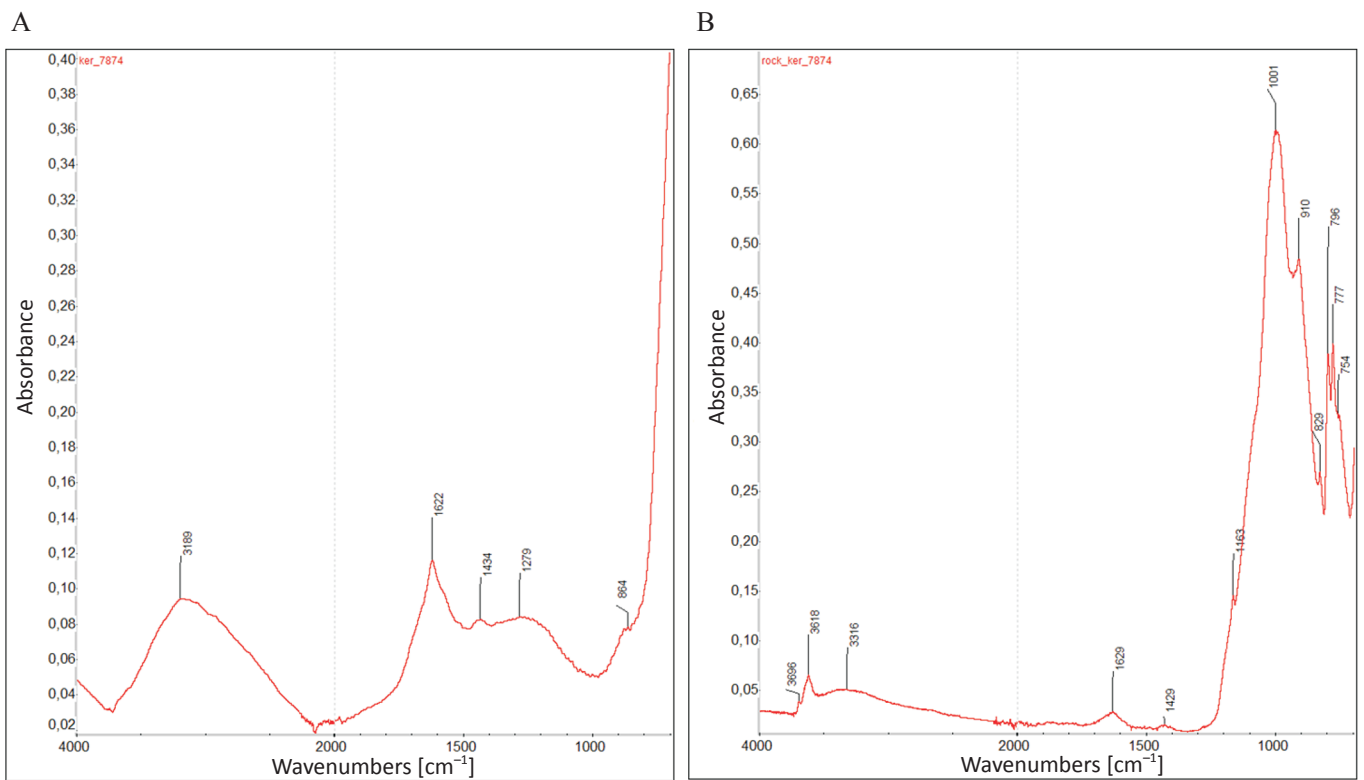B – spectrum of rock matrix together with kerogen. Sample represents type II kerogen

A

B

Fig. 7. FTIR-ATR spectra: A kerogen sample of extracted shale rock sample no 7874,
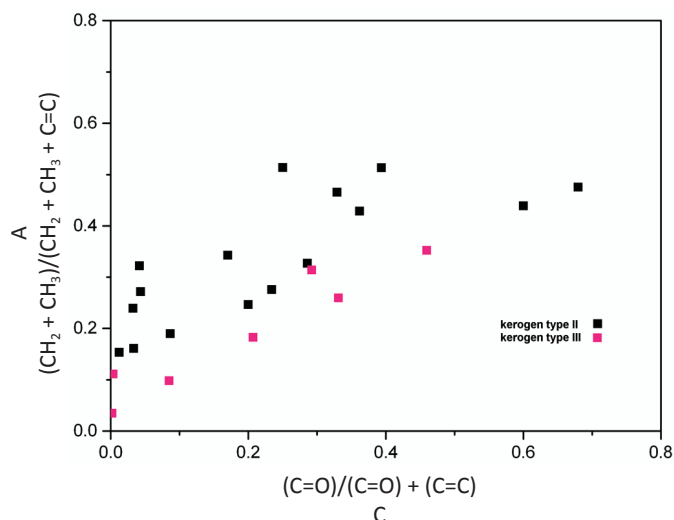B – spectrum of rock matrix together with kerogen. Sample represents type III kerogen

Fig. 8. Relations of the factors C and A calculated from bands intensities from FTIR-ATR analysis of extracted kerogen samples on the basis of Ganz and Kalkreuth paper [9] – kerogen types were analyzed by the Rock-Eval technique (from HI versus T_{max} diagram Fig. 9, Tab. 3)
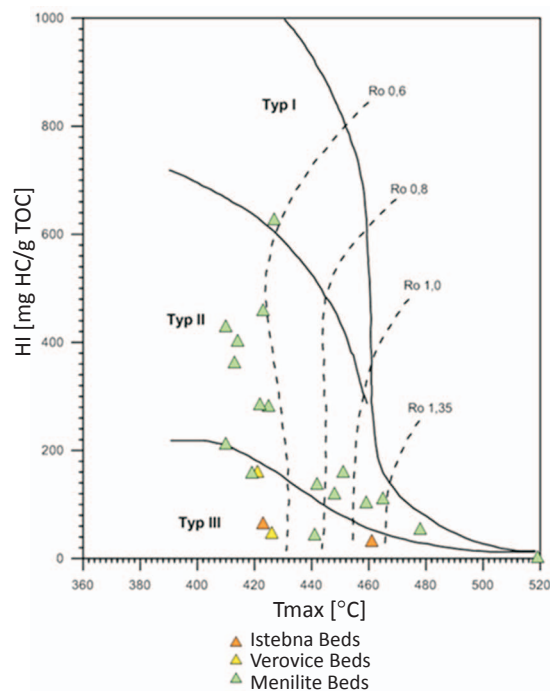

Fig. 9. HI versus T_{max} diagram results from the Rock-Eval analyses

Table 3. Spectroscopic results table with bands intensities and calculated factors presented with T_{max} and HI values from Rock-Eval method

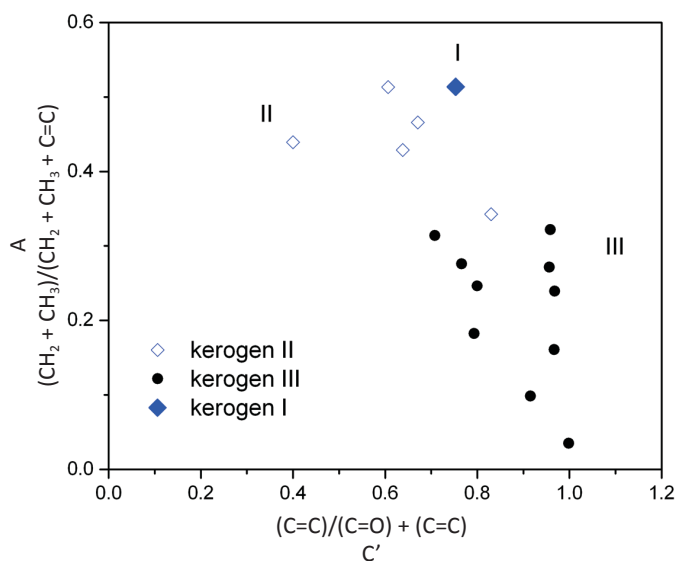| Sample code	Int C-H in CH_3 group 2912–2918 cm⁻¹	Int C-H in CH_2 group 2850 cm⁻¹	Int C=O 1710 cm⁻¹	Int C=C 1580–1620 cm⁻¹	Factor C' (C=C)/((C=O) + (C=C))	Factor C (C=O)/((C=O) + (C=C))	Factor A (CH_2+CH_3)/ $((CH_2)+(CH_3) +$ (C=C))	T_{max} [ºC]	HI
5517	0.034	0.019	0.017	0.030	0.638	0.362	0.429	410	427
5518	0.027	0.015	0.002	0.046	0.958	0.042	0.322	442	135
5519	0.033	0.014	0.026	0.063	0.708	0.292	0.314	400	65
5520	0.066	0.035	0.024	0.037	0.607	0.393	0.513	414	373
5521	0.048	0.027	0.034	0.085	0.714	0.286	0.327	410	209
5522	0.044	0.024	0.057	0.038	0.400	0.600	0.439	423	456
5523	0.018	0.015	0.011	0.036	0.766	0.234	0.276	465	109
5524	0.014	0.009	0.009	0.036	0.800	0.200	0.246	459	101
5525	0.050	0.029	0.070	0.033	0.320	0.680	0.475	425	280
5526	0.067	0.039	0.025	0.051	0.671	0.329	0.466	414	400
5527	0.051	0.028	0.017	0.083	0.830	0.170	0.343	413	360
5528	0.036	0.018	0.047	0.095	0.669	0.331	0.260	419	156
7864	0.004	0.001	0.000	0.027	0.996	0.004	0.111	451	158
7865	0.036	0.018	0.004	0.088	0.957	0.043	0.272	448	118
7866	0.021	0.011	0.002	0.060	0.968	0.032	0.239	441	41
7867	0.006	0.003	0.001	0.029	0.967	0.033	0.161	478	52
7868	0.098	0.056	0.020	0.060	0.750	0.250	0.514	427	625
7869	0.041	0.019	0.120	0.066	0.355	0.645	0.344	–	–
7875	0.023	0.010	0.009	0.095	0.913	0.087	0.190	422	283
7876	0.015	0.008	0.001	0.080	0.988	0.012	0.154	–	–
7871	0.033	0.019	0.040	0.047	0.540	0.460	0.352	421	158
7873	0.006	0.003	0.005	0.054	0.915	0.085	0.098	423	62
7874	0.011	0.005	0.012	0.046	0.793	0.207	0.182	461	29

Fig. 10. Relations of the modified factors C' and A calculated from bands intensities from FTIR-ATR analysis of extracted kerogen samples on the basis of Ganz and Kalkreuth paper [9], the samples of kerogen type assignment was based on Rock-Eval HI values
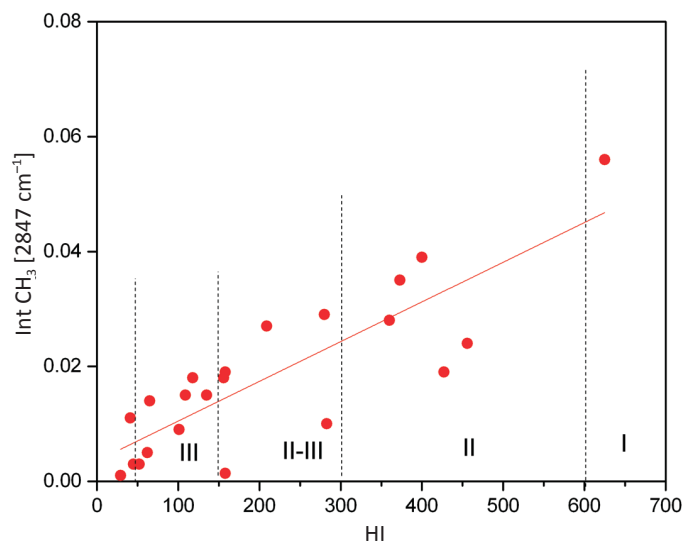

Fig. 11. Relation of CH_3 aliphatic groups bands intensities versus Hydrogen Index – linear dependence is confirmed by a relatively high Pearsons r coeficien $r = 0.84$ on the basis of the paper Landais et al. [12]

Summary/conclusion

1. A series of samples of various types of organic matter were examined by spectroscopic methods.

2. In addition, the samples were examined by the Rock-Eval and petrographic characterization for assessing qualitative composition of organic matter. This procedure allowed to verify spectroscopic results.

3. Based on literature reports the coefficients A, C and C' have been proposed to facilitate analysis and distinguish between the different types of organic matter by the FTIR technique.

4. Efficiency of organic matter analysis by the FTIR-ATR was confirmed by obtaining a correlation with indicators taken from commercial geochemical analyzes – Rock-Eval and FTIR-ATR results. Additional analyses on a larger number of samples is needed for the evaluation of the limits of application of methods.

5. The best correlation was obtained for CH_3 dependence of band intensities (FTIR-ATR method) versus hydrogen index HI (Rock-Eval method). Obtained value of the correlation coefficient (r-Pearson) was 0.84.

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