

FTIR SPECTROSCOPIC CHARACTERIZATION OF BITUMINOUS LIMESTONE: MAGANIK MOUNTAIN (MONTENEGRO)

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ABSTRACT. FTIR spectroscopy has been used to detailed study of bituminous limestone samples from two different locations at Maganik Mountain (Montenegro). Bituminous limestone at Maganik Mountain occurs as carbonate sediments in three levels and belongs to the early Cretaceous. Our specimens come from the oldest sediments of this limestone belonging to Barremian age. Particular attention has been given to investigation of isolated asphaltenes and kerogens. The FTIR technique provides fine determination of various organic and inorganic functional groups, as well as aliphatic and aromatic carbon and hydrogen. Due to the structural complexity of kerogens and asphaltenes, in this study we have done correlations of particular infrared absorptions to various functional groups. The asphaltenes of studied samples show higher contribution of aromatic structures than the kerogens. Notable differences in FTIR spectra of some samples that are reflected as shift of peak locations and a variety of intensities are attributed to eventual differences in the microbial precursors and/or depositional environments, conditions of sedimentation and/or genesis.

Keywords: FTIR analysis, kerogen, asphaltenes, Maganik Mountain

INTRODUCTION

The organic matter (OM) of bituminous limestone is composed mainly of two fractions – bitumen, the term assigned to soluble component (e.g. asphaltenes, resins, polar fraction) and kerogen, representing the insoluble component [1]. The solubility is here related to organic solvents.

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A careful study of the bituminous organic matter requires investigating the three main components: kerogen, bitumen, and mineral matrix [2]. Kerogens are complex, heterogeneous mixture of organic matter [3] produced primarily by geological processing of biologic materials [4]. They are classified into three types depending on its origin and maturity. Types I, II or III are associated to distinct depositional environments: lacustrine, marine, and continental, respectively [5-7]. These types display difference in the elemental composition, primarily in H/C and O/C ratios [8].

However, modern understanding of kerogen nature exceeds this way of classification [9]. On the other hand, asphaltenes are much smaller molecules compared to kerogens and represent fragments of kerogens structure. They are mostly composed of polycyclic-aromatic and naphthenic rings bonded by aliphatic chains and heteroatoms (N, O, and S). Due to the heterogeneity and complexity of kerogens, characterization of the structural functional groups can help understanding their nature and maturity. The asphaltenes of OM from bituminous limestone (locality Maganik) were also determined, because they exhibit close structural similarities to their precursors, kerogens [10, 11].

Fourier Transform Infrared spectroscopy (FTIR) is widespread used tool for molecular structure identification of the geological organic constituents. This technique provides fine determination of various organic and inorganic functional groups, as well as aliphatic and aromatic carbon and hydrogen. Due to the structural complexity of kerogens and asphaltens, in this study we have done correlations of particular infrared absorptions to various functional groups.

Geological setting and sampling

The specimens were sampled from geological section of Barremian age, occurring in the south-western flank of the Maganik Mountain. Maganik, 20 km long and 10 km wide mountain range is placed in the middle part of Montenegro, among the rivers of Zeta, Morača and Mrtica (Fig. 1). This massif represents a group of limestone formations of Cretaceous period. The base of this mountain massif from the side of the city of Nikšić and the Morača River valley is made up of Triassic limestone. Bituminous limestone at Maganik Mountain occurs as carbonate sediments in three levels and belongs to the early Cretaceous. Our specimens come from the oldest sediments of this limestone belonging to Barremian age.

The layers of bituminous limestone of Barremian age are thick, usually from 0.1 to 0.3 m, rarely up to 0.8 m. They are dark brown-to-black, depending on the proportion of bitumen, break with irregular fracture and always smell on bitumen when cracked with hammer. Basically, these rocks are of carbonate composition, but some layers contain ingredients of detrital aluminosilicate rocks (mostly clays). The bitumen is manifested as completely

impregnated in the layer of limestone, but of varying intensity in the same layer, as well as in all the layers that make up this formation. The texture of the limestone formation is laminated and striped.

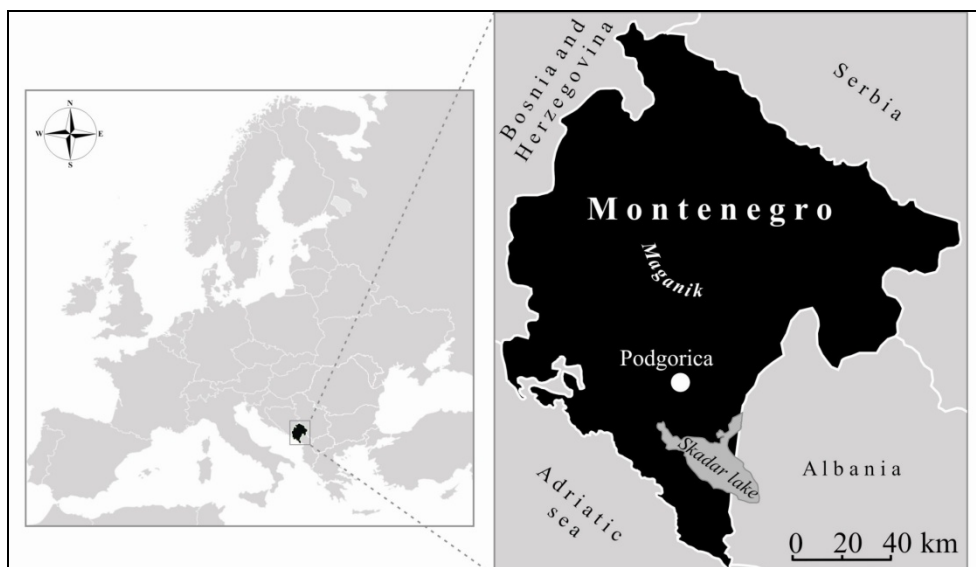


Figure 1. Geographical map of Maganik Mountain

The ESR spectroscopic investigation of vanadyl ions incorporated into the structure of kerogens from this locality has been performed by Premović et al. [12]. However, no comprehensive studies on the quantitative characteristics of the bituminous limestone and the qualitative characteristics of the isolated asphaltenes and kerogens were available to date.

In this study have been analyzed four samples (132, 425, 3149 and 3150) from the Maganik Mountain. Three of them (132, 3149, and 3150), have been collected from the locality Rekočica (altitude ca. 1550 m), and the fourth sample (425) has been collected from the locality Tuvrtina greda (altitude ca. 1530 m).

RESULTS AND DISCUSSION

Bituminous limestone samples 3150 and 425 contain relatively little OM (0.6 % and 2.5 %, respectively), sample 3149 has medium content of OM (17 %), whereas the sample 132 shows relatively high content of OM (54 %, Table I). Comparison of results of OM fractions represents that kerogen made 50-87 % of total OM in investigated samples. Kerogen concentration in the sedimentary rocks is considered to be reflection of the organic productivity

as well as the general sedimentation pattern during geological period of formation and diagenesis [1]. Asphaltenes are presented in range of 0.1 % (sample 3150) to 6.0 % (sample 132).

Table I. Fractional analysis of samples [± 5 wt%]

	Samples			
	132	425	3149	3150
Cold HCl	32.0	96.0	79.0	99.0
Hot HCl	2.0	0.5	1.0	0.1
HF/HCl	12.0	1.0	3.0	0.3
<i>Total of inorganic matter</i>	<i>46.0</i>	<i>97.5</i>	<i>83.0</i>	<i>99.4</i>
Polar fraction	0.5	0.1	0.5	0.1
Resin	0.5	0.1	1.0	0.1
Asphaltene	6.0	0.3	1.5	0.1
Kerogen	47.0	2.0	14.0	0.3
<i>Total of organic matter</i>	<i>54.0</i>	<i>2.5</i>	<i>17.0</i>	<i>0.6</i>

Comparing the FTIR spectra of the samples 425, 3149 and 3150 (Fig. 2) the dominance of inorganic fraction bands towards organic fraction bands is obvious, contrary to FTIR spectrum of sample 132, where organic fraction bands are significant. These results are in accordance with results of the fractional analysis.

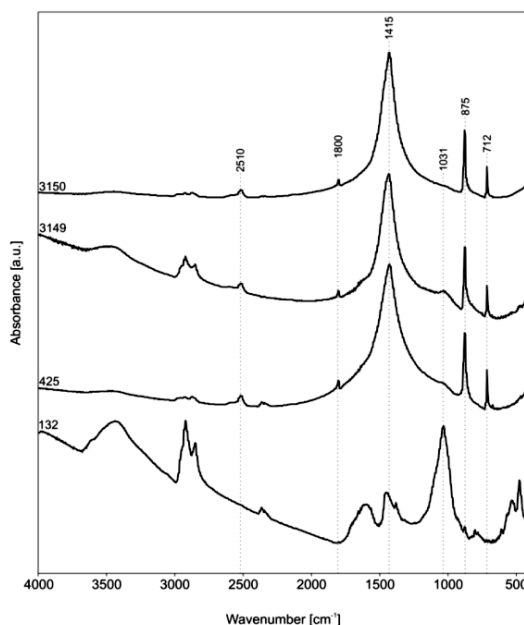


Figure 2. FTIR spectra of untreated samples 132, 425, 3149, and 3150

The FTIR spectra of the samples 425, 3149 and 3150 featured the following bands at: 2500, 1800, 1415, 875 and 712 cm^{-1} characteristic for carbonate minerals, precisely for calcite with minor aragonite [13]. These bands are absent in the FTIR spectrum of sample 132 indicating the inorganic fraction is, probably, composed mainly of silicate and aluminosilicate minerals.

Significant differences are evident in the relative intensity of the peak at 1031 cm^{-1} . This absorption is the most intense in the sample 3149 (if neglected sample 142), then in the sample 425, and at least in sample 3150. This is in accordance to analytical data of inorganic matter where the carbonate fraction (cold HCl soluble fraction) is the most existing in samples 3150, 425 and 3149, with 99 %, 96 % and 79 % of carbonate, respectively.

It should be mentioned that in the FTIR spectrum of sample 132 the bands of carbonate minerals are comparatively weak due to presence of intensive bands corresponding to silicate and aluminosilicate minerals, although there is higher account of the carbonate fraction (32 %) than of the silicate fraction (12 %).

FTIR spectra after treatment with (cold and hot) HCl

In the FTIR spectra of all the samples treated with cold/hot HCl featured the common bands, corresponding to the inorganic minerals, at: 3623, 1095, 1030, 920, 789, 777, 527, 470 and 417 cm^{-1} [13]. In Figure 3 are featured the FTIR spectra of the residues after treatment with cold/hot HCl, in the fingerprint region (1400-400 cm^{-1}), since the peak at 3623 cm^{-1} is not spectral interesting.

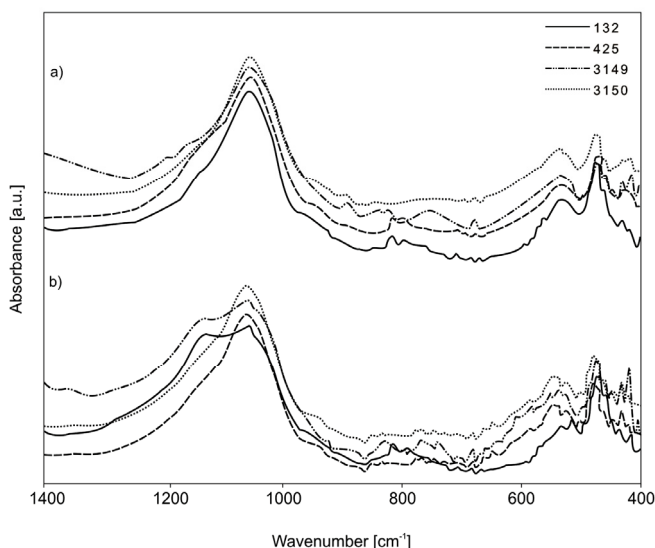


Figure 3. FTIR spectra of the studied samples in 1400-400 cm^{-1} region:
a) after treatment with cold HCl; b) after treatment with hot HCl

It is almost impossible unambiguously determinate minerals responsible for above mentioned bands, because they are insufficiently separated. Although, it could be claimed that these absorptions probably correspond to the following silicate/aluminosilicate minerals: montmorillonite, illite, secondary aluminous chlorite, interstratified montmorillonite/illite, interstratified montmorillonite/chlorite, cristobalite, and quartz. We believe that dominant species are secondary aluminous chlorite, interstratified montmorillonite/illite, and interstratified montmorillonite/chlorite. Quartz is presented in the traces. Our further studies will be performed in aim to get a more precise answer about nature of presented inorganic minerals.

Comparing the spectra of the residues after cold HCl treatment to those treated with hot HCl, the latter show neglected differences, primarily due to removal of less soluble carbonates and easily soluble silicate/aluminosilicate minerals. This difference is the most obvious in the spectra of the samples 132 and 3149 which is expected due to these samples have higher contribution of hot HCl soluble fraction, 2 % and 1 %, respectively.

Chemical characterization of asphaltenes

The FTIR spectra of carbonate isolated asphaltenes from all studied samples are presented at Fig. 4a. It can be seen that IR spectra show a combination of aliphatic and aromatic structures. The aliphaticity is presented by the intense bands in the regions between $2970\text{--}2850\text{ cm}^{-1}$ and $1455\text{--}1350\text{ cm}^{-1}$ [14]. The aromatic groups are indicated by the stretching vibrations at 3050 cm^{-1} and deformation vibrations between 900 and 700 cm^{-1} .

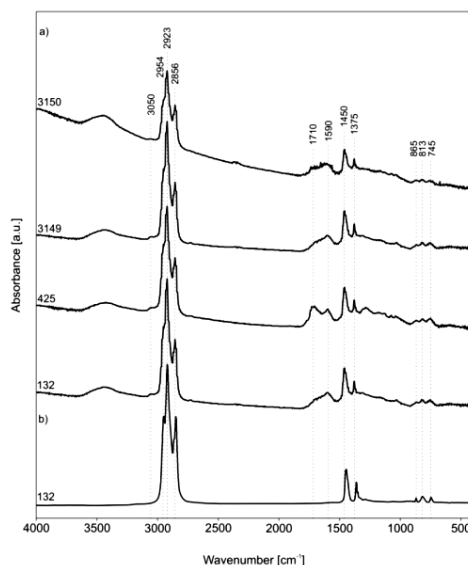


Figure 4. FTIR spectra of asphaltenes of studied samples
a) KBr pellets method, b) in Nujol

The absorption at 1710 cm^{-1} , observing in all samples spectra is assigned to stretching of carbonyl groups mainly occurring as free carbonyl-group, not as part of carboxyl-group, due to the absence of --OH band in the $3600\text{--}2500\text{ cm}^{-1}$ region (the broad band around 3300 cm^{-1} originated from moisture, what was confirmed by FTIR spectra of samples dispersed in Nujol as matrix, Fig. 4b). More intense band at 1710 cm^{-1} in the spectra of sample 425 in comparison to spectra of samples 132, 3149 and 3150 could be a sign of higher contribution of oxygen, and as follows the pronounced aromaticity of this asphaltene and its lower degree of evolution [15].

The presence of polyaromatic groups in the structures of all four samples is indicated by weak bands at 3050 , 865 , 813 and 745 cm^{-1} (Table II). The shoulder appearing in the domain 1700 and 1600 cm^{-1} corresponds to olefinic or aromatic ring $\text{C}=\text{C}$ stretching and is hard to observe it in the spectra due to the overlapping with deformation absorption of water, and $\text{C}=\text{O}$ vibration of aromatic quinines [14, 15].

Table II. Characteristic band assignments

Wavenumber (cm^{-1})	Assignment
3400	hydroxyl, OH^- stretching
3080-3000	aromatic C-H bonds
2956	asymmetric CH_3 stretching
2925	asymmetric C-H stretching of methylene group
2872	symmetric CH_3 stretching
2850	symmetric C-H stretching of methylene group
1745-1680	carbonyl $\text{C}=\text{O}$ stretching
	$\text{C}=\text{C}$ bonds, H_2O deformation, aromatic ring
1650-1580	stretching
1520-1500	aromatic rings
1450	asymmetric CH_2 and CH_3 bending
1380-1370	CH_3 and cyclic CH_2 vibrations
1250	phenolic C-O bond
1050	C-O bonds of alcohols
980-890	$\text{C}=\text{C}$ bonds
900-700	aromatic out-of-plane deformation
725-720	aliphatic chains longer than C_4

In our spectra this shoulder is shifted to 1590 cm^{-1} and represents the sum of the bands originated from $\text{C}=\text{C}$ stretching vibrations of polyaromatic structures, bending vibrations of molecular water and unsaturated hydrocarbons chains. This shift to lower frequencies could be the sight of higher level of maturity [15, 16].

As crucial for understanding the asphaltenes is the nature of their aliphatic and aromatic structures, the attention is paid to the absorptions that can provide information about these structures.

The analysis of aliphatic bands in the 3000-2800 cm^{-1} region

It was necessary to apply deconvolution in this region, because it helps to determine position, width and areas of each band (Fig. 5). The aliphatic bands in the 3000-2800 cm^{-1} region actually represent a sum of the following mutually overlapped single bands:

- asymmetric stretching of $-\text{CH}_3$ located at 2954 cm^{-1} ;
- asymmetric stretching of $-\text{CH}_2-$ located at 2923 cm^{-1} ;
- stretching of CH located at 2900 cm^{-1} ;
- symmetric stretching of $-\text{CH}_3$ located at 2870 cm^{-1} ;
- asymmetric stretching of $-\text{CH}_2-$ located at 2856 cm^{-1} .

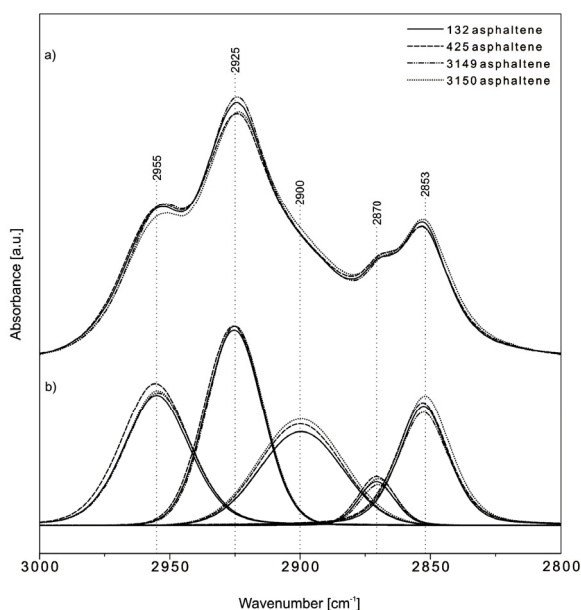


Figure 5. Deconvolution of region from 3000 to 2800 cm^{-1} ;
a) original spectra, b) deconvolution bands

The spectra show no differences in the peak positions, but only in their intensities. For interpreting the nature of the aliphatic structure is essential knowledge of the relationship between the methyl ($-\text{CH}_3$) and methylene ($-\text{CH}_2-$) groups which absorbed at 2955 cm^{-1} and 2925 cm^{-1} , respectively. The methyl/methylene bands ratio of the FTIR spectra were studied by curve-fitting analysis.

The ratio of these bands (I_{2955}/I_{2925}) gives an approximate picture of the aliphatic-chain length of hydrocarbons and the degree of branching of these structures [17, 18]. If this ratio has lower value the structure is dominated by long, straight aliphatic groups. The higher ratio values indicate existence of shorter and more branched aliphatic-chains. Increasing of this ratio is in accord to the decreasing of the H/C ratio which acts as a parameter of maturation, implying higher degree of maturation.

The analysis of aromatic bands in the 900-700 cm^{-1} region

In this region are occurring three bending aromatic bands at 865 cm^{-1} (corresponding to aromatic structures with isolated aromatic hydrogen), 813 cm^{-1} and 745 cm^{-1} , with two and four vicinal hydrogen atoms per cycle, respectively (Fig. 6) [19]. The number of vicinal aromatic hydrogen atoms per cycle could indicate the degrees of substitution and aromatic structure condensation. The intense band at 865 cm^{-1} accounts for the higher degrees of substitution and condensation, while weak bands at 815 cm^{-1} , and especially at 745 cm^{-1} show reversely. The spectra given in the Fig. 6 show no differences except in intensities of bands, and based on relative intensities of observed bands sample 3150 shows the highest degrees of substitution and condensation, followed by samples 3149, 425, and 132.

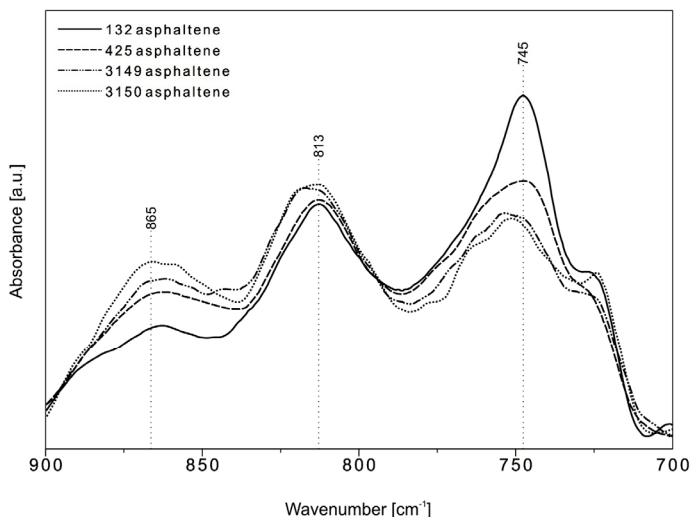


Figure 6. Enlarged FTIR spectra of asphaltenes of the studied samples in 900-700 cm^{-1} region.

In all spectra is presented comparative weak band around 720 cm^{-1} indicating low content of long aliphatic chains (with more than 4 methylene groups) in molecular structures of asphaltenes.

Chemical characterization of kerogens

The intense bands in the $2960\text{--}2850\text{ cm}^{-1}$ and $1455\text{--}1350\text{ cm}^{-1}$ regions are related to pronounced aliphatic structures into the kerogens of all four studied samples (Fig. 7). Also, the band at 1710 cm^{-1} corresponding to the carbonyl-group is presented in all spectra. This group is assigned mainly to free carbonyl-groups, out of carboxyl-group, due to the absence of --OH band in the $3600\text{--}2500\text{ cm}^{-1}$ region (as mentioned for asphaltenes, the observed broad band at about 3300 cm^{-1} originated from moisture, confirmed by FTIR spectra of kerogen dispersed in Nujol as matrix, Fig. 7b).

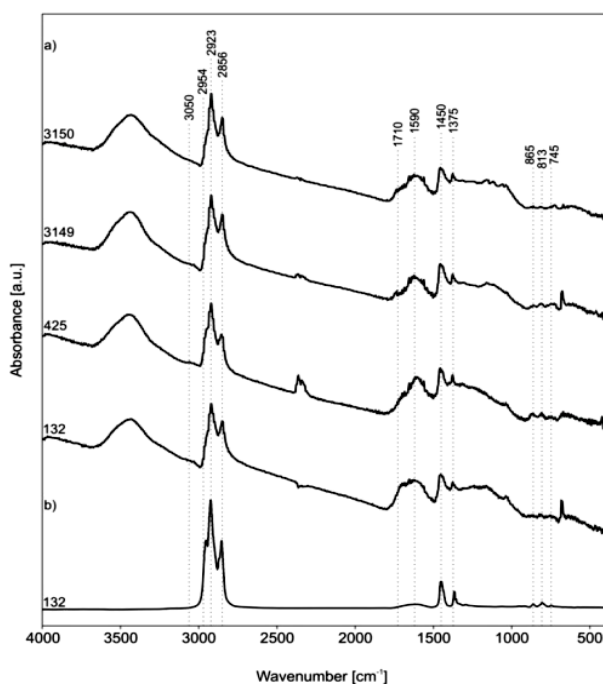


Figure 7. FTIR spectra of kerogens of studied samples
a) KBr pellets method, b) in Nujol

The presence of polyaromatic groups in the structures of all four samples is indicated by almost absent absorption at 3050 cm^{-1} and weak bands at 865 , 813 and 745 cm^{-1} . The band at 1590 cm^{-1} is result of overlapping the bands associated to: $\text{C}=\text{C}$ stretching vibrations of polyaromatic structures, bending vibrations of molecular water and unsaturated hydrocarbons chains. The knowledge of nature of aliphatic and aromatic structures of kerogens is crucial for their understanding, so our attention was paid to corresponding absorptions in the $3000\text{--}2800\text{ cm}^{-1}$ and $900\text{--}700\text{ cm}^{-1}$ regions.

The analysis of aliphatic bands in the 3000-2800 cm^{-1} region

The absorptions in the 3000-2800 cm^{-1} region assigned to aliphatic structures are result of composited, mutually overlapped bands (above mentioned, in section about asphaltenes) with presence of one more peak at 2833 cm^{-1} of unknown origin (Fig. 8).

The main differences in FTIR spectra of individual samples are the intensities of asymmetric stretching absorptions of methyl and methylene groups and symmetric stretching absorption of methylene group, resulting comparative high value for methyl/methylene ratio for sample 425 and low value of this ratio for sample 3150 (Fig. 9). This suggests that sample 425 is the most evolved cause methyl/methylene ratio tends to have higher value for kerogens with lower hydrogen content characteristic for the species of higher degree of maturity.

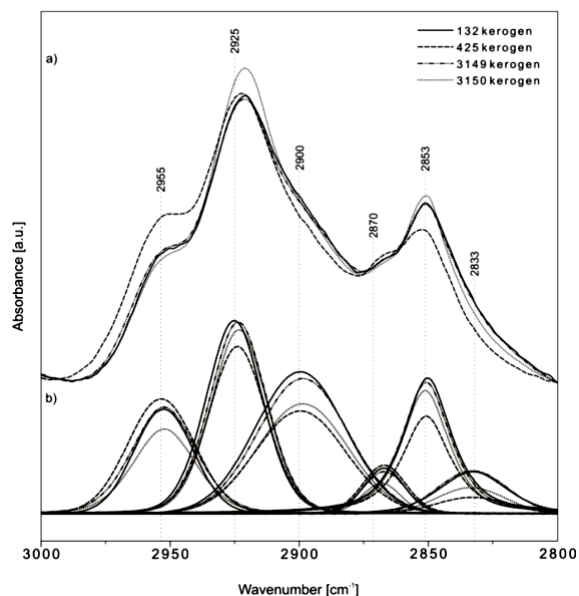


Figure 8. Deconvolution of region from 3000 to 2800 cm^{-1} ;
a) original spectra, b) deconvolution bands.

The methyl/methylene bands ratio, as well as for asphaltenes, shows lower value for the structure dominated by longer and straight aliphatic-chains, and higher values indicating dominating short and more branched aliphatic groups [17, 20, 21] in kerogen structure (Fig. 9). This ratio shows higher values for extracted asphaltenes indicating presence of shorter and more branched aliphatic structures, which is in correlation with the definition of these substances. However, one can observe that asphaltenes originating from kerogens give FTIR spectra similar to kerogens.

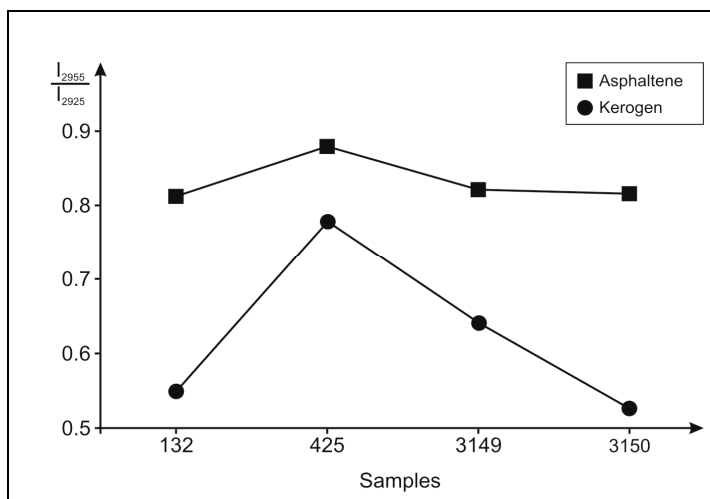


Figure 9. The I_{2955}/I_{2925} ratio for asphaltenes and kerogens of studied samples

The analysis of aromatic bands in the 900-700 cm^{-1} region

The differences in the peak positions, as well as in band intensities characterize the FTIR spectra of isolated kerogens in 900-700 cm^{-1} region (Fig. 10).

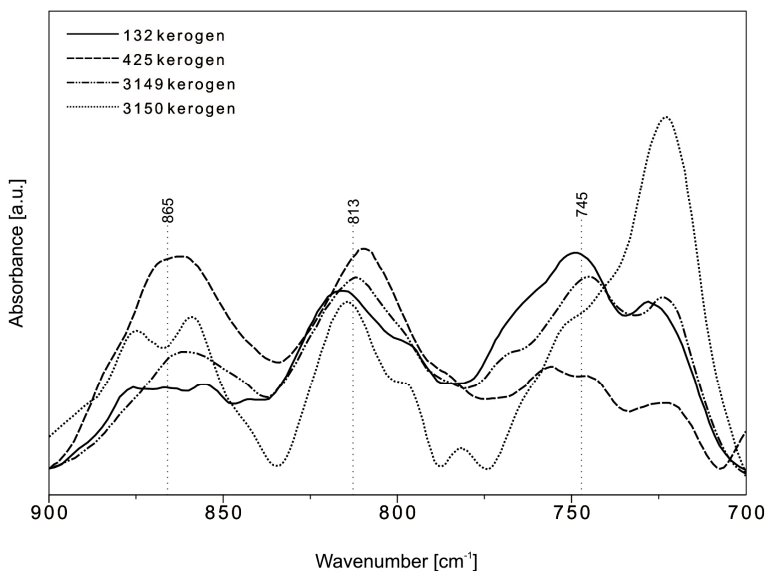


Figure 10. FTIR spectra of kerogens of the studied samples in 900-700 cm^{-1} region.

Bands that correspond to the aromatic out-of-plane deformation vibrations appear around 865, 813 and 745 cm^{-1} . In accordance with discussion for asphaltenes, the intense band at 865 cm^{-1} accounts for the higher degrees of substitution and condensation, while weak bands at 815 cm^{-1} , and especially at 745 cm^{-1} mean opposite. The sample 425 shows the highest degrees of substitution and condensation of aromatic structures, followed by samples 3149, 3150, and 132. It could be due to differences in the geological conditions of kerogen formation of sample 425. The FTIR spectrum of sample 3150 in this domain contains an intense band around 720 cm^{-1} due to CH_2 rocking vibrations in long chain aliphatic substances with more than 4 methylene groups, indicating high contribution of long, straight aliphatic-chains within kerogen structure.

Notable differences in FTIR spectra of samples 132 and 3150, such as peak locations and band intensities are attributed to eventual differences in the microbial precursors and/or depositional environments, conditions of sedimentation and/or genesis.

CONCLUSIONS

Successively dissolution and FTIR analysis show that the studied samples are mainly composed of inorganic matter (calcite with minor silicate and aluminosilicate minerals), except sample 132 that shows significant content of organic matter. Due to the FTIR spectra of untreated samples do not give useful information about the structures of organic matter because of interferences with the carbonate functional groups, extraction of asphaltene and kerogens have to be performed. According to the results of FTIR analysis of carbonate isolated organic matter, it may be concluded:

- The asphaltenes of studied samples show higher contribution of aromatic structures than the kerogens, and methyl/methylene ratio indicates existing shorter and more branched aliphatic-chains within the structures.
- The FTIR analyses of studied kerogens show very low aromaticity with aliphatic stretching vibrations in the 3000-2800 cm^{-1} as the most significant bands. The methyl/methylene ratio for kerogens, contrary to asphaltenes indicates higher contribution of longer and straight aliphatic-chains.

Notable differences in FTIR spectra of some samples that are reflected as shift of peak locations and a variety of intensities are attributed to eventual differences in the microbial precursors and/or depositional environments, conditions of sedimentation and/or genesis.

EXPERIMENTAL SECTION

Analysis and fractionation

Pre-treatment

Before extraction and treatment with mineral acids, the samples were grinded in a vibrating mill to particle size of 100 μm . To extract OM from source carbonate-bearing rocks, we followed the method of isolation by successively treating with HCl and HF [7, 22, 23] due to the presence of carbonates and clay minerals.

Demineralization of inorganic fractions

Ground samples of bituminous limestones were successively digested with appropriated mineral acids in order to remove carbonates and silicates. Dilution in HCl (6 M) at room temperature during 12 h was performed to remove most of the carbonates. The residues were then diluted in 6 M solution of HCl at 80 °C for 12 h for removing soluble silicates and less soluble carbonates and oxides. Insoluble residue after HCl-treatment was subjected to dissolution in mixture of (22 M) HF and (12 M) HCl (3:1, v/v) heated in a teflon glass at 80 °C. This mixture was used for removal of silicate minerals and silica.

Extraction of soluble OM

The separation of extractable OM from the insoluble residue after consecutive demineralization was performed in Soxhlet apparatus following the sketched fractionation procedure (Fig. 11).

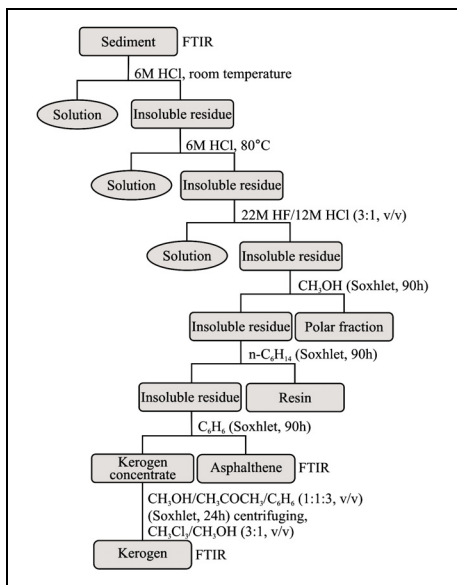


Figure 11. Flow chart of the fractionation procedure

The polar fraction was obtained from dried, finely powdered samples with methanol refluxing (Soxhlet) for 90 hours. The subsequent step was performed with n-hexane giving the resin fraction, and finally the asphaltene fraction was extracted with benzene. After solvent evaporation we get solid phase hereafter referred to as asphaltene.

Extraction of kerogen

In order to obtain the "cleaner" kerogen, the insoluble residue obtained after removal of the soluble fractions was extracted in Soxhlet apparatus with mixture of methanol/acetone/benzene (1:1:3, v/v) for 24 h. Also, the kerogen concentrate was subjected to centrifugation in the mixture of chloroform/methanol (3:1, v/v) in purpose to remove coarse pyrite and other HF/HCl insoluble minerals, as well as neoformed fluorides [24].

Fourier Transform Infrared (FTIR) Spectrometry

FTIR spectra were recorded, in absorbance mode, with a BOMEM Michelson Series MB FTIR spectrometer set to give undeformed spectra. Spectra were collected at room temperature, over the range of 4000-400 cm^{-1} with a spectral resolution of 4 cm^{-1} . 1.5 mg of a sample was ground with 150 mg of analytical quality KBr in a vibrating mill and sintered into a disk in a hydraulic press to obtain KBr pellets.

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