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Chemical, petrographic and thermoanalytical characterization of two Northbohemian low rank coals

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Abstract

Two low rank coal samples from Northbohemian region (Czech Republic) were studied using methods of chemical analysis, petrographic analysis and thermal analysis coupled with mass spectrometry. The results of thermal analysis are compared with the mass spectrometry results. The low rank coals were characterized from the viewpoint of their use as fossil fuel in power stations as well as raw materials for the chemical industry.

Keywords: Thermal analysis/mass spectrometry; DTA; Coal; Characterization; Fossil fuel

1. Introduction

The ecological problem of evolution of sulfur dioxide into the atmosphere during burning of low rank coals in power stations is well known all over the world. Lignites in the Northbohemian region (Sokolov basin) have been used as fossil fuel in the power stations of this region; this represents a serious source of environmental pollution.

In addition, taking into account the potential use of the lignites as raw materials in the chemical industry of Czech Republic, it has been suggested that the use of lignite as a fossil fuel in the power stations should be limited, with preference given to its use as a raw material for the chemical industry .

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In this paper the results of the investigation of two Northbohemian low rank coals are presented. The objective is to present chemical, petrographical and thermoanalytical low rank coal characteristics, useful for the decision makers.

2. Experimental

2.1. Methods of determining chemical characteristics

The basic chemical characteristics of brown coal samples include information obtained from proximate analyses, sulfur forms analyses and ultimate (elementary) analyses. International and Czech standards were used for determination of the proximate and ultimate analyses of the samples investigated.

The proximate analysis of coal samples is given in the following terms:

- (a) Moisture content, Czech standard CSN 44 1377
 - W_t^r , the bed-moisture content was measured by air-drying the equilibrated sample after weighing to constant mass at 30°C
 - W_a , the moisture in the analyzed sample (fine particle size <0.2 mm) was measured by drying at 110°C
- (b) Ash yield
 - A^d , the ash yield of coal is traditionally measured after the combustion of dry coal in a muffle furnace pre-heated to 815°C (Czech standard CSN 44 1378)
- (c) Calorific value, Czech standard CSN 44 1352
 - Q_s^{daf} , calorific value (MJ/kg) of the dry, ash free sample
- (d) Volatile matter content: Czech standard CSN 44 1351
 - V^{daf} , the volatile matter is determined by heating of coal, out contact with air, in a muffle furnace at 900°C

Sulfur and sulfur forms analyses, Czech standards CSN 44 1370 and CSN 44 1379:

- S_t^d , total sulfur in dry coal is determined by the Eshka method
- $S_{SO_4^d}$, sulfate sulfur in dry coal
- S_p^d , pyrite sulfur in dry coal

Ultimate analysis of coal comprises the determination of the carbon (C^{daf}), hydrogen (H^{daf}), nitrogen (N^{daf}), sulfur (S_O^{daf}) and oxygen (O^{daf}) contents of organic coal substance. The first four elements are determined directly (Czech standards CSN 44 1355 and CSN 44 1356). Oxygen is usually estimated by difference.

2.2. Methods of petrographic characteristics

Qualitative and quantitative microscopic maceral analyses were carried out in normal white light and under ultraviolet excitation (HBO lamp and FI 09 filters, reflector) on a polished section of the samples. For the petrographic analysis a reflected light microscope-microphotometer UMSP 30 Petro (Opton-Zeiss) equipped with oil immersion objective lens (40×) was used. The coals were prepared for microscopic analysis according to the ISO Standard 7404 and CZ standard CSN 44 1344, to prepare an epoxy-bound crushed coal pellet with one polished surface. Maceral composition was determined by

the procedures of Stach et al. [1] and CZ standards (CSN 44 1343), with 1000 points counted per sample. The degree of coalification of low rank coal samples was determined by measuring the huminite reflectance. The light reflectance (mean reflectance) was measured according to standards ISO 7404 and CSN 44 1343 on homogenous surfaces of huminite macerals at the wavelength of 546 nm with immersion objective (magnification 40×) and in oil immersion ($n = 1.518$).

2.3. *Methods of thermal analyses*

A simultaneous DTA/TG/mass spectrometry system NETZSCH STA 429 coupled with Balzers QMG 420 quadrupole spectrometer was used for thermoanalytical characterization of the coal samples. The sample mass was ca. 50 mg. The samples were heated in an argon atmosphere from ambient temperature up to 1200°C, applying a heating rate of 5 K min⁻¹. Through a special interface system, the gases released from the sample were introduced into the mass spectrometer for the simultaneous recording of the MS spectra (every 20 K). The high vacuum pressure was adjusted to 10⁻³ Pa, being controlled automatically during the measurement.

3. Results and discussion

The Sokolov basin is second in importance among the brown coal mining areas in the Czech Republic. Low rank coal from the Sokolov basin is a source of energy (briquetting, combustion, gassification). Brown coal from the Sokolov basin is also a suitable feedstock for chemical processing [2].

3.1. *Chemical characterization*

Chemical composition of brown coal expressed by determination of moisture, ash content, total sulfur and sulfur forms content and elementary analysis (C, H, N, S, O) is given in Table 1; the basic characteristics of calorific value and amount of volatile matter are also included.

Bed-moisture content, calorific value and carbon content are good indicators of the degree of coalification in brown coal. Both samples are low rank coal of equal degree of coalification. The differences in values of chemical parameters (Table 1) are given by the higher content ($A^d = 14.09\%–31.17\%$) and composition of mineral matter. Clay minerals, carbonate and low content of sulfate and sulfide are predominantly finely dispersed in the coal matter of sample from locality Druzba. A higher content of total sulfur ($S_t^d = 3.28\%$), organic sulfur ($S_o^{daf} = 2.97\%$) and inorganic sulfur forms ($S_p^d = 1.25\%$, $S_{SO_4^d} = 0.70\%$) was found in the sample from the Jiri locality. It was found microscopically that the most frequent mineral component are the framboids and euhedral crystals of Fe disulfide dispersed in coal matter (Jiri). Massive syngenetic Fe disulfides are less frequent.

Table 1

Results of proximate analyses, sulfur forms and ultimate analyses of the low rank coal samples

Parameter		Locality	
		Jiri JP 5/91	Druzba 80/211
<i>Proximate analyses</i>			
Bed moisture content	$W^s/\%$	40.01	43.3
Moisture content of sample	$W^a/\%$	25.20	11.03
Ash yield	$A^d/\%$	14.09	31.17
Calorific value	$Q_{sd}^{daf}/\text{MJ kg}^{-1}$	29.44	26.93
Volatile matter content	$V^{daf}/\%$	49.86	52.27
<i>Sulfur form analyses</i>			
Content of total sulfur	$S_t^d/\%$	3.28	1.08
Content of sulfate sulfur	$S_{SO_4}/\%$	0.70	0.27
Content of pyrite sulfur	$S_p/\%$	1.25	0.19
<i>Ultimate analyses</i>			
Carbon content	$C^{daf}/\%$	70.79	67.16
Hydrogen content	$H^{daf}/\%$	5.21	5.53
Nitrogen content	$N^{daf}/\%$	1.00	0.95
Organic sulfur content	$S_{od}^{af}/\%$	2.97	0.90
Oxygen content	$O^{daf}/\%$	20.03	25.46

The methods of determination of above parameters are described in Section 2.

3.2. Petrographic characterization

The determination of the petrographic composition of the coal is based on morphological and optical properties of coal microcomponents (macerals, clay minerals, carbonates, sulfides, sulfates, quartz) and their distribution. Huminite, liptinite and inertinite are the main maceral groups of brown coals. The microphotographs illustrating the petrographic characteristics of the coal samples investigated are shown in Figs. 1–5. The results of the petrographic analysis are summarized in Table 2.

From a technological viewpoint, huminite is from the most common and the most important macerals group. It originates from plants material, and can be subdivided into various huminite macerals (attrinite, densinite, textinite, ulminite, gelinite, korpo-huminite). The huminite macerals differ in degree of gelification.

The inertinite group consists of highly reflective plant material which is relatively inert. Its content in Middle European brown coals is below 10% [3].

The liptinite group consists of material which is fluorescent under blue light. This group consists of nine macerals, including those derived from spores, pollen, cuticle and resin. An increased liptinite content leads to higher values of hydrogen, carbon, volatile matter, and calorific value. The huminite and liptinite macerals are reactive upon coal combustion, carbonization and processing as could [4].

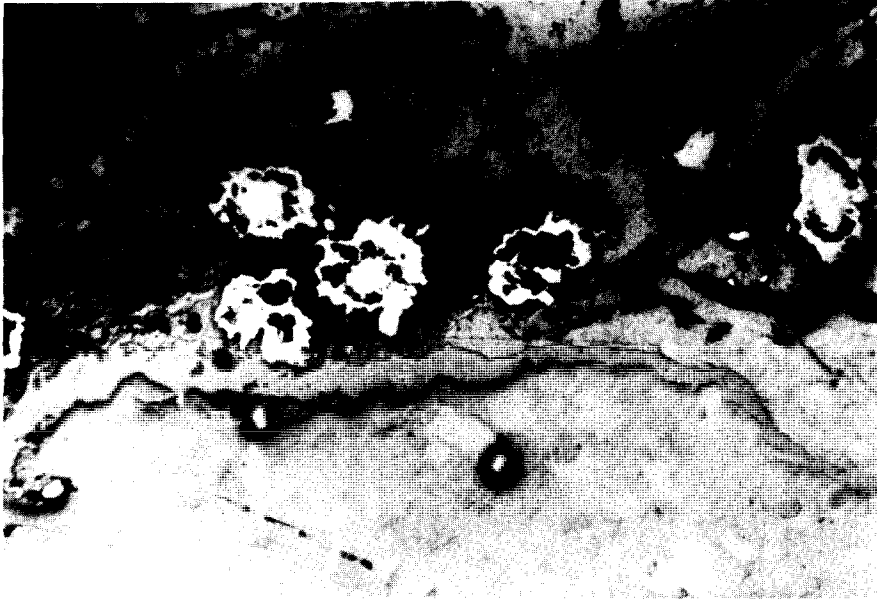


Fig. 1. Photomicrographs of clay minerals and siderite corn in humic detritus. Incident light, dry objective; actual length of each field of view = 0.28 mm.

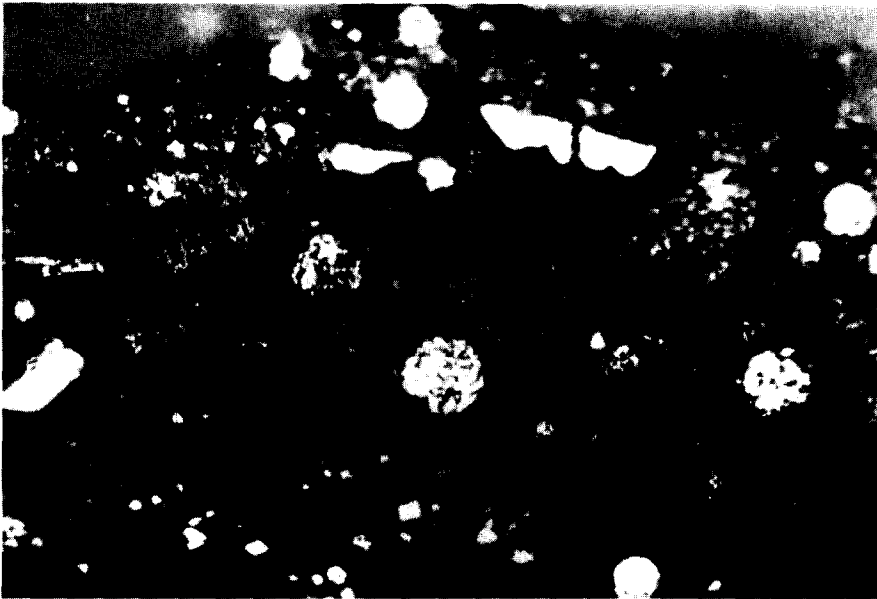


Fig. 2. Photomicrographs of example of Fe sulfide forms: euhedral crystals, framboids and massive corn. Incident light, oil immersion, actual length of field of view = 0.14 mm.

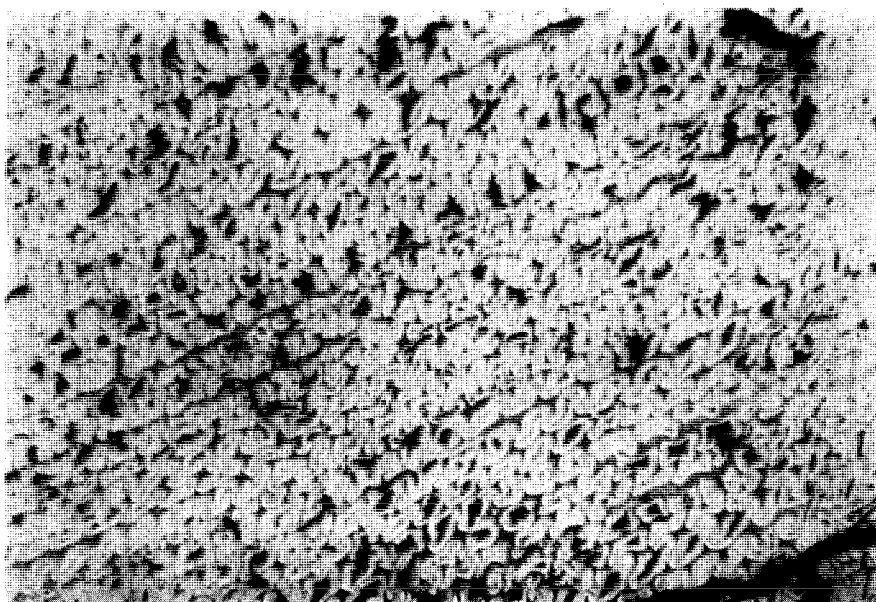


Fig. 3. Photomicrographs of texto-ulminite, macerals of the huminite group. Incident light, oil immersion; actual length of each field of view = 0.22 mm, i.e. 1 cm of the photomicrographs representing 20 μm .

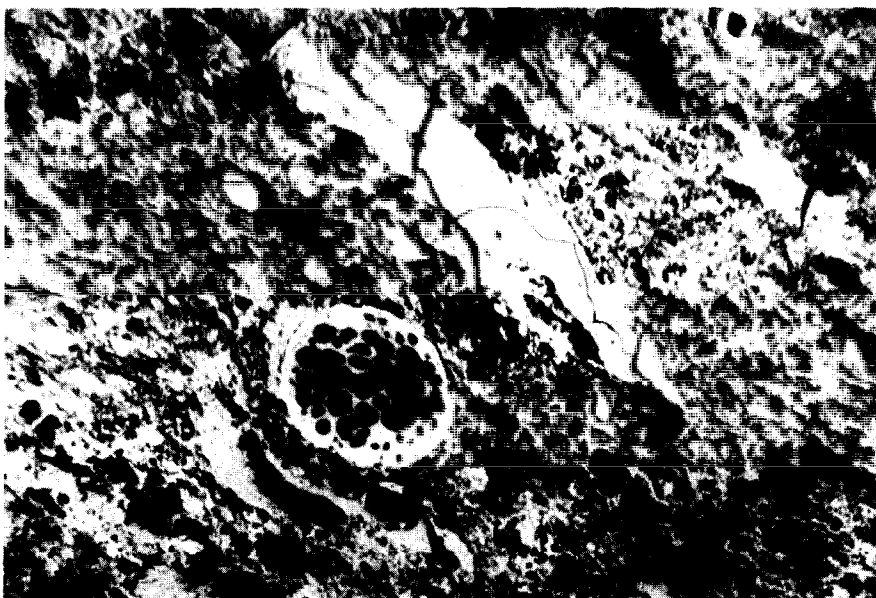


Fig. 4. Photomicrographs illustrating of composition of attrinite (maceral of huminite group): humic detritus, fragments of ulminite (huminite group), sporinite and liptodetrinite (liptinite group) and the inclusion of sklerotinite (inertinite group). Incident light, oil immersion; actual length of each field of view = 0.22 mm.

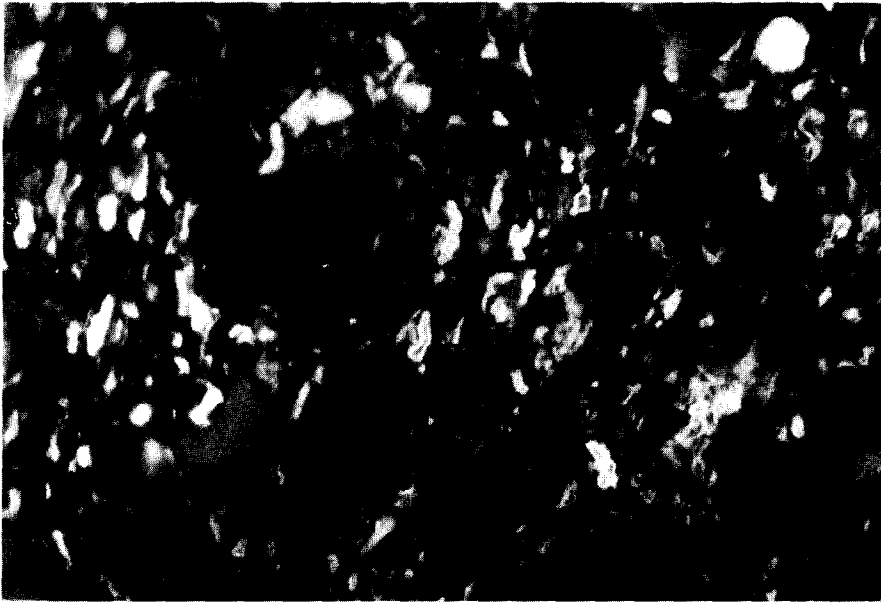


Fig. 5. Photomicrographs of liptoderinite with resinite (maceral of liptinite group). Incident light in fluorescence mode, oil immersion; actual length of each field of view = 0.22 mm.

The coal samples denoted after their localities Druzba and Jiri represent detroxylic coals with an abundance of ulminite (44% and 25% gelified plant tissues). Ungelified

Table 2
Petrographic characteristics

Parameter	Locality	
	Jiri	Druzba
Mean reflectance R_p /%	0.33	0.31
Content of		
Huminite group/%	86	56
Attrinite/%	12	12
Densinite/%	18	9
Textinite/%	3	4
Ulminite/%	44	25
Gelinite/%	13	4
Korpohuminite/%	3	2
Liptinite group/%	3	3
Inertinite group/%	1	2
Mineral matter/%	10	39

The methods of determination of above parameters are described in Section 2.

plant tissue with preserved cell structure, textinite, is present to a low degree in both samples (3–4%).

The attrinite and densinite are a mixture of gelinite, ulminite, textinite, corphuminite, resinite, sclerotinite and fusinite fragments in the porous binding matter. Attrinite (12%) of both samples contain liptodetrinite and bituminite (liptinite group) in the binding matter. In the more gelified densinite of sample Jiri (18%) there are sporadically dispersed macerals of liptinite (sporinite, cutinite, fluorinite, resinite) and those of inertinite groups.

The coal sample from the locality Jiri contains more gelinite (13%) than the sample from the locality Druzba. The isolated grains of gelinite are often broken by desiccation fissures.

3.3. Thermoanalytical characterization

Simultaneous thermal analysis and mass spectrometry have already been used in the study of thermal behavior of coals by Ohrbach et al. [5] and Matuschek et al. [6].

In this study, the thermal characteristics of two low rank coal samples were obtained by means of thermogravimetry and differential thermal analysis during heating in argon from 20 to 1200°C. The NETZSCH STA 429 equipment for simultaneous measurements of TG and DTA was coupled with a quadrupole spectrometer, making it possible to record simultaneously mass spectra of the volatile products released from the sample in the course of the whole temperature interval.

The results of the TG/DTG and DTA of the two low rank samples from the localities Jiri and Druzba are presented in Figs. 6 and 7, respectively. It follows from Figs. 6 and 7

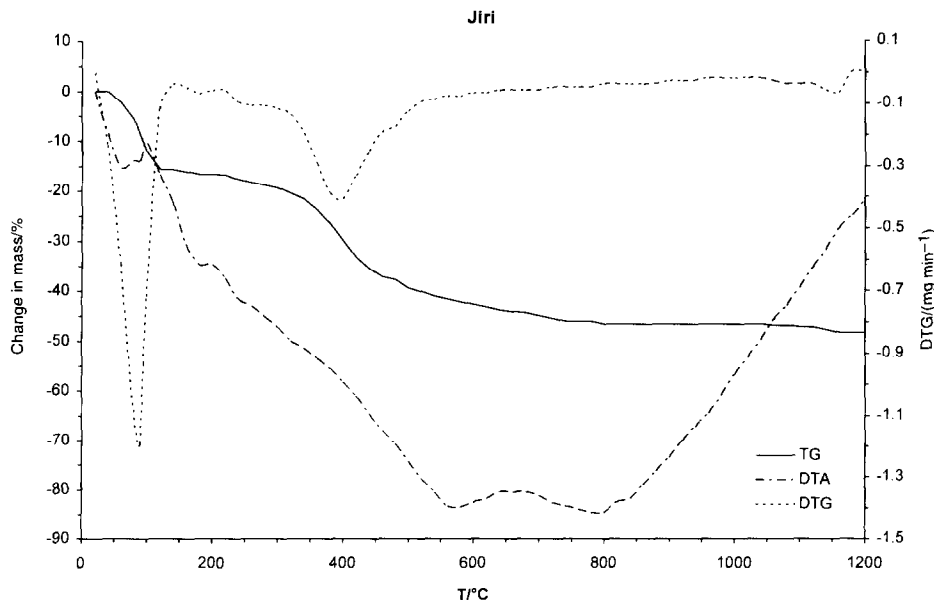


Fig. 6. TG/DTG and DTA curves of lignite sample, locality Jiri, measured during heating in argon (heating rate 5 K min⁻¹).

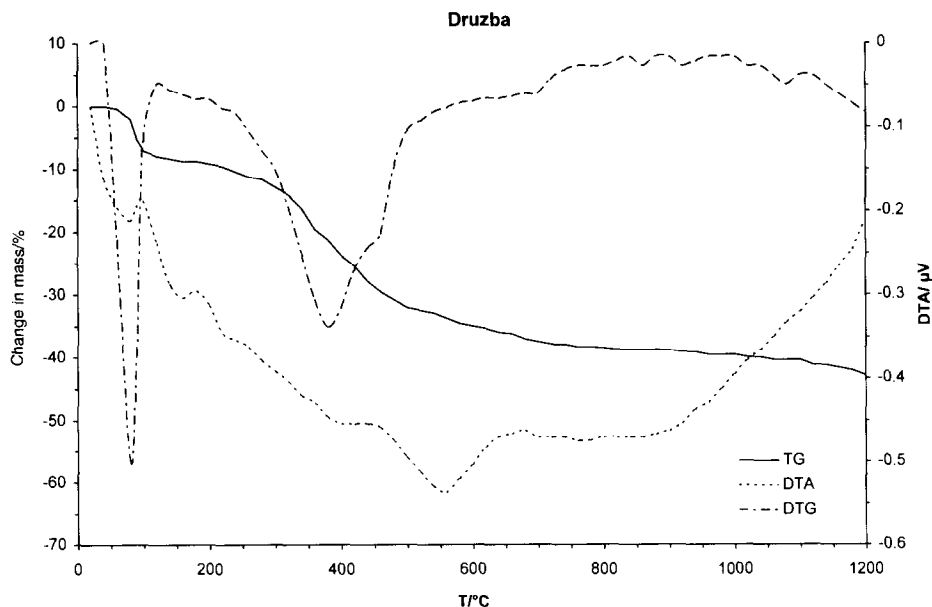


Fig. 7. TG/DTG and DTA curves of the lignite sample, locality Druzba, measured during heating in argon (heating rate 5 K min^{-1}).

that two temperature regions exist with both samples where the mass loss takes place, namely: the temperature range $20\text{--}100^\circ\text{C}$ where the release of physically bound water takes place; the range $300\text{--}450^\circ\text{C}$ where the pyrolysis of the coals takes place, accompanied by the release of volatile products.

The representative MS spectra of the volatile products released from the coal samples denoted JIRI and DRUZBA heated to the temperatures of 100°C and 400°C are presented in Figs. 8(a,b) and 9(a,b), respectively.

Taking into account both environmental and technological objectives of this investigation, the volatiles products of the following masses were simultaneously measured during heating of the coal samples: 17, 18, 28, 34, 44, 55, 64, 67, 91, 92, ...

The release of the volatiles was simultaneously measured for the selected m/z in the course of heating the sample in argon.

In Figs. 10(a–c) and 11(a–c) the temperature dependence of the ion current densities for the measured fragments of the selected m/z are presented. It follows from Figs. 6 and 7 that the two lignite samples investigated differ in the mass loss taking place at the temperatures $20\text{--}120^\circ\text{C}$ (corresponding to the release of physically adsorbed water) as well as in the total mass loss measured after heating to 1200°C . The results of TG shown in Figs. 6 and 7 as well as the results of the MS shown in Figs. 10 and 11, are summarized in Table 4.

It follows from Figs. 10(a) and 11(a) that the release of water takes place in two steps: in the temperature range up to 100°C (corresponding to the release of physically adsorbed water) and in the temperature interval $400\text{--}500^\circ\text{C}$ (corresponding to the release of chemically bound water).

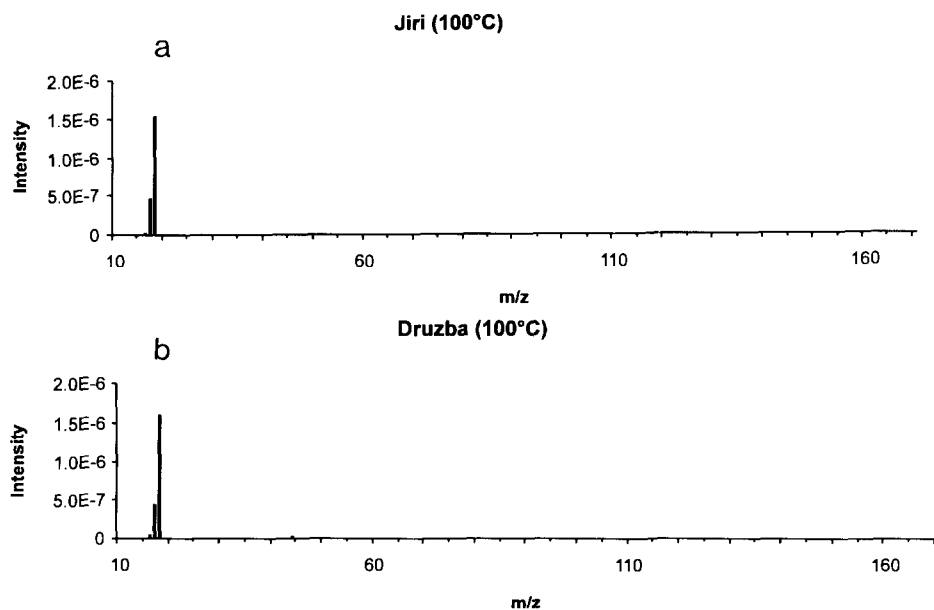


Fig. 8. MS spectra of the volatile products released from the lignite localities Jiri (a) and Druzba (b) corresponding to the sample temperature of 100°C.

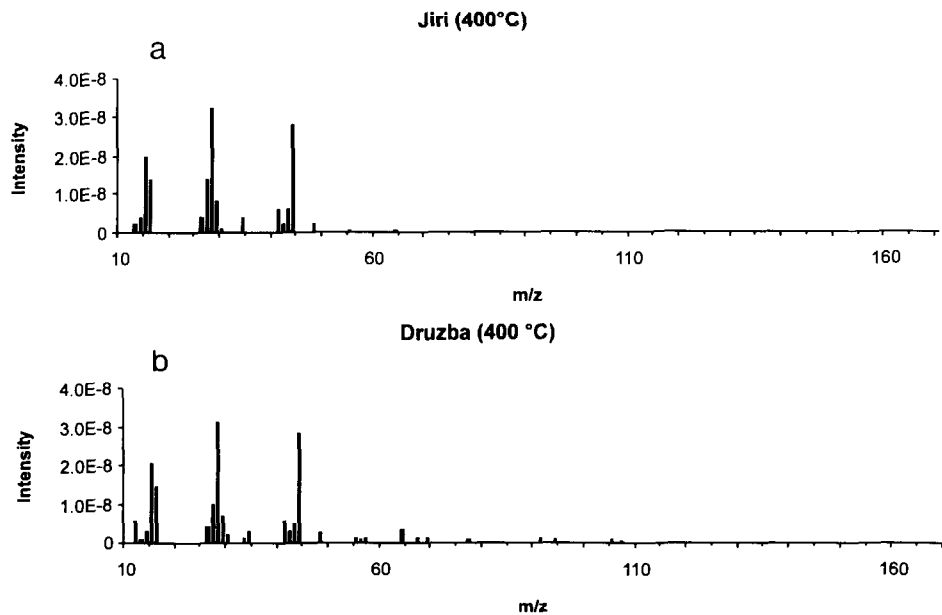


Fig. 9. MS spectra of the lignite samples localities Jiri (a) and Druzba (b) corresponding to the sample temperature 400°C.

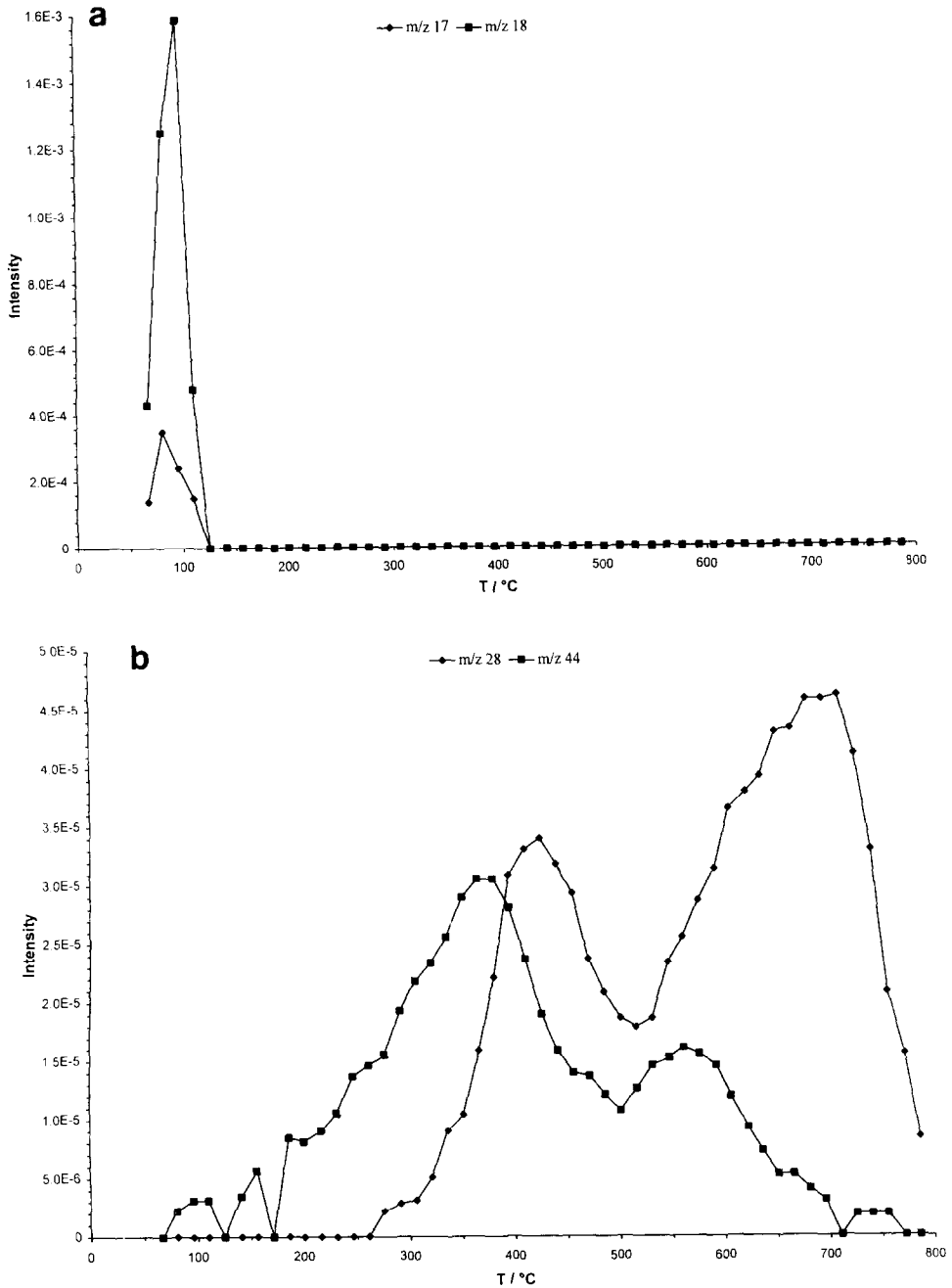


Fig. 10. Temperature dependence of the ion current intensities for the measured fragments of the $m/z = 17, 18$ (a), $m/z = 28$ and 44 (b), $m/z = 34, 64$ (c), $m/z = 55$ and 91 (d) released during heating of the lignite (locality Ľirí).

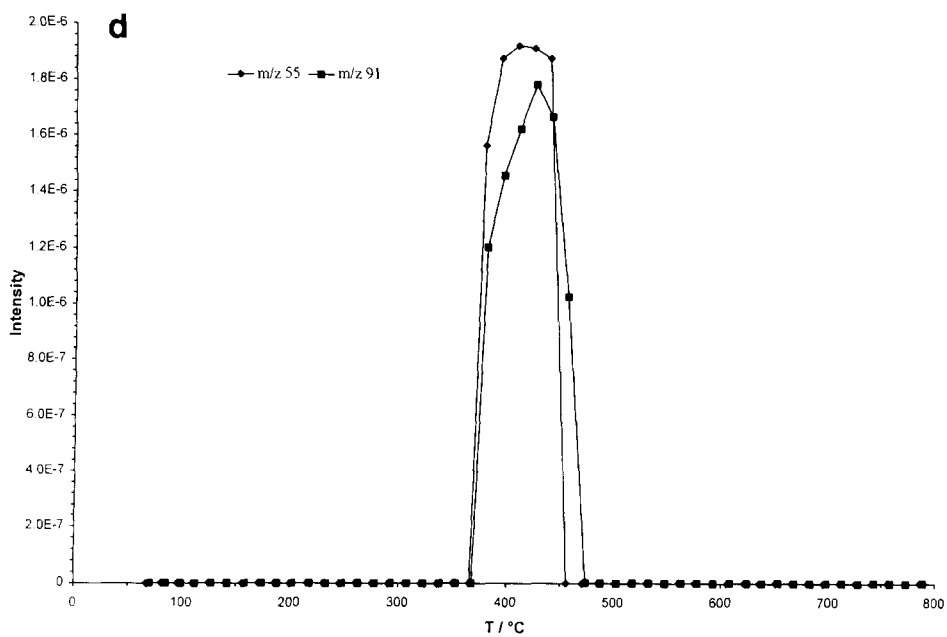
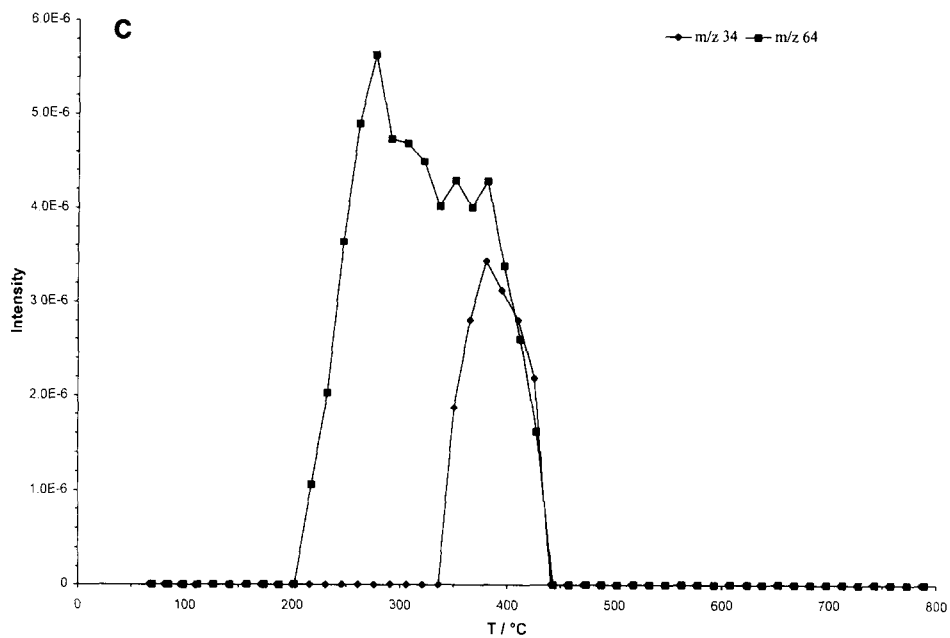


Fig. 10(c,d).

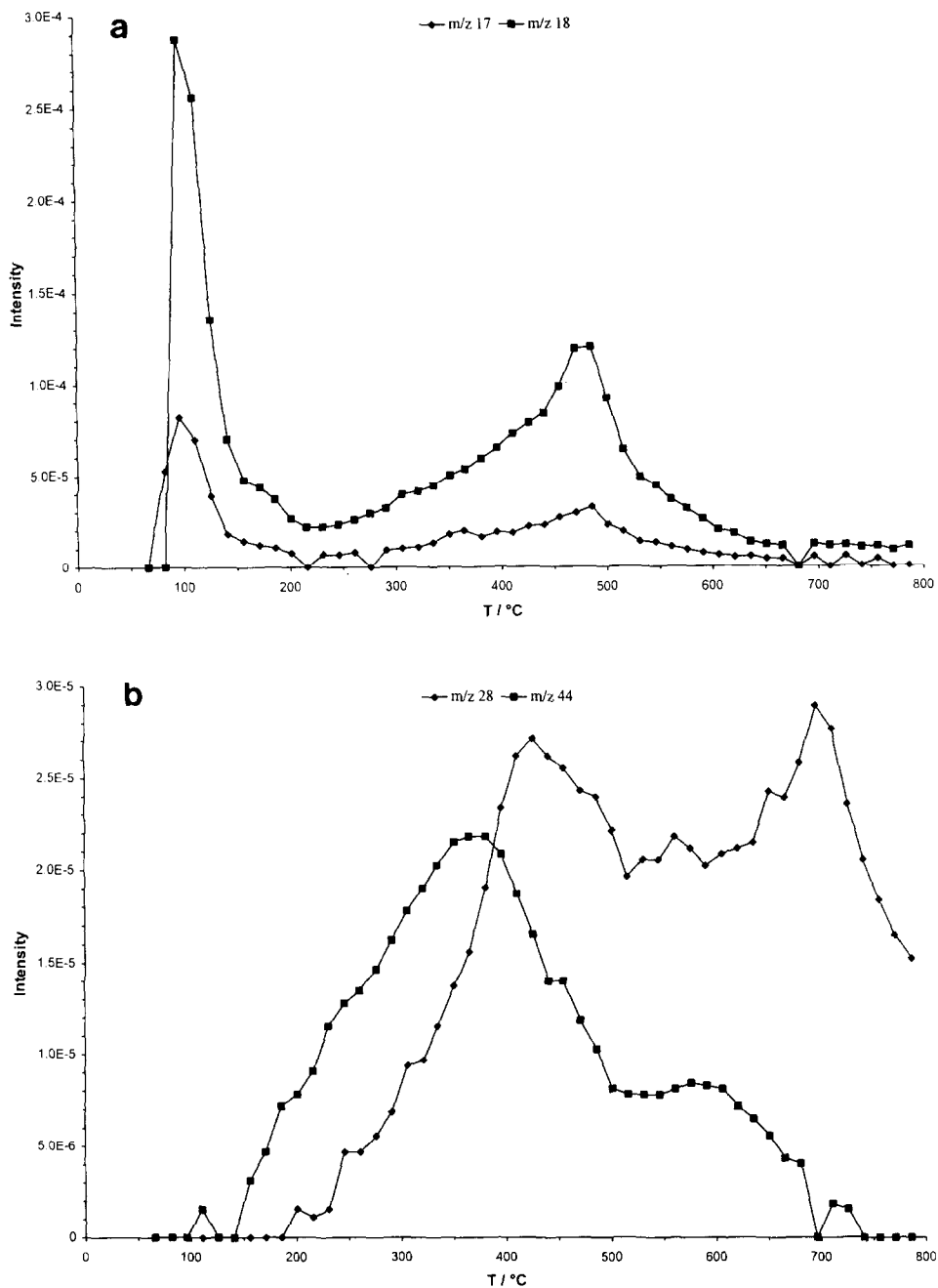


Fig. 11. Temperature dependence of the ion current intensities for the measured fragments of the $m/z = 17, 18$ (a), $m/z = 28$ and 44 (b), $m/z = 34, 64$ (c), $m/z = 55$ and 91 (d) released during heating of the lignite (locality Duzba).

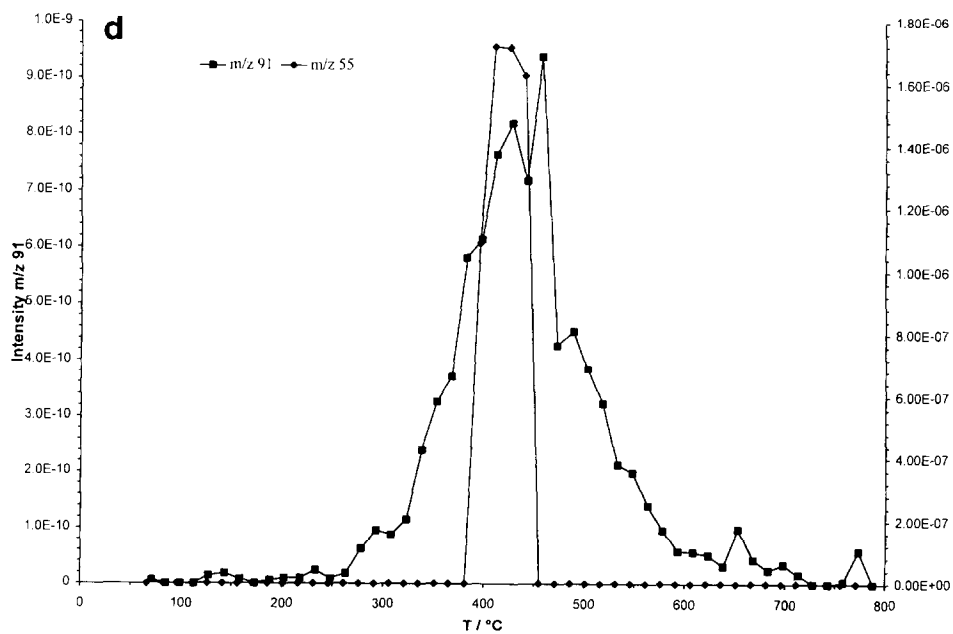
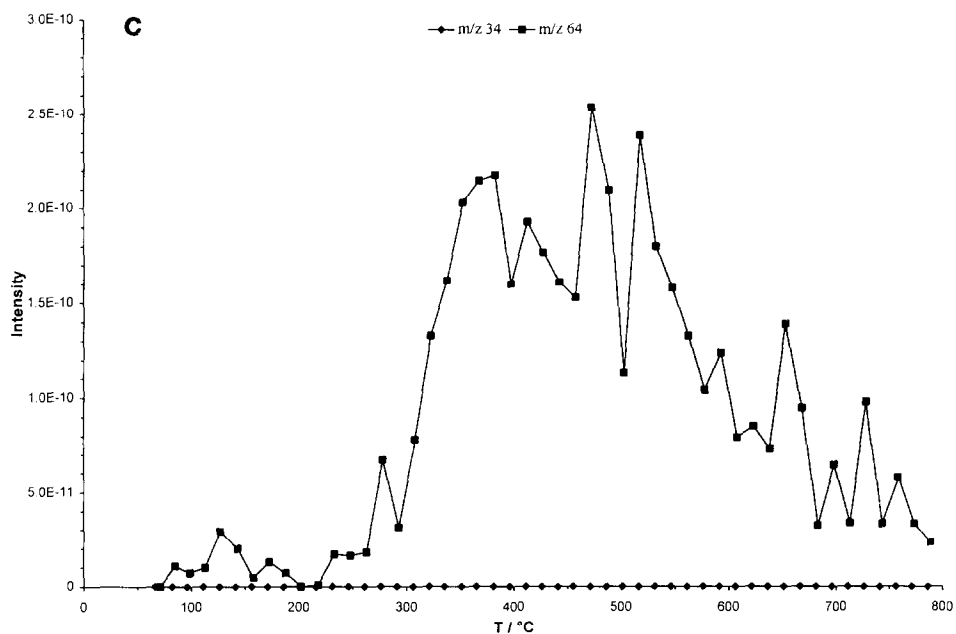


Fig. 11(c,d).

Table 3

Mass fragments and structural related compound measured during the thermal characterization of low rank coals

<i>m/z</i>	Sum formula	Compound on fragment of molecule
17, 18	HO ⁺ , H ₂ O ⁺	Water
28	CO ⁺	Carbon monoxide
34	H ₂ S	Sulfur hydrogen
44	CO ₂ ⁺	Carbon dioxide
55		Typical aliphatic fragment
64	SO ₂ ⁺	Sulfur dioxide
78	C ₆ H ₆ ⁺	Benzene
91, 92	C ₇ H ₇ ⁺	Typical aromatic fragments (tropyllium)

From Figs. 10(b) and 11(b) it follows that the release of CO and CO₂ was observed in two steps with both samples. This corresponds to the decomposition of organic components of the lignite.

The release of SO₂, resulting from the decomposition of sulfates, takes place in one step; the maximum at 275°C was observed with the sample Jiri, the maximum at 400°C was observed with the sample Druzba.

Table 4

Characterization of thermal behaviors of two low rank Northbohemian coals

Thermal processes	Locality of the coal samples	
	Jiri	Druzba
Total mass loss determined by TG after heating up to 1200°C/%	48	38.
Moisture content determined by TG after heating to 120°C/%	16.5	8
Release of water determined by MS (<i>m/z</i> = 18) in two steps	First maximum 100°C Second maximum 480°C	First maximum 100°C Second maximum 480°C
Release of carbon monoxide determined by MS (<i>m/z</i> = 28) in two steps	First maximum 385°C Second maximum 700°C	First maximum 430°C Second maximum 700°C
Release of carbon dioxide determined by MS (<i>m/z</i> = 44) in two steps	First maximum 375°C Second maximum 560°C	First maximum 380°C Second maximum 620°C
Release of sulfur dioxide determined by MS (<i>m/z</i> = 64) in one step	Max. 275°C	Max. 400°C
Release of aliphatic fragments determined by MS (<i>m/z</i> = 55) in one step max. 420°C	Max. 400°C	
Release of aromatic fragments determined by MS (<i>m/z</i> = 91) in one step	Max. 420°C	Max. 420°C

In the mass spectra of low rank coals from the localities Jiri and Druzba we have observed (see Figs. 10(c) and 11(c)) significant effects corresponding to the $m/z = 34$ (being ascribed to the release of sulfur hydrogen H_2S or aliphatic sulfides) which use to be released from the coal sample heated in a non-oxidative atmosphere as the result of reduction of organic sulfur [7] and partially during the reduction of finely dispersed crystals of FeS_2 (submicrometre and micrometre size).

The question of the sulfur bonding in the organic coal mass will be discussed in the next paper. The detailed study of this question requests the separation of organic and inorganic coal components. The investigation of the separated inorganic and organic (iron sulfide free) components can be performed apart from the mass spectrometry, by means of high pressure temperature programmed reduction [8].

The release of organic molecules corresponding to the $m/z = 55$ (aliphatic fragments) and $m/z = 91$ (aromatic fragments), takes place in one step with the maximum at temperatures of 400–420°C (see Figs. 10(c) and 11(c)) for both coal samples investigated.

The methods of thermal analysis, coupled with mass spectrometry used reflect fairly well the differences in the two Northbohemian low rank coals from the localities Jiri and Druzba.

The higher content of huminite groups and the higher degree of gelification of the coal from the locality Jiri is characterized by a higher concentration of aromatic volatiles released from the sample during pyrolysis. The higher content of the finely dispersed mineral component (clay minerals, carbonates) as well as of bituminous mass in the coal from the locality Druzba is characterized by a higher amount of released CO , CO_2 and fragments of the aliphatic compounds, released during the pyrolysis of this sample.

It is obvious from these results that simultaneous measurements of the volatiles released and TG and DTA curves are very suitable tools for the characterization of the thermal behavior of the coal samples.

4. Conclusion

We have found that two lignite samples from the localities Jiri and Druzba are different in basic chemical characteristics, especially in the content of moisture, the yield of ash, and the content of sulfur. The temperature intervals of the release of moisture, organic and inorganic volatiles were determined from the TG and DTG curves.

It was demonstrated that the use of thermal analysis coupled with mass spectrometry gives the upgraded characteristics of the low rank coal samples. Thermal behavior of samples from two different localities of the Northbohemian region was distinguished. From the MS results of SO_2 release compared to the petrographic and chemical analysis of the coal samples, the origin of sulfur (ex-pyrite, ex-sulfate or organic origin) can be made.

The thermal characteristics obtained can be used as the basis for the optimization of the thermal treatment of the low rank coal, as well as for assessment of the environmental risk caused by the use of the low rank coals as fossil fuel in power stations.

Acknowledgement

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