

Aniela MATUSZEWSKA  
Uniwersytet Śląski, Katowice

## PRELIMINARY RESULTS OF GEOCHEMICAL AND PETROGRAPHIC INVESTIGATIONS OF HARD COAL FROM MINE „SOŚNICA”, HEAT-AFFECTED BY IGNEOUS INTRUSION

**Summary.** The preliminary results are presented of geochemical and petrographic investigations of coal from 416-bed of hard coal mine „Sośnica” (Upper Silesia Basin), heat-affected by igneous intrusion. The geochemical parameters were estimated on the basis of the mass chromatograms obtained with the use of GC/MS method for hydrocarbon fractions of the molecular phase of coal. For diversification of the chemical structure in a function of the distance of sampling of the parent coals from intrusion, the most useful were parameters basing on aromatics, of various degree of alkyl substitution and condensation. The aromatisation process of coal structure is in turn a reason of variations in physical coal properties, as e.g. increasing of vitrinite reflectance. The degree of thermal transformations of coal organic matter may be also characterised well by changes occurring of amounts of dibenzothiophene type compounds. Their presence, as well as some geochemical and mineralogical data, can indicate, moreover, the hydrothermal conditions of transformations in the zone of heat flow of intrusion.

## WSTĘPNE WYNIKI BADAŃ GEOCHEMICZNYCH I PETROGRAFICZNYCH WĘGLA Z KWK „SOŚNICA”, PRZEobrażonego DZIAŁANIEM INTRUZJI MAGMOWEJ

**Streszczenie.** Przedstawiono wstępne wyniki badań geochemicznych i petrograficznych węgla z pokładu 416 w KWK „Sośnica” (GZW), który uległ przeobrażeniu termicznemu pod wpływem intruzji magmowej.

Parametry geochemiczne wyznaczono na podstawie chromatogramów masowych wykonanych przy użyciu metody GC/MS dla węglowodorowych frakcji fazy molekularnej węgla. Najlepszą charakterystykę zmian chemicznej struktury w funkcji odległości pobrania węgla macierzystych od intruzji uzyskano, stosując wskaźniki określające zmiany zawartości węglowodorów aromatycznych o różnym stopniu kondensacji i substytucji podstawnikami alkilowymi. Proces aromatyzacji węglowej struktury jest z kolei przyczyną zmian obserwowanych we własnościach fizycznych węgla, m.in. wzroście refleksyjności witrynit. Stopień termicznych przemian organicznej substancji węgla charakteryzują także wskaźniki wykorzystujące zmiany zawartości związków z grupy dibenzotiofenu, których obecność może

wskazywać ponadto, obok niektórych danych geochemicznych i mineralogicznych, na hydrotermalne warunki przeobrażeń węgla w strefie strumienia ciepła intruzji.

## Introduction

The symptoms of volcanism in the saddle layers of the „Sośnica” mine were already described by Gabzdyl et al. [1], Duźniak et al. [2] and Kapuściński et al. [3], which indicated a probability of occurrence of hydrothermal processes, simultaneously with volcanism. Chodyniecka and Hanak [4] have presented a detailed characteristics of transformations of coals and coal shales from the “Sośnica” mine (414/413-bed), heat-affected by intrusion. The authors have stated that coal layers from the contact zone contain mainly natural coke but there are also non coked grains of the anthracite nature. They underlined also that in this region the pneumatholytic hydrothermal solutions could be active. The intrusive rocks show, because, a considerable degree of hydration and carbonatisation.

In the work presented here the investigations were also taken up of coal samples from the „Sośnica” mine, affected and transformed by an intrusive body. Geochemical and petrographic analyses have been performed for characterisation of changes of physicochemical properties which occurred during process of accelerated coalification in the natural „stove”, with intrusion as a source of heating. The gradient of changes of parameter values estimated in this case is much higher, than observed for common coalification process, occurring when a heat flow from Earth abyss influences by a longer geological time and with a lower thermal gradient.

Literature data indicate that investigations of transformation of sedimentary organic matter were made in a broad range. The analyses served as well the cognitive as also the practical purposes. A main aspect of application is an estimation of oil potential of rocks and description of conditions of organic matter migration. These problems are important from a point of view of studies of oil pools formation. It is a reason of a great number of works on the geochemistry of organic matter dispersed in the rocks. Geochemistry of the kerogen and oil is simultaneously a significant scientific basis for the carbochemistry domain. The limitation are here, however, resulting from a relatively high degree of transformation of organic coal substance, especially when treated by additive heating of intrusion.

As well in a case of a slow influx of the heat flow from the Earth abyss, as in the result of impetuous heat affection by igneous intrusion, an action of elevated temperature and other co-

operating factors, causes transformation of sedimentary organic matter in the direction of thermodynamically advantageous structures up to final stage – the graphite structure.

In these natural thermolytic processes the trends can be expected similar to these well known and investigated, occurring during industrial thermal treatment of coal, such as semicoking, coking and at last- graphitisation. It seems to be especially interesting, therefore, a further comparison of the occurrence of natural and technological thermolysis, with consideration of diversification of the conditions of these processes course. Natural thermal alteration characterises by a longer time of progress, and by contribution of natural catalysts and possible hot water convection occurring in hydrothermal conditions. There is also other important factor: an influence of elevated pressure which can slowing down the processes of degassification. The temperature factor is, however, usually dominating and it is because a degree of transformation of sedimentary organic matter is called the degree of thermal maturation.

There is a great variety of the methods of instrumental analysis making possible a characteristics of thermal maturation process of sedimentary organic substance. Among them are methods of thermal analysis, spectroscopic and chromatographic methods as well as methods applying the microscopic images. However, higher is transformation degree, fewer parameters can be used in consideration of lower and lower degree of preservation of a primary matter structure. Moreover, a progress of physicochemical changes takes place in the direction of increasing similarity of structural traits. It is because the processes proceed of cyclisation and aromatisation of the structure. For this reason in geochemical analyses of hard coal the parameters are used, basing, above all, on the estimation of aromatic compounds of various degree of alkyl-substitution and condensation. For broader comparisons, these parameters are completed, however, by the use of chosen relation between aliphatic compounds, commonly used for characterisation of organic matter dispersed in the rocks.

## Experimental

### The apparatus used

Photomicroscope III, of the Opton firm was utilized for petrographic analyses, using a monochromatic, non polarized, reflected light and oil immersion; magnification was 512 x.

For analysis of hydrocarbon fractions of coal molecular fraction (extracts) the capillary gas chromatography-mass spectrometry method was applied, using a Hewlett-Packard gas chromatograph (with HP-column) coupled to a HP-mass spectrometer.

Data were processed with the Hewlett Packard Chemstation software. All compounds were identified by their mass spectra, and comparison of retention times of their peaks to these of standard compound and literature data, and interpretation of MS fragmentation patterns.

### Characteristics of analysed samples

Three samples were chosen here to comparisons from a series of coals sampled from a close environment of an intrusive body occurring in bed-416 in Sośnica coal mine (Upper Silesia Coal Basin). The dike diameter was about 1,5 meter. One of samples (Z) was taken from a contact zone, second (Y)- from the distance of about one meter from the dike and third (X)- from the distance of about two meters from intrusion. The classification of (X) – coal as the flame type (31.2, in Polish classification) ( $V^{daf}$  : 28.6%;  $Q^{daf}$  : 33 129 kJ/kg (14,232 BTU/lb); RI: 0) suggests that it was not influenced (or to a low degree) by intrusion heat. Sample (Y) was classified in Polish classification as a 38-type coal ( $V^{daf}$  : 25.1%;  $Q^{daf}$  : 33 050 kJ/kg (14,198 BTU/lb); RI :0 ). The data obtained from mine “Sośnica” characterise sample taken from the contact zone ((Z)-coal) as an anthracite type.

The results of an X-ray analysis described earlier [5], indicate a predomination of the dolomite in (Z)-sample (about 60%) and lower contents of the halite and small amounts of quartz, kaolinite and pyrite. In (Y)-coal sample the mineral matter of about 23% is formed mainly by quartz, halite and kaolinite. (X)-coal sample contains about 10% of mineral matter. The identified there predominating minerals were: dolomite, quartz, halite and pyrite.

Geochemical investigations were performed on a basis of coal dichloromethane extracts separated, using preparative thin layer chromatography, onto aliphatic , aromatic and polar fractions. The GC/MS analysis were made of the obtained aliphatic and aromatic hydrocarbon fractions. A series of parameters has been estimated with the use of relative intensities of the obtained mass chromatograms peaks of characteristic compounds.

Abundanc

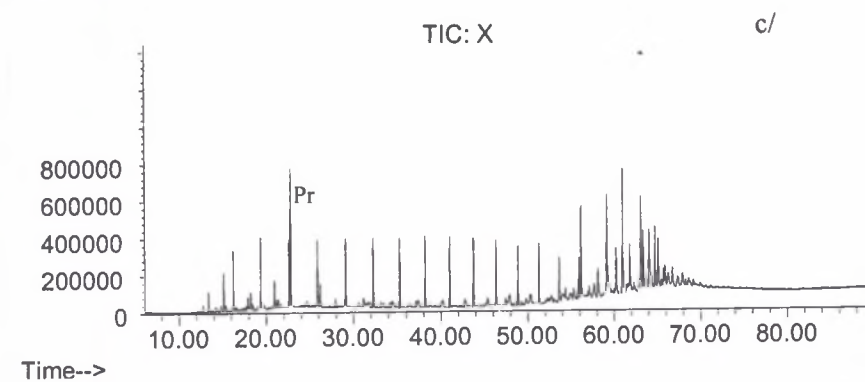
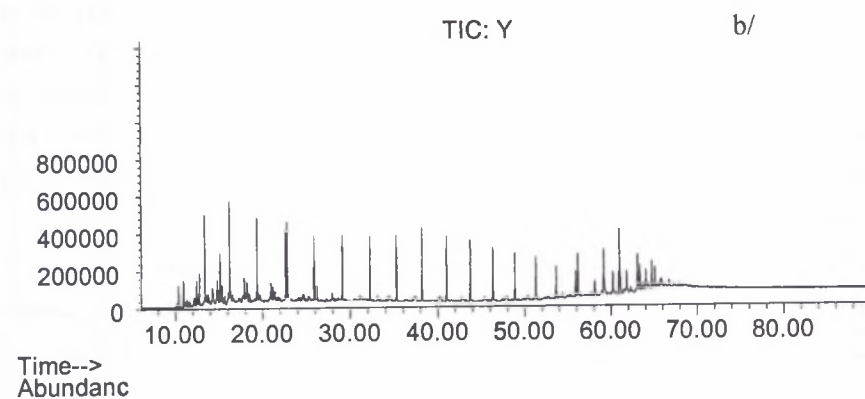
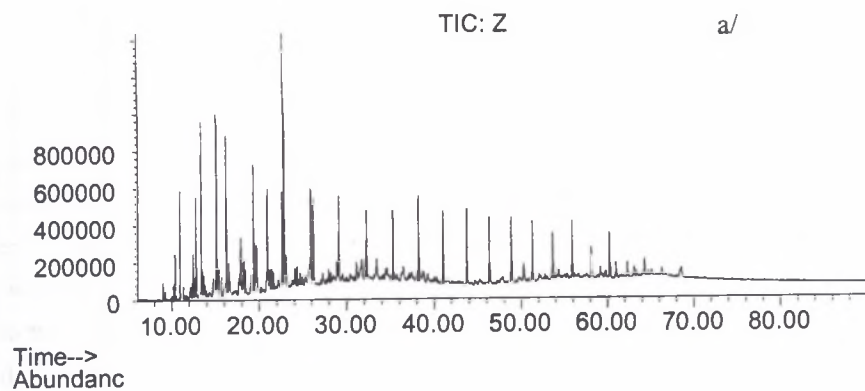


Fig. 1. Total ion chromatograms (TIC) of aliphatic fractions of extracts of coals: a/ (Z), b/ (Y), c/ (X)

## Discussion of the results

### The parameters calculated using GC/MS data for aliphatic fraction of analysed coal extracts

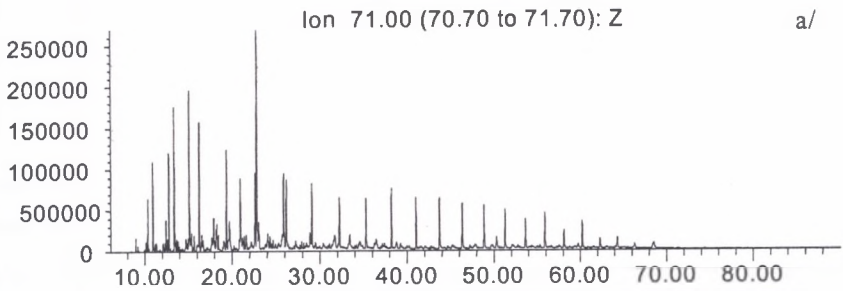
Characteristics of the analysed aliphatic fractions is given in Fig.1, presenting their total ion chromatograms (TIC). All of the aliphatic fractions are characterized by a similar range of n-alkanes containing from about 13 (14) to 36 carbon atoms. The shapes of n-alkane distribution are, however, different, as well as the relative intensity of particular peaks in the total ion chromatogram (TIC). The most characteristic in the case of the sample from (X)-coal (Fig.1 c) is a predomination of the pristane (Pr) peak intensity and relatively high content of triterpane and sterane type compounds (in the range of retention time of about 50-70 min). It is in accordance with the shape of TIC attributed to sedimentary organic matter of relatively low thermal maturity [6]. With increase of thermal degradation of coal samples the decrease of relative intensity is observed of triterpane and sterane peaks (Figs 1b,a). In turn, the relative intensity growth can be seen of the peaks in the range of low values of the retention time. It is a result of a destruction progress of long alkane chains with temperature increase, as the parent coals approached to the intrusion.

*n-Alkane distribution.* Fig. 2 a-c presents the mass chromatograms of  $m/z$  71 characteristic for n-alkanes. The n-alkane distribution (C14-C34) in the case of (X) sample extract (Fig. 2c) is monomodal and has the rather equalized intensities in the range of hydrocarbons with carbon atoms number of 15 to 27. Hunt [6] has stated that the distribution like this can testify to the high maturation degree of the parent fossil organic matter. It is a result of generally high stage of transformation of parent plant mater at the coalification stage equal to hard coals. The n-alkane distribution for the sample (Y) (Fig. 2b) is slightly bimodal with two maxima : at C<sub>22</sub> and C<sub>15</sub>. The shape of this distribution testifies a progress of thermal degradation of the parent (Y)-coal sample in relation to (X)-coal sample.

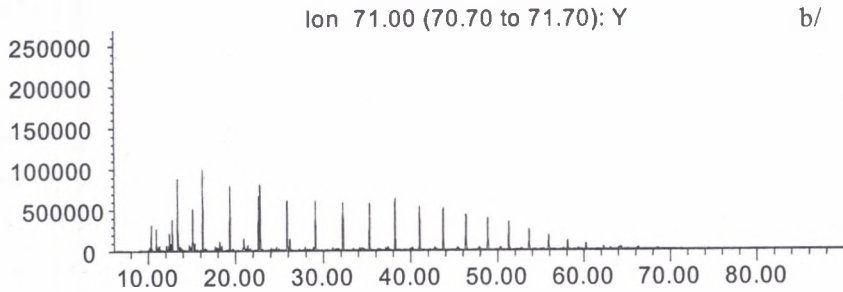
Fig.2a presents more clear bimodal character of n-alkane distribution with the maxima at C<sub>22</sub> and C<sub>14</sub>. The narrow distribution range of predominating n-alkane group (C<sub>13</sub>-C<sub>16</sub>) in the extract of the (Z)-coal testifies, after Hunt [6], to the postmaturity of analyzed organic matter.

*Carbon Preference Index (CPI).* This parameter has been at first defined as relative contribution of chosen n-alkanes with odd and even number of carbon atoms and was utilized for the characteristics of sources and thermal maturity of oils and dispersed organic matter [7]. Here this ratio has been calculated by summation of peak intensities for n-alkanes with odd and even number of carbon atoms of : 15-33 and 14-32, respectively. The sums obtained

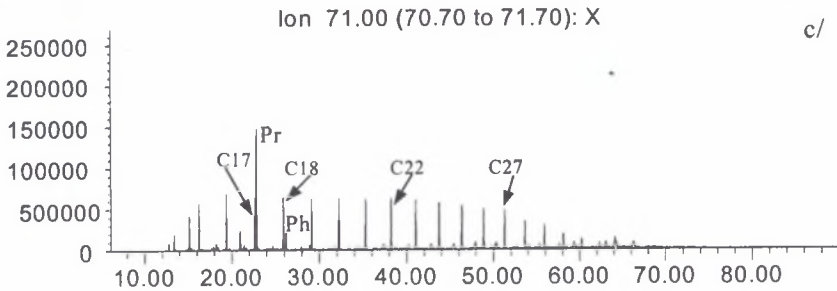
Abundanc



Time--  
Abundanc



Time--  
Abundanc



Time--

Fig. 2. Mass-chromatograms ( $m/z$  71) of aliphatic fractions of extracts of coals: a/ (Z), b/ (Y), c/ (X). Some peaks are marked of n-alkanes (in  $C_n$  symbols  $n$  signifies a number of carbon atoms in alkane chain) as well as isoprenoids : pristane (Pr) and phytane (Ph)

were next divided. The mass chromatograms of  $m/z$  71 of aliphatic fractions of extracts were used to the calculations (Fig. 2a-c). The results given in Table 1 (equal to about 1.0 for all analyzed samples) show no carbon number preference and indicate complete maturation of coaly organic substance in relation to other forms of fossil organic matter of lower coalification degree [6]. This parameter does not diversify, however, the coal samples influenced in a various degree, by high temperature of igneous intrusion.

*Pristane to phytane ratio Pr/Ph.* Isoprenoids: pristane (Pr) and phytane (Ph) are formed during diagenesis of fossil organic matter probably from phytol side chain of chlorophyll a. Pristane may be formed during the process of oxidation and decarboxylation. Phytane can be formed e.g. in a process of hydrogenation and reduction [8]. It is because the relation between the isoprenoids can be an indicator of the deposition conditions. For oils, the values of  $Pr/Ph \geq 3$  ratio were also attributed to terrestrial parent organic matter. In the case of coals investigated here, the ratio of  $Pr/Ph > 3$  for all analyzed extracts may also signify the terrestrial provenance of parent organic matter accumulated in sediment in oxic environment.

Other parameters were also estimated on the basis of the peak intensities of isoprenoids in relation to these ones of n-alkanes appearing on the mass chromatograms at approximate retention times. The ratios of isoprenoids Pr and Ph to the relative n-alkanes (n-C17, n-C18) decrease during thermal maturation process because of generation of n-paraffins, as a result of cracking processes [9,10]. For a sedimentary organic matter affected by the igneous dike Clayton and Bostick [11] also stated decreasing of these parameters:  $Pr/n-C_{17}$  from about 1.3-0.3 over the range 0.4-1.3% Ro, and  $Ph/n-C_{18}$  from about 0.4 in the unaltered zone to about 0.2 at  $Ro=2.1\%$ . In the case, however, of organic matter of analysed coals, decreasing tendency of the ratio  $Pr/n-C_{17}$  is observed from sample X to Y, and then- a clear growth for the Z-sample. Also the value of  $Ph/n-C_{18}$  ratio increases for the Z-sample. (Table 1). The anomalies can be results of high temperature degradation as well as of hydrothermal migration processes controlling probably also relative changes of the contents of isoprenoids (Pr, Ph) and neighbouring n-alkanes (n-C17, n-C18).

*Pentacyclic triterpanes* undergo, with maturation progress, the conversion of sterical configuration R at the carbon atom C<sub>22</sub> (for triterpanes above C<sub>30</sub>) to the mixture of diastereoisomers (22R) and (22S) [12]. It make possible to utilise other else parameter of thermal maturity, calculated for homohopanes as a ratio of peak intensities of diastereoisomers: 22S and 22R of aliphatic hopanoid homologues C<sub>31</sub> and C<sub>32</sub>. For analysed samples the peaks mentioned can be seen in Fig.3, presenting mass-chromatograms ( $m/z$  191) recorded for aliphatic fractions of extracts of investigated coals. Seifert and



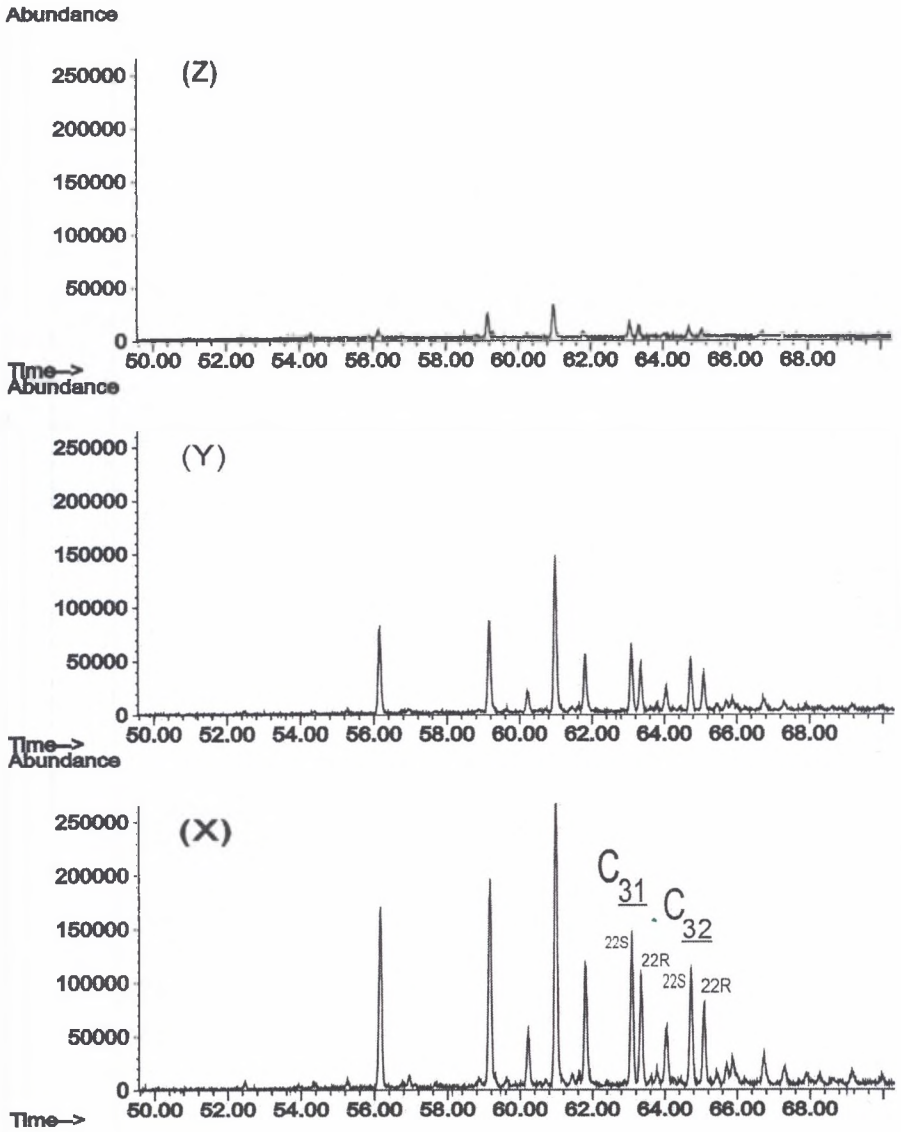


Fig. 3. Distribution of hopanes (m/z 191) in aliphatic fractions of extracts of coals (Z), (Y), and (X). The peak descriptions signify diastereoisomers 22S and 22R of aliphatic hopanoids C 31 and C 32

Table 1  
Geochemical parameter values calculated from mass chromatograms of the aliphatic fraction of extracts from analysed coals: X, Y, Z.

Aliphatic fraction of extract from coal:	Pr/Ph	Pr/(n-C <sub>17</sub> )	Ph/(n-C <sub>18</sub> )	Pr+Ph (n-C <sub>17</sub> +n-C <sub>18</sub> )	CPI <sub>(14-33)</sub>	Cholestane C <sub>29</sub> α 20S (20S+20R)	hopanoid C <sub>31</sub> 22S (22S+22R)	hopanoid C <sub>32</sub> 22S (22S+22R)	tricyclic terpane ratio: C <sub>27</sub> /C <sub>21</sub>
X*/	6.9	2.3	0.3	1.3	1.02	0.62	0.60	0.59	1.40
Y*/	5.3	1.2	0.3	0.8	0.97	0.44	0.59	0.60	1.30
Z*/	3.1	2.8	0.9	1.9	1.06	0.46	0.62	0.58	1.74

X\*, Y\*, Z\* - the distance of investigated coals from intrusion was, respectively: 0-0.15 m, 1.00-1.10 m, 1.70-1.80 m

Table 2  
Geochemical parameter values calculated from mass chromatograms of the aromatic fraction of extracts from analysed coals: X, Y, Z.

Aromatic fraction of extract from coal:	DNR 1	MPR	MPR 1	MPI 1	MPI 3	PAI 1	DPR	MDBT (m/z198)	MDBT (AM1) (m/z198)	MDBT (AM2) (m/z198)	MDBT (AM3) (m/z184 +m/z198)	DMDBT (m/z212)
X	0.55	0.96	0.43	0.56	0.76	1.69	0.31	0.7	0.5	2.3	2.0	0.18
Y	0.92	1.15	0.35	0.60	0.86	1.61	0.34	0.8	0.7	3.6	4.9	0.25
Z	1.21	2.53	0.08	0.30	1.86	0.35	0.70	0.9	1.1	7.2	7.8	0.46

Table 3  
Petrographic data estimated for analysed coals: X, Y, Z.

Petrographic data / Coal sample	Average reflectance data:				Petrographic composition:			
	for vitrinite		for lipinite (sporinite)		for inertinite (semifusinite+ fusinite)		MM [%]	
	R <sub>o</sub> Vt [%]	S [%] **/ R(L) [%] ***/	R(L) [%] **/ R(I) [%] ***/	R(I) [%] ***/	Vt [%]	L [%]	I [%]	MM [%]
X	0.98	0.143	0.20	2.43	47	16	37	0
Y	1.32	0.404	0.40	2.33	39	22	38	1
Z	5.79	0.375	n.d./*	n.d.	n.d.	n.d.	n.d.	n.d.

n.d./\* not detected

S[%]/\*\* - standard deviation of R<sub>o</sub> Vt [%] data

R(L) [%], R(I) [%] \*\*\*/ - average values of reflectance, respectively, of (L): lipinitite (sporinite) and (I): inertinite (semifusinite and fusinite)

Moldovan [13] have stated that values of parameters after formula:  $[22S / (22S + 22R)]$  rise from 0 to about 0.6 with thermal maturity of sedimentary organic matter. Samples showing this ratio in the range of 0.50 to 0.54 have barely entered oil generation, while ratios in the range of 0.57 to 0.62 indicate that the main phase of oil generation has been reached or surpassed. Two last mentioned ranges are adequate for the hard coal state, and the higher one – for coals thermally altered by igneous intrusion (Table 1). For comparison, other own results can be quoted, obtained earlier [14] for some analysed coking coals from the Rybnik Coal Basin. The values were generally lower than these presented here in Table 1. For example, for coal sample from Jastrzębie mine the results were obtained as: 0.58 (for  $C_{31}$ ) and 0.55 (for  $C_{32}$ ). For coal sample from Borynia mine the respective values were of 0.56 and 0.58. For the neighbouring coal roof-shales these values were similar, as e.g.: 0.57 and 0.58 for the sample from Jastrzębie mine

*Steranes* and their rearranged analogues- *diasteranes* are main diagnostic molecular biomarkers in aliphatic fraction and are identified on the mass chromatograms at  $m/z$  217.

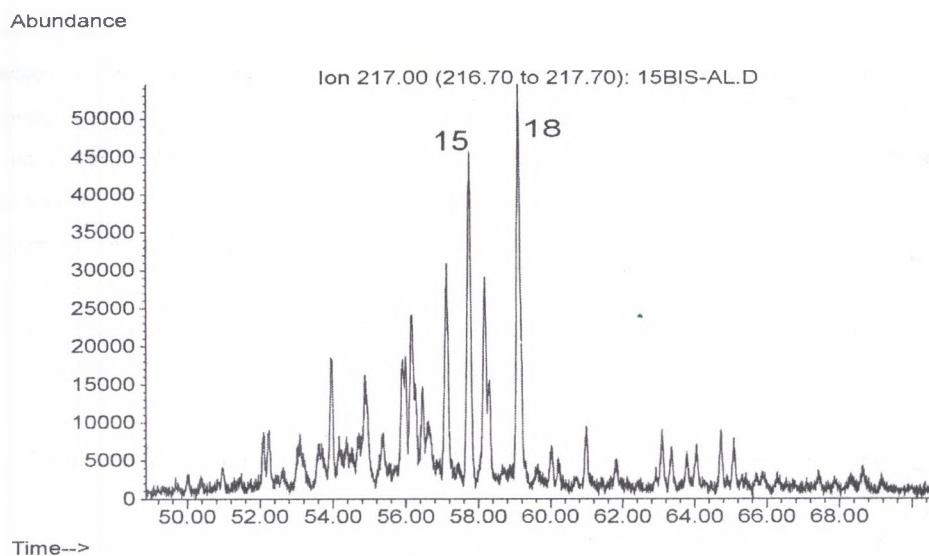


Fig. 4. Distribution of steranes ( $m/z$  217) in aliphatic fractions of extract of (X) coal sample. Marked numbers signify peaks of: 15/  $C_{29}$  (20S)-5 $\alpha$ (H),14 $\alpha$ (H),17 $\alpha$ (H)-24-ethylcholestane; 18/  $C_{29}$  (20R)- $\alpha$ (H),14 $\alpha$ (H),17 $\alpha$ (H)-24-ethylcholestane

Fig. 4 presents their distribution for aliphatic fraction of (X)- coal extract. After Bendall et al. [15] two peaks have been marked: No 15 ( $C_{29}$  (20S) - 5 $\alpha$  (H),14 $\alpha$ (H),17 $\alpha$ (H)-24-ethylcholestane) and No 18 ( $C_{29}$  (20R) - 5 $\alpha$  (H), 14 $\alpha$  (H), 17 $\alpha$  (H) - 24 -ethylcholestane).

Cholestanes are the  $14\alpha$  (H) –steranes. The configuration:  $5\alpha,14\alpha,17\alpha$  , 20R is an original, biological form of the sterane C<sub>29</sub> and can transform to the 20S configuration. The changes of the ratio values of amounts of stereoisomer 20S and 20R can, therefore, characterize transformations in the coal structure. On the basis of the intensities of relative peaks the parameters may be estimated such as:  $C_{29} \alpha\alpha \quad 20S/(20S+ 20R)$ . The results obtained for extracts from analyzed coals (Table 1) show that the value of the parameter under discussion is the highest for the sample from (X)-coal unaffected (or in very low degree) by intrusion heat. The markedly lower values were calculated for samples from coals (Y) and (Z) taken from a nearer distance to the intrusion. For the two last mentioned samples the parameter values are, moreover, very similar. The direction of changes was unexpected because the values should growth, after literature data. The decreasing of the parameter values calculated here is probably a result of a fast increase of temperature caused by intrusion action. Two parent coal samples: (Y) and (Z) are , moreover, highly mineralized what can additively influence the amounts of both stereoisomers mentioned [16].

*Tricyclic terpanes* have been here also taken into account because Peters and Moldowan [8] described them as thermally stable compounds. The distribution of terpanes in the aliphatic fraction was determined from m/z 191 ion chromatograms on the basis of two peaks at the retention times of 40.95 and 35.75 min, corresponding to C<sub>23</sub> and C<sub>21</sub> tricyclic terpane, respectively. The identification of respective peaks was made after George [17].The tricyclic terpane ratio  $C_{23}/C_{21}$  calculated after Ekweozor and Strausz [18] decreases with increasing maturity from sample X to Y . For the sample Z, however, the marked growth was observed of this parameter, probably because of a strong thermal transformation of (Z)-coal by intrusion (Table 1). It should be also underlined, that for sample Z this group of compounds have shown the relative highest peaks intensity.

### **The parameters calculated using GC/MS data for aromatic fraction of analysed coal extracts**

A very important group enabling estimation of thermal maturation indexes are aromatic compounds. The parameter values calculated after the literature data, basing on naphthalenes and phenanthrenes contents, indicate trends of changes, as it was expected. With temperature increasing the growth is observed of the contribution of unsubstituted aromatics and degree of alkylsubstitution tends to decrease.

*Dimethylnaphthalene Ratio.* This parameter was calculated after relation given by Radke et al. [19, 20]:  $DNR\ 1 = ([2,6\text{-DMN}] + [2,7\text{-DMN}]) / [1,5\text{-DMN}]$  , on the basis of respective

peaks intensity ratio. Identification of the peaks in ion chromatograms  $m/z$  156 was made after Leroy [21]. Dimethylnaphthalenes of 2,6- and 2,7-dimethylsubstitution are more stable in relation to the 1,5-substituted one. In accordance with this fact, the calculated values of this ratio growth with degree of thermal transformation from the sample X (0.55) up to Z (1.21) (Table1).

*Phenanthrene Indexes.* Methyl Phenanthrene Index MPI 1 was estimated on the basis of intensities of respective peaks in the mass chromatograms recorded at  $m/z$  192 characteristic for methyl-substituted phenanthrenes:  $MPI\ 1 = 1,5(2-MP + 3-MP)/(P + 1-MP + 9-MP)$ , where P signifies phenanthrene, and 1-, 2-, 3-, 9- MP are methylphenanthrenes. Among them these of 2- and 3- methyl substitution are more stable, whereas these ones of 1- and 9- methyl substitution form structures of lower stability [19,20,22]. An enhancement in the relative concentration of the isomer 2- and 3- and depletion of the isomers 1- and 9- of the methylphenanthrenes is observed with increasing thermal maturity of the parent coals. However, the unsubstituted phenanthrene dominates in relation to methylphenanthrenes for all samples of aromatic fractions of analysed extracts especially for the sample Z. It is a reason of the tendency of decrease of values of the parameter under discussion from about 0.6 for samples X and Y up to 0.3 for sample Z. It is in accordance with the literature data [22] indicating that MPI 1 growth up to end of oil window and then decrease.

Identification of peaks was made after Leroy [21] and presented in Fig. 5.

Radke et al.[23] have stated that in a broad range MPI 1 index correlates well with vitrinite reflectance, according to relations:

$$R_c [\%] = 0.60 MPI\ 1 + 0.40 \text{ (for } R_r \leq 1.35\%)$$

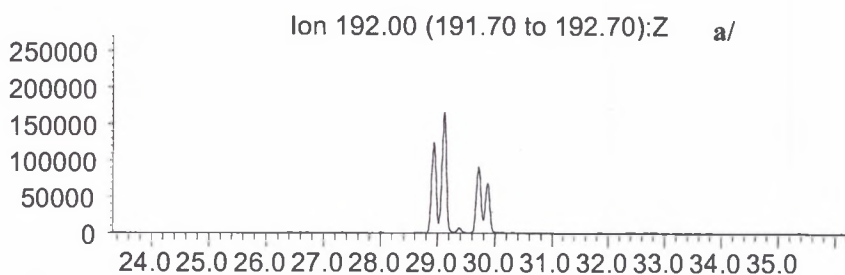
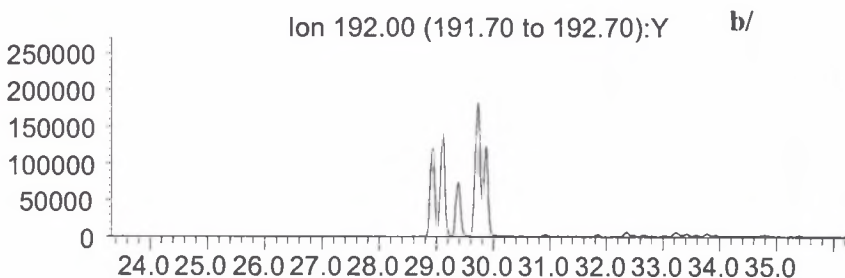
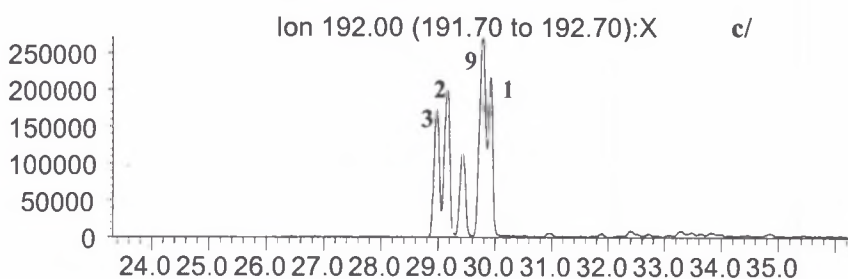
$$\text{or } R_c [\%] = -0.60 MPI\ 1 + 2.60 \text{ (for } R_r > 1.35\%)$$

Using the data calculated from ion chromatograms of aromatic fraction of extracts of analysed X,Y and Z-coals, the  $R_c$  values have been estimated: 0.74, 0.76 and 2.42%, respectively. These calculated data differ considerably in relation to experimental ones (Table 3).

The test was also made of the use of another relation between vitrinite reflectance and methylphenanthrene index, given by Radke [24]:  $R_m [\%] = 0.95 + 1.10 \log MPR$  (correlation coefficient  $r = +0.95$ ). MPR is the index given by Radke et al. [19]:  $MPR = 2-MP/1-MP$ , where (1-) is an alkyl substitution position of lower stability than the (2-) one.

The values of the parameter MPR estimated for analysed samples, presented in Table 2, enabled to calculate values of vitrinite reflectance of: 0.93, 1.02 and 1.39 %, respectively for samples X,Y,Z.

Abundan

Time--  
AbundanTime--  
Abundan

Time--

Fig. 5. Distribution of 1-, 2-, 3-, and 9-methylphenanthrenes in aromatic fractions of extracts of coals: a/ (Z), b/ (Y), c/ (X)

Abundance

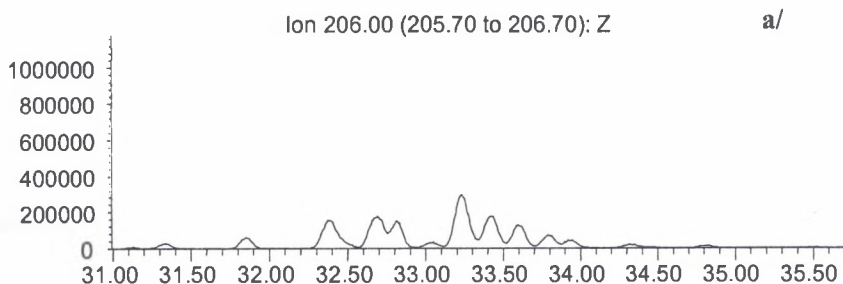
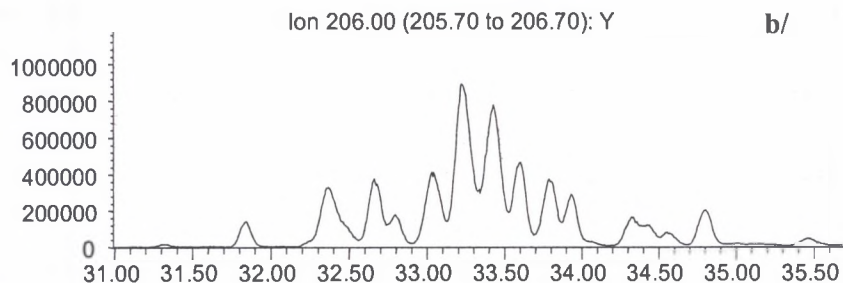
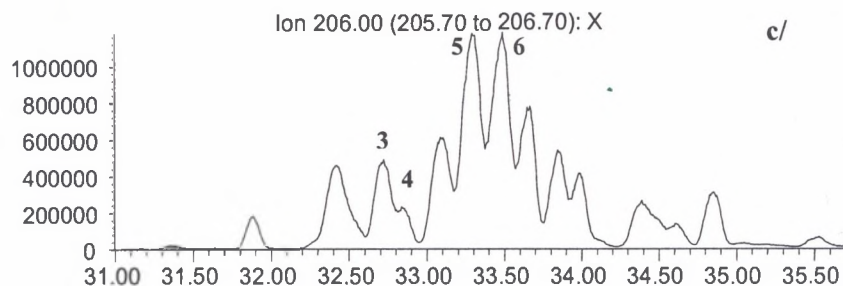
Time-->  
AbundanceTime-->  
Abundance

Fig. 6. Distribution of dimethylphenanthrenes in aromatic fractions of extracts of coals: a/ (Z), b/ (Y), c/ (X). The peaks are marked of dimethylphenanthrenes taken to calculation of DMP – parameter : 3 : 2,6-dimethylphenanthrene; 4: 2,7-dimethylphenanthrene; 5: 2,9- + 2,10- + 3,10- + 1,3-dimethylphenanthrene; 6: 1,6- + 2,9- dimethylphenanthrene

The differences between calculated (using MPI 1 and MPR parameters) and experimental data of vitrinite reflectance for analysed coals could be explained by the fact that investigated coals undergone a thermal shock caused by intrusion, whereas relation between R[%] and methylphenanthrene indexes were estimated for normal thermal maturation process occurring much more slowly in the geological time. It is confirmed by the value Ro of 0.93 % (mostly approaching the experimental value: 0.98 %), calculated on the basis of MPR parameter for (X)-coal affected at the weakest by intrusion.

Simplified relation between stable (2-, 3-) and unstable (1-, 9-) methylphenanthrenes mentioned earlier, presents a parameter MPI 3 [19]:

$$\text{MPI 3} = ([2\text{-MP}] + [3\text{-MP}]) / ([9\text{-MP}] + [1\text{-MP}])$$

The values of this parameter grow with thermal maturity of parent coal samples (Table 2). This relation is also visible clearly in Fig.5 in the direction from sample from coal (X) (Fig. 5c) up to (Z) (Fig. 5a).

Other else useful methylphenanthrene indexes were proposed by Radke et al. [20]

$$\text{MPR 1} = 1\text{-MP} / \text{P}$$

and so called Phenanthrene Alkylation Index:

$$\text{PAI 1} = ([1\text{-MP}] + [2\text{-MP}] + [3\text{-MP}] + [9\text{-MP}]) / [\text{P}].$$

The values calculated (Table 2) decrease with growth of thermal maturity from parent coal sample (X) up to (Z), what is in accordance with the known tendency, in this direction, of contribution decreasing of alkyl-substituted versus unsubstituted aromatic rings. .

Dimethylphenanthrene Ratio DPR =  $([DMP3] + [DMP4]) / ([DMP5] + [DMP6])$

(where numbers of: 3,4,5,6 signify dimethylphenanthrenes with dimethyl substitution as follows: 2,6-, 2,7-, (1,3- + 2,10 + 3,9- + 3,10-) and (1,6- + 2,9-) , respectively, ([25]) was calculated after estimation the intensities of respective bands on mass chromatograms m/z 206 (Fig. 6) of aromatic fractions of extracts from analysed coals. The dominating more stable structures having contribution to the values of a nominator of this ratio caused his growth from 0.31 for sample X to 0.70 for sample Z (Table 2). This fact was attributed a thermal rearrangement of the unstable dimethylphenanthrenes to the sterically more stable ones.

*Dibenzothiophenes.* The geochemical indexes used most frequently, presented above, have been completed by some other parameters based on the dibenzothiophene group of compounds, well diversifying thermal altered organic matter. The compounds indicate as well the thermal processing as its hydrothermal conditions [20, 23].

In Table 2 the values are presented of some parameters calculated after relations taken from literature as well as own ones. The parameters were calculated similarly as presented



earlier, by estimation of intensities of the respective peaks on the specific ion chromatograms. Ion chromatograms, recorded at  $m/z$  198 for aromatic fraction of extracts of investigated coals, were used for calculation methyl dibenzothiophene index MDBT after relation given by Radke et al. [26]. The values of this parameter growth rather regularly as distance from intrusion decreases of parent coal sampling.

Own indexes were also applied with the use of the ratios between intensities of peaks of various methyl dibenzothiophenes existing on the ion chromatogram  $m/z$  198 at the retention times: 28.26 and 27.30 minutes (index MDBT (AM 1)) as well as at : 27.63 and 28.99 minutes (index MDBT (AM 2)) (Table 2). Third own index MDBT (AM 3) was based on two normalised ion chromatograms  $m/z$  184 and  $m/z$  198 . Values of the index were calculated as a ratio of intensities of dibenzothiophene peak (retention time: 24.45minutes) and methyl dibenzothiophene peak appearing at the retention time of 27,63 minutes. All these own parameters seem to be useful for comparisons because their marked growth is observed with intensity of heat-affecting of the parent coals (from X to Z sample) (Table2).

Another parameter (DMDBT) was calculated from ion chromatogram  $m/z$  212, using relation for dimethyl dibenzothiophenes given by Radke et al. [26]. The values change also markedly as a function of the distance of parent coal to intrusion (Table 2).

## Petrographic parameters

The petrographic composition of analysed samples was measured (Table 3) but it was very difficult to differentiate particular macerals in (Z)-coal because of a high thermal alteration. The vitrinite reflectance increased from 0.98 up to 5.79% , indicating considerable structural changes from coal sample (X) to (Z) as a function of the distance from intrusion and, therefore, as the function of temperature of heating. Broadening of histograms described by  $S[\%]$  parameter is also indicative for occurring changes. Liptinite reflectance (determined for sporinite) shows a tendency of increase, whereas inertinite reflectance (determined for semifusinite and fusinite) changes slightly in the investigated range from the (X) to the (Y)-coal. Very interesting microscopic image differences were also observed for particular coal samples as e.g. gradual growth of degassification pores.

A slight vesiculation was already observed for the X- coal vitrinite what signifies that heat flow have reached also this coal. Low coalification degree (a flame stage) indicates, however, low degree of the heat affection. In this case a long time factor was rather important of low-

temperature changes as well as a pressure influence of the cap-rock, being capable to inhibition of degassification processes.

## Conclusions

Geochemical and petrographic investigations enabled to state a high degree of a heat-affectation of the analysed coal from the contact zone what indicates a high primary temperature of the intrusive body.

The vitrinite reflectance shows the considerable structural changes, increasing from 0.98% at a the distance of about two meters from intrusion up to 5.79% in a contact zone. Simultaneous alteration of vesiculation degree was observed in microscopic image, what characterises well a progress of degassification controlling alterations of the coal structure in a function of the distance from intrusion.

Geochemical parameter values estimated on a basis of mass chromatograms for the molecular phase of coals (i.e. for coal extract fractions) were useful to characterisation of thermal alterations occurring in a coal structure as a whole, being in a well accordance with thermal changes degree estimated by petrographic analysis. The most useful for description of the changes in chemical structure of metamorphosed coals are indexes basing on the contents of aromatic compounds of various degree of alkyl substitution and condensation.

The mineral constituents as well as a presence of dibenzothiophenes seem to suggest the hydrothermal conditions accompanying the heat affluence of the intrusion on investigated coal transformations.

## BIBLIOGRAPHY

1. Gabzdyl, W., Dudziak, T., Tomica, J.: Przejawy wulkanizmu w strefie nasunięcia michałkowickiego i fałdu orłowskiego w NW części GZW, *Przegl. Geol.*, 3, 1969, s.139-142.
2. Duźniak S., Gabzdyl W., Kapuściński T.: Intruzja bazaltowa i jej wpływ na węgiel w pokładzie 507 Kopalni Sośnica, *Przegląd Górniczy*, 12, 1976, s. 524-528.
3. Kapuściński T., Proberz K., Strzałkowska E., Kubik A., Drobiazgiewicz W.: O występowaniu intruzji magmowej w warstwach siedłowych kopalni Sośnica (Górnośląskie Zagłębie Węglowe) i jej wpływie na węgiel pokładu 501/3, *Zeszyty Naukowe Politechniki Śląskiej*, s. Górnictwo, z. 187, Nr 1066, 1990, s.97-115.

4. Chodyniecka, L., Hanak, B., Intruzja z pokładu 414/3 w kopalni Sośnica (GZW) i jej wpływ na otaczający ją węgiel. Zeszyty Naukowe Politechniki Śląskiej , s. Górnictwo, z. 246, 2000, s.55-72.
5. Matuszewska A.: Charakterystyka stopnia metamorfizmu wybranych węgli z KWK „Sośnica” w GZW na podstawie składu pirolizatów węglowych, Materiały XXVI Sympozjum nt. Geologia Formacji Węglonośnych Polski, AGH, Kraków, 2003, s.97-102.
6. Hunt J. M.: Petroleum Geochemistry and Geology, W. Freeman and Co., New York ,1996.
7. Bray E. E., Evans E.D.: Distribution of n-parafins as a clue to recognition of source beds, *Geochim. Cosmochim. Acta*, 22, 1961, s.2-15.
8. Peters K. E., Moldowan J.M.: The Biomarker Guide. Interpreting Molecular Fossils in Petroleum and Ancient Sediments, Prentice Hall, Englewood, Cliffs, New Jersey, 1993.
9. Tissot B. P., Welte D.H.: Petroleum Formation and Occurrence, 2<sup>nd</sup> Edn., Springer-Verlag, Berlin, 1984.
10. Tissot B., Califet-Debyser, Y., Deroo G., Oudin J.L.: Origin and evolution of hydrocarbons in early Toarcian shales, Paris Basin, France, *American Association of Petroleum Geologists Bulletin*, 55, 1971, s.2177-2193.
11. Clayton J.L., Bostick N.H.: Temperature effects on kerogen and on molecular and isotopic composition of organic matter in Pierre Shale near an igneous dike, *Org. Geochem.*, 10, 1986, s.135-143.
12. Ensminger A., van Dorsselaer A., Spycykerelle C., Albrecht P., Ourisson G.: Pentacyclic triterpenes of the hopan type as ubiquitous geochemical markers: Origin and significance. In: *Advances in Organic Geochemistry, 1973* (B.Tissot and F.Bierner, eds.) Éditions Technip., Paris, 1974, s. 245-260.
13. Seifert W.K., Moldowan J.M.: Use of biological markers in petroleum exploration. In: *Methods in geochemistry and geophysics* (ed. R.B. Johns), 24, 1986, 262-290.
14. Matuszewska A.: Geochemical interpretation and comparison of biomarker composition of bitumens obtained from coals and surrounding rocks , *Proceed. of the IV European Coal Conference*, Polish Geol. Inst. Special Papers, Warszawa, 7, 2002, s. 169-180.
15. Bendall M.R., Volkman J.K., Leaman D.E., Burrett C.F.: Recent developments in exploration for oil in Tasmania, *APEA J.*, 31, 1991, s.74-84.
16. Matuszewska A.: Diagnostyka stopnia przeobrażenia depozytów materii organicznej poprzez badanie zróżnicowania składu frakcji węglowodorowej w fazie molekularnej kaustobiolitów, *Sprawozdanie z grantu KBN Nr 1087/PO4/97/12*, Warszawa, 1999.
17. George S.C.: Effect of igneous intrusion on the organic geochemistry of a siltstone and an oil shale in the Midland Valley of Scotland, *Org. Geochem.*, 18, 705-723, 1992.
18. Ekweozor C.M., Strausz O.P.: Tricyclic terpanes in the Athabasca oil sands: Their geochemistry. In: *Advances in Organic Geochemistry 1981*, (Bjørøy et al. , Eds.) Wiley, Chichester, 1983, s.746-766.
19. Radke M., Willsch H., Leythaeuser D., Teichmüller M.: Aromatic components of coal: relation of distribution pattern to rank. *Geochim. Cosmochim. Acta*, 46, 1982, s. 1831-1848.
20. Radke M., Welte D.H., Willsch H.: Geochemical study on a well in the Western Canada Basin: relation of aromatic distribution pattern to maturity of organic matter, *Geochim. Cosmochim. Acta* , 46, 1982, s.1-10.
21. Leroy E.: Aromatic hydrocarbons in crude oil and sediments , Doctor`s Thesis, Curtin University of Technology, October, 1994.
22. Radke M., Welte D.H.: The methylphenanthrene index (MPI): a maturity parameter based on aromatic hydrocarbons. In: *Advances in Organic Geochemistry 1981* (Ed. by Bjørøy M. et al., Wiley, Chichester,1983.

23. Radke M., Welte D.H., Willsch H.: Distribution of alkylated aromatic hydrocarbons and dibenzothiophenes in rocks of the Upper Rhine Graben, *Chem. Geol.*, 93, 1991, s.325-341.
24. Radke M.: Application of aromatic compounds as maturity indicators in source rocks and crude oils, *Marine and Petroleum Geology*, 5, 1988, s. 224-236.
25. Radke M., Leythaeuser D., Teichmüller M.: Relationship between rank and composition of aromatic hydrocarbons for coals of different origins., *Org. Geochem.*, 6, 1984, s.423-440.
26. Radke M., Welte D.H., Willsch H.: Maturity parameters based on aromatic hydrocarbons: influence of organic matter type, *Organic Geochemistry*, 10, 1986, s.51-56.

Recenzent: Dr hab. inż. Krystian Probiez prof. nzw. w Pol. Śl.

### Abstract

The preliminary results are presented of geochemical and petrographic investigations of coal from 416-bed of hard coal mine „Sośnica” (Upper Silesia Basin), heat affected by igneous intrusion. The thermal changes of coal structure and properties were analysed, as a function of sampling distances from igneous intrusion. The intrusion caused a considerable thermal transformation, up to the anthracite stage, of coal from contact zone. Coal sampled from a distance of about 1 m. from intrusion was classified as the 38-type and coal taken from the distance of about 2 m. was a flame coal of the 31.2-type. Flame stage was probably a primary for analysed coals before intrusion influence. The two-meter distance seems to be approximate distance of intrusion affection because of low stage of coal sampled there and its physicochemical characteristics. A high thermal gradient in this range is characterised well by the values of vitrinite reflectance changing here from 5.79% for the sample from contact zone up to 0.98% for coal taken at two-meter distance from intrusion. Microscope observation of simultaneous growth of reflectance of other macerals, splits appearing and increase of degassing pores, enabled to compare a degree of thermal transformation of coals versus the distance from intrusion.

The petrographic characteristics was compared with the changes of values of chosen geochemical parameters. These parameters were estimated on the basis of the mass chromatograms obtained with the use of GC/MS method for hydrocarbon fractions of the molecular phase of coal. The phase was separated from coals by solvent extraction process. The parameters calculated characterise thermolytic changes occurring in the aliphatic group of

compounds (chosen biomarkers including) and in aromatics. It was simultaneously confirmed, that for diversification of a broad coalification range, the most useful are, however, parameters basing on aromatics, especially, when deep thermal processes are to investigation. During thermolysis, the aromatic compounds change by alkyl substitution as well as by condensation degree. The changes observed are a result of thermodynamically advantageous direction of transformation leading to cyclisation and next to aromatisation of heated organic matter. The aromatisation process of coaly structure is in turn a reason of variations in physical coal properties, as e.g. increasing of vitrinite reflectance. The degree of thermal transformations of coal organic matter may be also characterised well by changes occurring of amounts of dibenzothiophene type compounds. Their presence can also confirm, as well as some geochemical and mineralogical data, the hydrothermal conditions of transformations in the zone of heat flow of intrusion.