

**SOME ASPECTS OF THE USE OF PY–GC–MS  
TO INVESTIGATE THE COMPOSITION  
OF THE AROMATIC FRACTION  
OF HARD COAL PYROLYSATES**

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**SUMMARY**

Py–GC–MS has been used to compare the extent of transformation of hard coals from a bed thermally affected by magmatic intrusion. The coal samples under investigation originated from bed 416 of the “Sośnica” coal mine (USCB, Poland). They were taken at different distances from the intrusion and were thus subjected to different amounts of metamorphosis. To assess changes in chemical structure caused by the intrusion comparative analysis was performed by GC–MS of pyrolysates obtained at different temperatures – 358, 480, 610, 770, and 980°C. Comparisons were based on the distribution of aromatic compounds, chiefly naphthalene and its methyl derivatives. The trend was for the amount of methyl substitution of the naphthalene rings to decrease with increasing temperature with, moreover, a relative preference for the more stable  $\beta$  substitution position rather than the  $\alpha$  position. Some comparative numerical data, ratios of the intensities of the GC–MS peaks, were calculated.

**INTRODUCTION**

In geochemical investigations the origin, sedimentation conditions, and the extent of diagenesis, catagenesis, or metamorphism of fossil organic matter can be described on the basis of the distribution of characteristic compounds or groups of compounds. The compounds usually investigated for this purpose are aliphatic and aromatic hydrocarbons and so-called biomarkers – compounds of different nature which indirectly characterize the features of precursor organic matter and the extent of its transformation. In studies of this type modern analytical methods, for example GC–MS,

furnish more detailed information about the complex composition of organic substances of natural origin.

The structure of many organic fossils, including hard coal, includes a macromolecular network not accessible to direct investigation. Information on structures such as these can be obtained indirectly by analysis of the molecular phase separated from the pores of macromolecules by an extraction process. Another means of investigation is partial destruction of the macromolecules by thermal splitting (pyrolysis, Py) of their peripheral fragments. For this purpose combined Py–GC–MS enables direct introduction of the obtained pyrolysates into analytical GC–MS equipment. Py–GC–MS enables a pyrolysis of samples at different temperatures by use of ferromagnetic filaments made of alloys with different Curie-point temperatures – the temperature at which a metal loses its ferromagnetism, becomes paramagnetic, and the heating effect decreases substantially. The intrinsic feature of this method is flash pyrolysis in a short time, i.e. up to several seconds. This in turn leads to substantial preservation of the primary structure of fragments split from the pyrolysed macromolecule.

This paper reports the use of Py–GC–MS for analysis of hard coals thermally affected by magmatic intrusion, a phenomenon known as “contact metamorphism” and defined as a process occurring as the consequence of high temperature resulting from contact with an intrusive body [1]. In this work the extent of thermal changes in the chemical structure of coals chiefly depended on the distance of the coal deposit from the heat source and the objective of the investigation was to determine how the chemical composition of the analysed coals depended on the extent of metamorphism, by comparing results obtained by Py–GC–MS of coal samples at different pyrolysis temperatures.

The organic matter in hard coal has undergone advanced transformation as a result of a variety of geological factors. Investigation of aromatic compounds is, because of their high thermodynamic stability, a very effective means of characterising fossil organic matter on the basis of the stage of coalification, especially after additive heating by intrusion. For this reason this group of compounds was studied in this work. The naphthalene compounds were chosen for detailed discussion because of the distribution of naphthalene and its methyl-substituted derivatives. For comparative purposes mass chromatograms were used to calculate numerical values of ratios of peak intensities.

## EXPERIMENTAL

### Characteristics of the Samples Analysed

Three hard coal samples from the “Sośnica” mine in the Upper Silesian Coal Basin (USCB, Poland) were selected for investigation. They were taken from the 416 bed, at different distances (1.7, 1.0, and 0.00–0.15 m) from an intrusive body. The intensity of heating of these samples of coal by the intrusion, and thus the extent of metamorphism, was, therefore, different. Sample no. 15 taken 1.7 m from the intrusion was probably affected very weakly (or even not at all) by the heat; it was described technologically as a flame coal (31.2 type in the Polish classification, 500 type in the international classification). Sample no. 8, taken 1.0 m from intrusion was a lean coal (38 type in the Polish classification, 400 in the international classification). Sample no. 1, taken in direct proximity to the intrusion was from a position described in the mine documents as a zone of anthracite with high mineralisation. X-ray analysis of sample no. 1 enabled assessment of the level of dolomite – the main mineral component in this sample – as approximately 65%.

For comparative purposes the samples were first extracted in a Soxhlet apparatus with dichloromethane–methanol, 97:3 (v/v), as solvent. The extracts obtained were separated into aliphatic, aromatic, and polar fractions by preparative TLC on precoated silica gel plates (Merck) with *n*-hexane as mobile phase. Aromatic fractions were then isolated and analysed by GC–MS.

The raw coal samples were then submitted to Curie-point pyrolysis, which takes advantage of ferromagnetic filaments inductively heated to their Curie points. Different filaments were used to enable pyrolysis at different temperatures – 358, 480, 610, 770, and 980°C. The pyrolysates obtained were analysed by GC–MS coupled on line to the pyrolyser.

### Instrumentation

#### *Gas Chromatography–Mass Spectrometry*

Gas chromatography was performed with a Hewlett–Packard (HP) chromatograph equipped with a 60 m × 0.25 mm i.d., 0.25 μm film, HP-5 column and coupled to an HP mass spectrometer. Helium was used as carrier gas. The column oven temperature was held isothermally at 50°C for 2 min, then programmed at 10° min<sup>-1</sup> to 175°C, then at 6° min<sup>-1</sup> to 225°C, and finally at 4° min<sup>-1</sup> to 300°C which was held for 20 min. The

mass spectrometer was operated in electron-impact ionization mode, electron energy 70 eV, and scanned from 650 to 50 da. Data were acquired in full-scan mode and processed with HP Chemstation software. Compounds were identified from their mass spectra, by comparison of the retention times of peaks with those of standard compounds, by use of literature data, and by interpretation of MS fragmentation patterns.

#### *Flash Pyrolysis–Gas Chromatography–Mass Spectrometry*

A Pye–Unicam Curie-point pyrolyser, type 795050, was coupled to an HP gas chromatograph equipped with a 60 m × 0.32 mm i.d., 0.52 µm film, HP-1 column and coupled to an HP mass spectrometer. Helium was used as carrier gas. The column oven temperature was programmed from 50°C to 175°C at 10° min<sup>-1</sup>, then to 225°C at 6° min<sup>-1</sup>, and finally to 300°C at 4° min<sup>-1</sup>. The mass spectrometer was operated in electron-impact ionization mode, electron energy 70 eV, and scanned from 650 to 50 da. Data were acquired in full-scan mode and processed with HP Chemstation software.

## **RESULTS AND DISCUSSION**

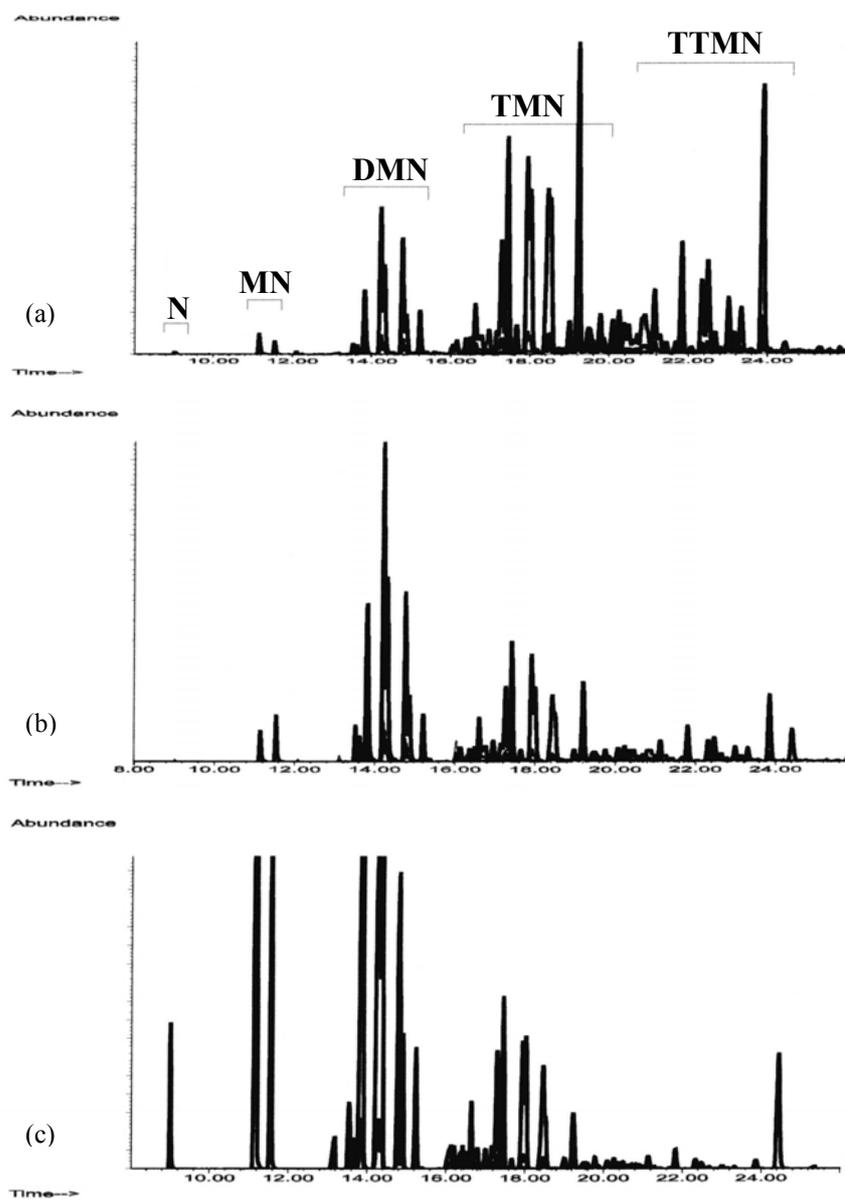
The coal samples under investigation, taken at different distances from the intrusion (no. 15, 1.7 m; no. 8, 1.0 m; no. 1, direct contact with the intrusive body), were characterised by different amounts of primary thermal transformation by the heat from the intrusion. The changes of the properties of the coal were, to some extent, a function of the distance from the intrusion, as the source of the heat. In this work the extent of the differentiation was characterised by secondary thermolysis – by means of a pyrolyser coupled to GC–MS equipment. Pyrograms of different shape were expected, depending on the extent of primary thermolysis in the coal seam. Separate sub-samples of each coal sample were pyrolysed at 358, 480, 610, 770, and 980°C. The mass chromatograms recorded were indicative of substantial differences between the pyrolysates obtained from the different coals and at the different temperatures. Differences between the results obtained from samples 8 and 15 were, however, much less marked than differences between results from sample 1 and the other two samples. Differences between the distribution of compounds obtained by pyrolysis tended to be less for samples pyrolysed at 980°C.

From among the compounds present in the pyrolysates, a group of aromatic compounds was selected for discussion. Aromatic compounds are

especially characteristic of the hard coal stage of coalification and are generated from coals in substantial amounts during different types of thermal processing. They are also compounds regarded as undesirable products of thermal processing of coal, and interesting in terms of environmental protection. Preliminary analysis indicated that 1- and 2-ring aromatic compounds predominated, followed by smaller amounts of tricyclic compounds and much lower amounts of 4- and 5-ring condensed aromatic systems. Characteristic polycyclic aromatic hydrocarbons identified in coal include pyrene, fluoranthene, chrysene, benzo(*a*)anthracene, benzofluoranthenes, benzo(*a*)pyrene, and perylene. It should be emphasised that only vestigial amounts of this type of aromatic compound was present in the pyrolysates obtained from sample no. 1, probably because of incorporation of polycyclic aromatic hydrocarbons (PAH) into the coal macromolecule during the intense heating resulting from direct contact with the intrusion. Literature data [2–5] confirm the possibility of incorporation of the PAH into the structure of coke during different coal thermolysis processes. Further heating during laboratory pyrolysis probably has a similar effect and might explain the relatively small amount of PAH in the pyrolysates obtained from the other analysed coals, as mentioned earlier.

Phenanthrene and its alkyl derivatives afforded more intense peaks than the PAH but benzene and naphthalene derivatives predominated. The substantial amounts and diverse distribution of naphthalene and its methyl derivatives were the reason for selection of this group of compounds for the more detailed studies.

For comparative purposes an initial assessment was made of differences between the molecules present in solvent extracts obtained from the coal samples. Differences between the amounts of naphthalene-group compounds in the aromatic fractions obtained from the extracts are shown in Figs 1a–c. Mass chromatograms were recorded at  $m/z$  128 (for identification of naphthalene, N), 142 (methylnaphthalenes, MN), 156 (dimethylnaphthalenes, DMN), 170 (trimethylnaphthalenes, TMN), and 184 (tetramethylnaphthalenes, TTMN). The general tendency was an increase in the relative amount of unsubstituted naphthalene and a decrease in the amount of methyl substitution from the extract obtained from sample 15 (probably not thermally affected by the intrusion or affected only slightly) to the extract from sample 1 (from the contact zone). Substantial amounts of di-, tri-, and tetramethyl-substituted naphthalenes are apparent in Fig. 1a, from coal no. 15. Dimethylnaphthalenes predominate in extracts from sample 8 (Fig. 1b). An intense peak for unsubstituted naphthalene was obtained from the



**Fig. 1**

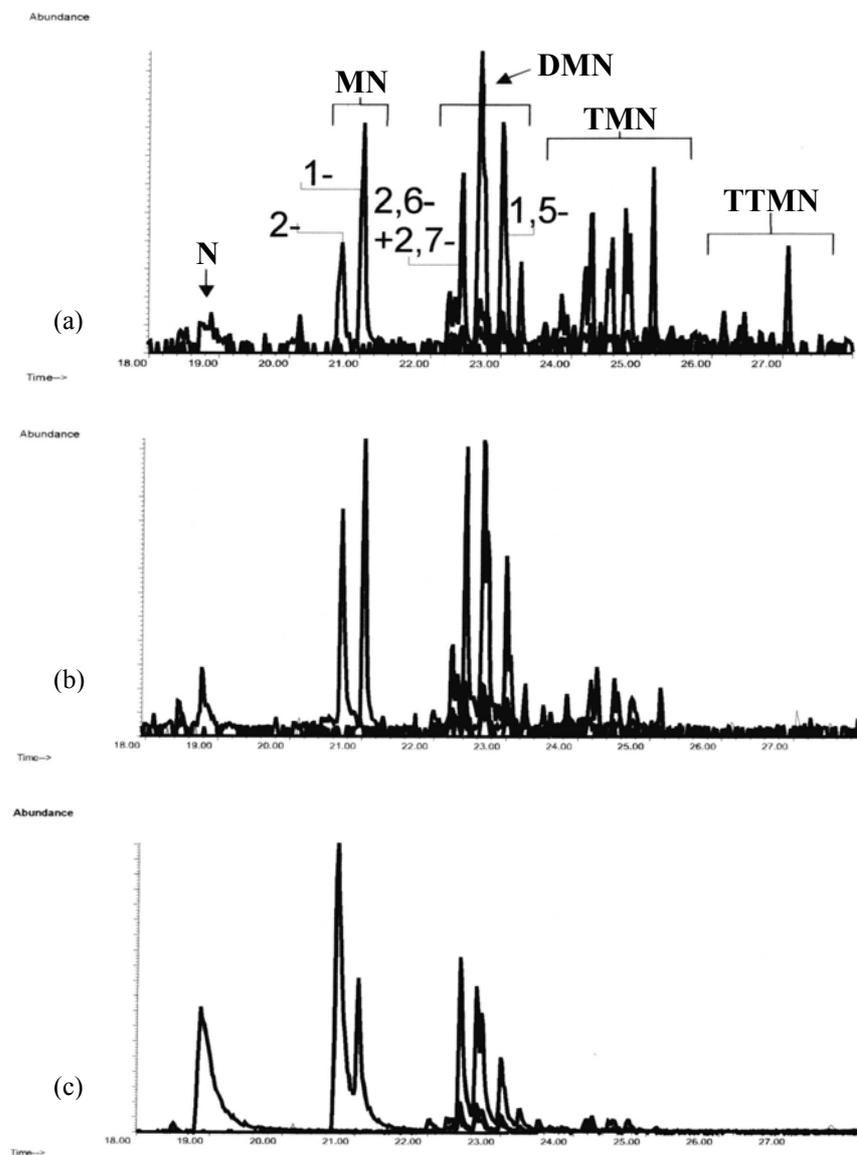
Mass chromatograms of naphthalene group compounds recorded for extracts obtained from coal samples 15 (a), 8 (b), and 1 (c). N, naphthalene ( $m/z$  128); MN, methylnaphthalenes ( $m/z$  142); DMN, dimethylnaphthalenes ( $m/z$  156); TMN, trimethylnaphthalenes ( $m/z$  170); TTMN, tetramethylnaphthalenes ( $m/z$  184)

extract from sample 1 (this is one of more characteristic features of the thermal treatment of coal) and much monomethyl and dimethyl substitution of the naphthalene ring is also apparent (Fig. 1c). In general, the thermal effect of magmatic intrusion in a coal bed is thus similar to changes in the distribution of aromatic fractions which result from the technological processes used for thermal treatment of coal [6].

A series of mass chromatograms of naphthalene and methyl-substituted naphthalenes was recorded for the pyrolysates in the same way as reported earlier for the solvent extracts. Changes in the distribution of these compounds with pyrolysis temperature and the dependence of these differences on the nature of the parent coal samples are shown in Figs 2–6.

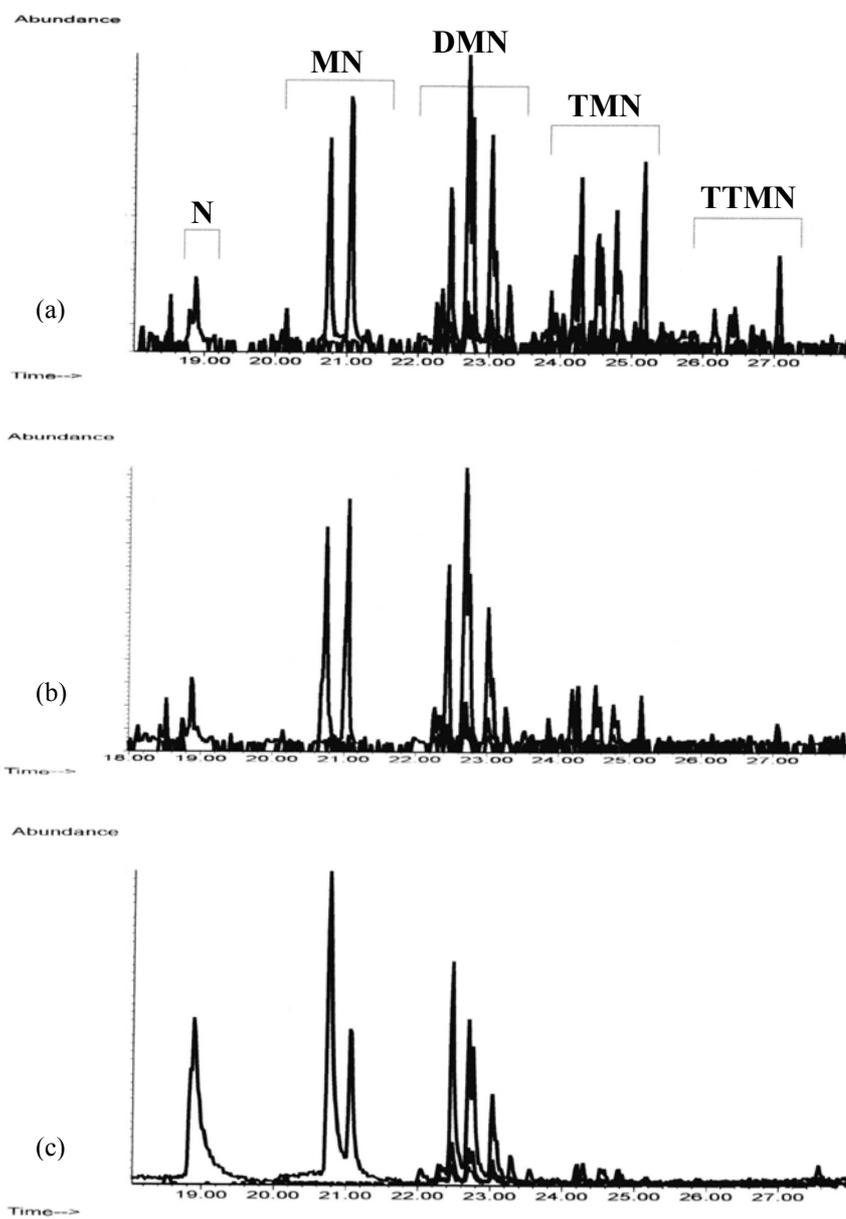
Figure 2 shows the mass chromatograms obtained from the naphthalene compounds under discussion for pyrolysates obtained at 358°C. Differences among the general shapes of the mass chromatograms obtained from the pyrolysates seem to characterise well the geological thermal history of the parent samples, in the same way as the mass chromatograms obtained from the solvent extracts. Compared with the mass chromatograms obtained from the solvent extracts, however (Fig. 1), the increase in the relative intensities of peaks of monosubstituted naphthalenes in the pyrolysates obtained from samples 15 and 8 as a result of the high pyrolysis temperature should be noticed.

No differences can be distinguished between the pyrogram obtained at the higher temperature of 480°C (Fig. 3) and that obtained at 358°C. When pyrolysis is performed at 610°C more significant changes are observed in the pyrograms obtained from samples 15 and 8, but not so for that obtained from sample 1 (Fig. 4). For the pyrolysates from samples 15 and 8 a further shift toward a lower degree of substitution, i.e. toward monomethyl substituted naphthalenes, is observed. The great similarity of the pyrograms obtained from these two samples in this temperature range should also be noticed. The lack of noticeable changes in the profiles of the pyrograms obtained from sample 1 up to a pyrolysis temperature of 610°C suggests, moreover, that the probable temperature of the intrusion was also above 600°C. Although this is only hypothesis, and requires confirmation by other methods, the suggestion is in agreement with data given by other authors [7] for coals from other beds in the same mine. There were probably several intrusions during the tertiary period in different parts of the mine. For coal from seam 501/3 of this mine the temperature of the intrusive body was assessed (on a basis of petrographic data) as above 500–600°C [7].



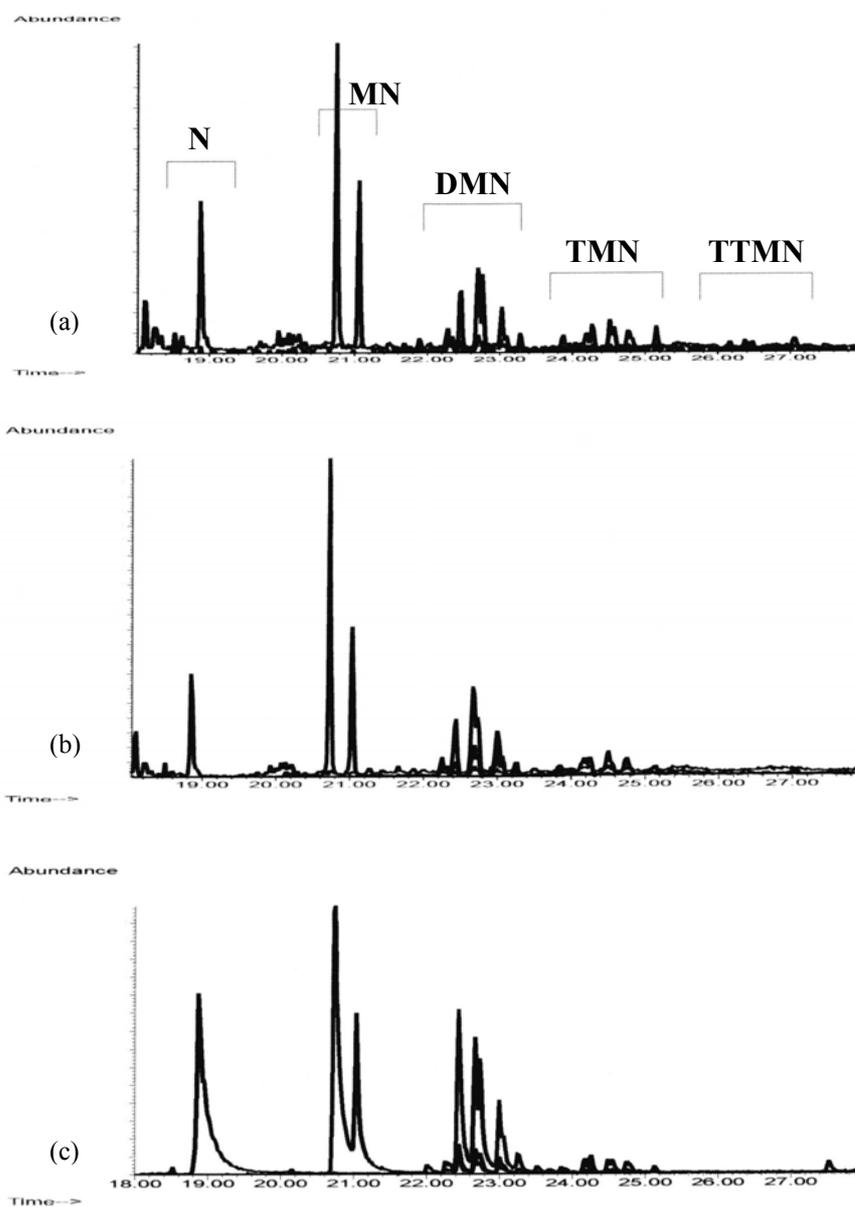
**Fig. 2**

Mass chromatograms of naphthalene group compounds recorded for pyrolysates obtained at 358°C from coal samples 15 (a), 8 (b), and 1 (c). N, naphthalene ( $m/z$  128); MN, methylnaphthalenes ( $m/z$  142), 2- and 1- are 2- and 1-methylnaphthalene, respectively; DMN, dimethylnaphthalenes ( $m/z$  156), 2,6-, 2,7-, and 1,5- are 2,6-, 2,7- and 1,5-dimethylnaphthalene, respectively; TMN, trimethylnaphthalenes ( $m/z$  170); TTMN, tetramethylnaphthalenes ( $m/z$  184)



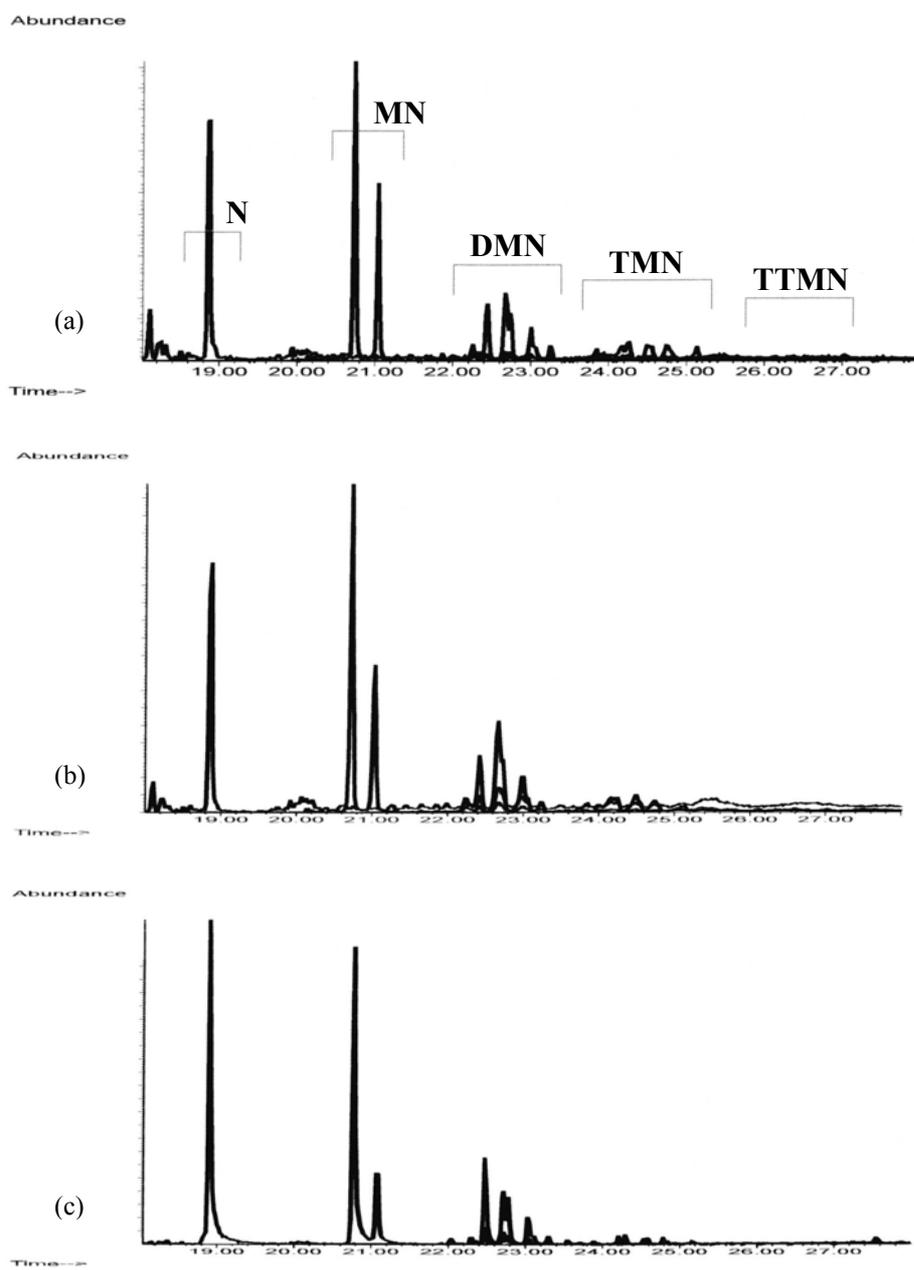
**Fig. 3**

Mass chromatograms of naphthalene group compounds recorded for pyrolysates obtained at 480°C from coal samples 15 (a), 8 (b), and 1 (c). Peak identities as for Fig. 1



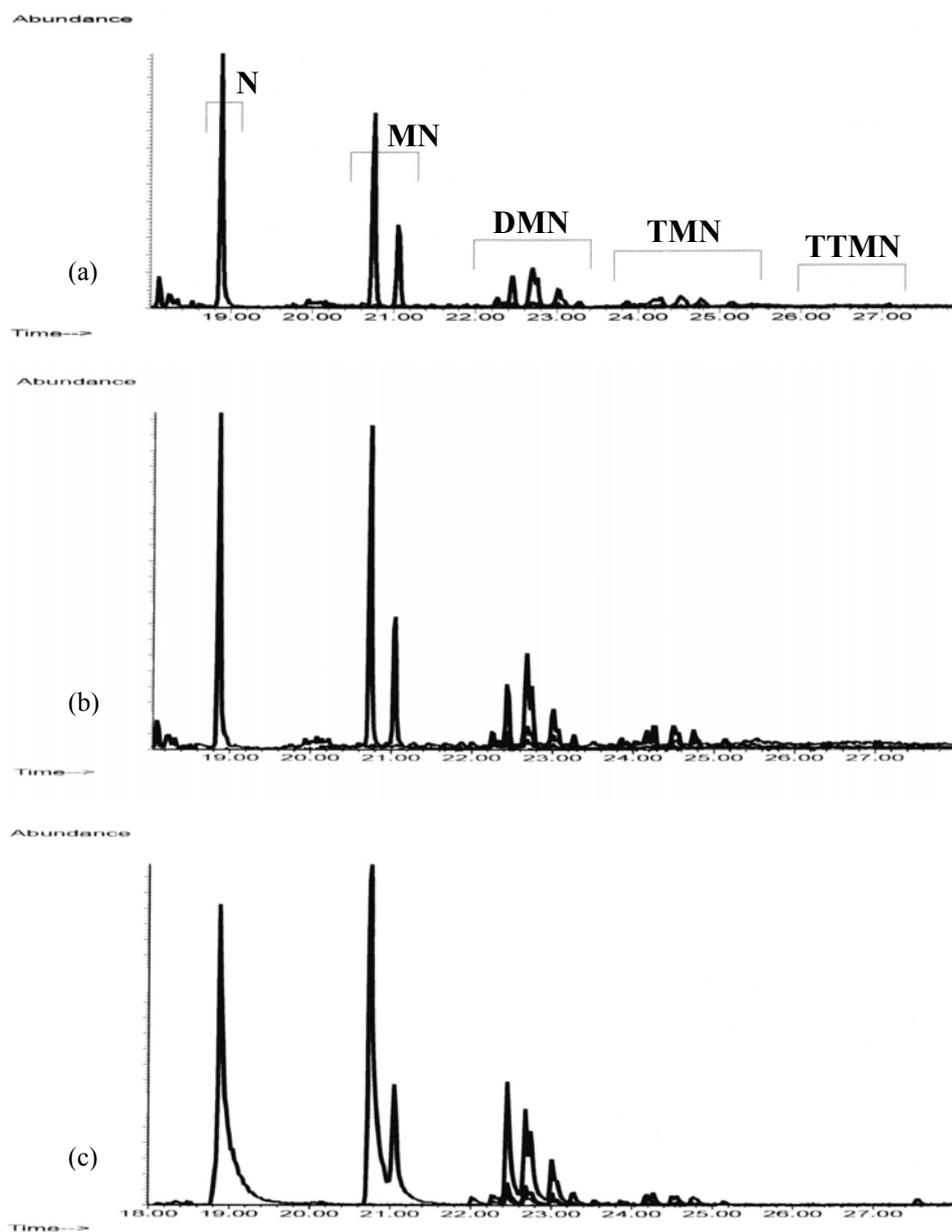
**Fig. 4**

Mass chromatograms of naphthalene group compounds recorded for pyrolysates obtained at 610°C from coal samples 15 (a), 8 (b), and 1 (c). Peak identities as for Fig. 1



**Fig. 5**

Mass chromatograms of naphthalene group compounds recorded for pyrolysates obtained at 770°C from coal samples 15 (a), 8 (b), and 1 (c). Peak identities as for Fig. 1



**Fig. 6**

Mass chromatograms of naphthalene group compounds recorded for pyrolysates obtained at 980°C from coal samples 15 (a), 8 (b), and 1 (c). Peak identities as for Fig. 1

Pyrolysis at 770°C resulted in greater changes in the pyrogram obtained from sample 1, i.e. that from the contact zone. The intensity of the unsubstituted naphthalene peak increased and the size of peaks from monosubstituted naphthalenes increased relative to those from disubstituted naphthalenes (Fig. 5). The only changes in the shapes of the pyrograms obtained from samples 15 and 8 were distinctive increases in the sizes of the naphthalene peaks, although the general shapes of both pyrograms were similar.

Figure 6 shows the pyrograms obtained from pyrolysis at 980°C. The relative intensities of the respective peaks are similar for all the samples. The high temperature has resulted in similar results from samples of coal of very different structure.

Analysis of the changes in the shapes of the pyrograms also revealed other trends in the changes in the structures of the aromatic compounds with increasing temperature, in particular changes in the amount of substitution at positions of different thermal stability. It is well known that with increasing temperature methyl groups become mobile and that  $\alpha$  methyl groups move to the  $\beta$  position, which is more thermally stable. This process has also been observed for the organic matter in coal during the natural thermal maturation process [8,9]. The relationship between the amount of methyl substitution at these stable and unstable positions enables calculation of numerical data which can be effective means of characterising the parent samples and of assessing changes during thermal treatment of coals. Values of the ratios of peak intensities for 2-methyl- and 1-methyl-substituted naphthalene, equivalent to  $\beta$ - and  $\alpha$ -substitution, respectively, on  $m/z$  142 mass chromatograms, are listed in Table I. Values of this ratio increase with increasing temperature. The changes are more distinct for pyrolysates from coals 15 and 8 which were either unaffected or only slightly affected

**Table I**

Ratios of the intensity of the 2-methylnaphthalene peak to that of the 1-methylnaphthalene peak on  $m/z$  142 mass chromatograms obtained by pyrolysis of the coals at different temperatures

No. of parent coal sample	Pyrolysis temperature (°C)				
	358	480	610	770	980
15	0.5	0.8	1.8	1.7	2.3
8	0.8	0.9	2.1	2.2	2.4
1	1.9	2.0	1.7	4.2	2.9

by the thermal transformation which resulted from the intrusion. For pyrolysates from sample no. 1, from the contact zone, the changes are irregular, with the maximum value being that for the pyrolysate obtained at 770°C. It is possible that this sample was preheated to a high temperature by the intrusion and during secondary, laboratory pyrolysis was subjected to further changes. In the temperature range under discussion noticeable amounts of aromatic compounds can still be generated from coal [10]. Naphthalenes can also be created, especially those of greater stability, because of the high temperature of the process.

Similar trends were observed in changes of the ratios of the intensities of peaks obtained from dimethyl-substituted naphthalenes. Table II shows values of the ratio of the sum of the intensities of the 2,6- and 2,7-dimethyl-substituted naphthalene peaks ( $\beta$  substitution, of higher stability) to that of the 1,5-dimethylnaphthalene peak ( $\alpha$  substitution, of lower stability), on  $m/z$  156 mass chromatograms obtained from the pyrolysates. The more detailed identification presented in Fig. 2 (performed in accordance with Leroy [11]) indicates the peaks taken into account.

**Table II**

Ratios of the sum of the intensities of the 2,6- and 2,7-dimethylnaphthalene peaks to that of the 1,5-dimethylnaphthalene peak on  $m/z$  156 mass chromatograms obtained by pyrolysis of the coals at different temperatures

No. of parent coal sample	Pyrolysis temperature (°C)				
	358	480	610	770	980
15	0.8	0.8	1.3	1.8	2.3
8	1.6	1.3	1.9	1.6	1.6
1	2.3	2.4	2.3	3.2	2.8

The data shown in Table II reveal the general tendency of values of this ratio to increase with increasing temperature, except for sample 8, for which the values do not change regularly. Comparison of differences between values calculated for particular samples at a given temperature enables the samples to be distinguished, so this information can be valuable in more than one application

## CONCLUSIONS

Py–GC–MS was a very effective and useful tool for characterisation of organic substances in samples of coal with different amounts of metamorphosis. This method also enabled successful characterisation of changes in the macromolecular structure of coals during pyrolysis at a wide range of temperatures.

The trend in structural changes with increasing pyrolysis temperature, specifically dealkylation of aromatic structures, is a characteristic feature of the thermal transformation of the organic structure of coal and can be used to assess the extent of thermal degradation of hard coals both in natural and in laboratory processes.

The relatively low concentration of polycyclic aromatic hydrocarbons in the pyrolysates probably results from incorporation, during pyrolysis, of these aromatic compounds into the macromolecular network making up the coke structure. This indicates the possibility of considerable reduction of emissions of PAH into the environment by application of different thermolytic processes to the coal under appropriate processing conditions.

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