GAS CHROMATOGRAPHIC AND MASS SPECTROMETRIC CHARACTERIZATION OF PYROLYSIS PRODUCTS OF FOSSIL ORGANIC MATTER FROM LOCALITIES OF THE CZECH REPUBLIC

Jiri CEJKA[a], Lubos HOLY[b], Bohdan KRIBEK[c] and Vaclav SEDLACEK[d]

[a] *J. Heyrovsky Institute of Physical Chemistry, Academy of Sciences of the Czech Republic,*
182 23 Prague 8, Czech Republic; e-mail: cejka@jh-inst.cas.cz
[b] *ECOCHEM – Analytical Centre, Dolejskova 3, 182 23 Prague 8, Czech Republic;*
e-mail: ecochem.pha@lbc.pvtnet.cz
[c] *Czech Geological Survey, Klarov 3, 118 21 Prague 1, Czech Republic*
[d] *Department of Geochemistry and Mineral Raw Materials, Charles University, 128 40 Prague 2,*
Czech Republic

Received February 6, 1996
Accepted May 1, 1996

The composition of fossil organic matter of different origin and thermal maturation was studied based on the gas chromatographic-mass spectrometric characterization of their pyrolysis products. Increase in the pyrolysis temperature from 300 to 500 °C was found to cause the cracking of aliphatic hydrocarbons resulting in a shortening of the n-alkane chains. High yields of pyrolysis products can be obtained at temperatures above 350 °C; the cracking reactions can be suppressed by applying relatively short duration of pyrolysis. The chromatographic patterns then clearly reflect the origin of the organic matter and degree of its thermal maturation in rocks.

Key words: GC-MS; Pyrolysis; Fossil organic matter; Thermal maturation.

It is well-known that heating of fossil organic matter in an inert atmosphere yields complex mixtures of various aliphatic and aromatic hydrocarbons and their oxygenated derivatives ranging from C_5 to C_{40} at least (refs[1–3]). The composition of such mixtures depends highly on the nature of the material being pyrolysed as well as on the conditions in which the pyrolysis is carried out.

Pyrolysis-gas chromatography-mass spectrometry, benefiting from the unique separation capabilities of high resolution capillary columns combined with the possibility of identifying the individual pyrolysis products, is frequently used "on-line" or "off-line" for the analysis of compounds belonging to various chemical classes such as phenolic compounds and polysaccharides[4], tannins in plant materials[5], terpenes and sesquiterpenes in amber[6], beeswax in Egyptian painting layers[7], cellulosic materials[8,9] and humic brown coal[10].

In the field of organic geochemistry, pyrolysis in combination with GC-MS has been successfully used for characterization of the volatile fraction of coal tar pitch by Blanco et al.[11] and for screening of aliphatic and aromatic hydrocarbons in urban aerosols by Aceres and Grimalt[12,13]. Supercritical fluid extraction has been employed by Martin et al.[14] to investigate the nature and composition of fossil organic matter in bitumens. Conversion of alkanes to aromatics at temperatures higher than 650 °C has been reported by Moliner et al.[15].

The objective of this paper is to identify the products of pyrolysis of fossil organic matter from different localities of the Bohemian massif using "off-line" pyrolysis coupled with gas chromatography and mass spectrometry (GS-MS) and to assess the potential of "off-line" pyrolysis-GC-MS in the characterization of such organic materials. The effect of the pyrolysis temperature and duration on the product composition is examined on a selected sample with a view to identifying the optimal pyrolysis conditions for such fossil organic materials. The pyrolysate yield is compared with the results of conventional pyrolysis of the Rock–Eval type, which is commonly used to characterize the chemical composition of the fossil organic matter[16,17].

EXPERIMENTAL

Materials

In order to characterize the pyrolysis products of organic matter of different origin and different degree of thermal maturation, a representative set of samples was collected from (i) high-ash coal and claystone of the Sokolov Brown Coal Basin, (ii) coal from the Plzen Coal Basin, and (iii) Silurian black shales from the Beroun Area. The sample description, pyrolysate yield and values of the Rock–Eval hydrogen index (*IH*) and mean reflectivity of the organic matter, which characterize the degree of its thermal maturity, are given in Table I.

Apparatus

The thermal maturity of the organic fossil matter was determined based on its optical reflectance values[17,18]. Polished samples of the sediments or coals were studied under polarized reflected light with a wavelength of 546 nm through an oil immersion (n = 1.5180) objective connected to an MPV-2 Leitz microscope. The average maximum and minimum reflectance was determined, and the mean reflectance R_0, which increases with increasing degree of thermal maturation of the organic matter in rocks, was calculated.

Pyrolysis was carried out in a fixed bed glass reactor. The individual samples (weight of 8 g) were heated in a vacuum of 660 Pa applying a temperature program of 8 K/min up to temperatures of 300 to 500 °C. The final temperatures and duration of the pyrolyses are given in Table I. The gaseous products were trapped in a glass receiver cooled at 0 °C. Since most of the natural kerogens undergo pyrolytic cracking at temperatures above 300 °C, the product mixture is apparently a mixture of distillation and pyrolysis products; for the sake of brevity, however, the mixtures will be referred to as the pyrolysis products. The pyrolysate yield is the amount of pyrolysis products obtained.

The pyrolysis product yield, estimated gravimetrically after removal of water, was compared with the results of the Rock–Eval type of pyrolysis, which is widely used to characterize fossil organic

TABLE I
Characteristics of investigated samples, conditions and results of pyrolysis

Sample No.	Litology	Age	Location	Temperature °C	Duration min	Yield mg/g C_{org}	C_{org} wt.%	*IH* mg/g C_{org}	Mean reflectivity R_0, %
1A	Sapropelitic claystone	Miocene	Sokolov Basin	300	60	10	11	900	0.28
1B	Sapropelitic claystone	-"-	-"-	400	60	600	11	900	0.28
1C	Sapropelitic claystone	-"-	-"-	500	60	995	11	900	0.28
1D	Sapropelitic claystone	-"-	-"-	450	10	37	11	900	0.28
2	Sapropelitic claystone	-"-	-"-	450	60	750	6.8	691	0.28
3	High-ash coal	-"-	-"-	450	60	362	16.6	350	0.3
4	Coal	Carboniferous	Plzen Basin	450	60	220	39.1	206	0.45
5	Shale	Silurian	Beroun Area	450	60	115	2	81	1.62

matter. The Rock–Eval pyrolysis was carried out by the Laboratory of Organic Geochemistry, Czech Geological Survey, Brno. Homogenized samples (0.05–0.1 g) were analyzed applying a temperature gradient of 25 K/min up to maximum temperature of 550 °C. The results of this analysis are expressed as *IH*, corresponding to the H/C ratio in the fossil organic matter[19].

The pyrolysis products were analyzed by gas chromatography (Hewlett–Packard 5890 Series II) and identified by using a quadrupole mass spectrometric detector (Hewlett–Packard 5971A). Separation was achieved on a high resolution capillary column (SPB-1, Supelco, 30 m, 0.2 mm i.d., film thickness 0.2 μm). The injector and detector temperatures were set at 250 °C, and the temperature program was run from 60 to 275 °C at a rate of 5 K/min. The mass spectrometer was calibrated with perfluorotributylamine (PFTBA), and the spectra were recorded in the electron impact mode at an ionization energy of 70 eV over the *m/z* range of 25–450. Standards of individual substances ($C_{25}H_{52}$, $C_{28}H_{58}$, $C_{30}H_{62}$, $C_{33}H_{68}$) and a spectral library were employed to elucidate the spectra recorded.

RESULTS AND DISCUSSION

Effect of Pyrolysis Temperature and Duration on the Character of Pyrolysate

The effect of the pyrolysis temperature on the character of the gas chromatograms of the pyrolysates was examined using sample **1**, an organic matter-rich claystone of Cypris Beds (Miocene, Sokolov Basin). The chromatograms of pyrolysates obtained applying different temperature regimes are shown in Fig. 1. The chromatograms shown in Fig. 1 are total ion current chromatograms, which overestimate the concentration of compounds rich in fragmented ions. Hence, no straightforward quantitative correlations can be drawn from the chromatograms, and only a comparison of the chromatographic profiles is therefore made here. The most intense chromatographic peaks represent mainly various long-chain alkanes and 1-alkenes. Particularly for compounds higher than $C_{25}H_{52}$, their molecular ions were not observed and their identification was based on the use of an internal standard and on the retention times. It is evident from Fig. 1 that at higher pyrolysis temperatures, the maxima of peak intensities of alkanes and the corresponding 1-alkenes are shifted towards lower carbon numbers. Moreover, the n-alkene to n-alkane ratio seems to increase with increasing temperature.

The products of pyrolysis at 300 °C give a chromatogram where the highest intensities are observed for the C_{21}–C_{22} alkanes (Fig. 1, sample **1A**). While the patterns remain virtually unchanged at 400 °C (Fig. 1, sample **1B**), considerable changes are observed if the pyrolysis temperature is increased to 500 °C (Fig. 1, sample **1C**): the maximum of the envelope shifts to C_{11}–C_{17} alkanes and is much broader.

The chromatogram of the pyrolysis products at 300 °C is dominated by alkanes ranging between C_{19}–C_{25}, and exhibits a relatively small amount of short-chain alkanes and alkenes. Moreover, 1-pristene and 2-pristene, which presumably arise from the thermal breakdown of macromolecularly bound tocopherols[20], were also identified among the pyrolysis products in non-negligible concentrations. This indicates that a partial dehydrogenation and cracking of long alkanes proceeds at temperatures as low as 300 to 400 °C.

Short-time (10 min) pyrolysis at 450 °C gave a profile similar to that obtained by pyrolysis at 400 °C (Fig. 1, samples **1B** and **1D**). This indicates that the optimal temperature for pyrolysis lies between 400–450 °C, although a compromise must be sought in view of the fact that lower pyrolysate yields are obtained at lower temperatures whereas substantial changes in the character of the pyrolysis products occur at higher temperatures, complicating the evaluation of the origin of the fossil organic matter in-

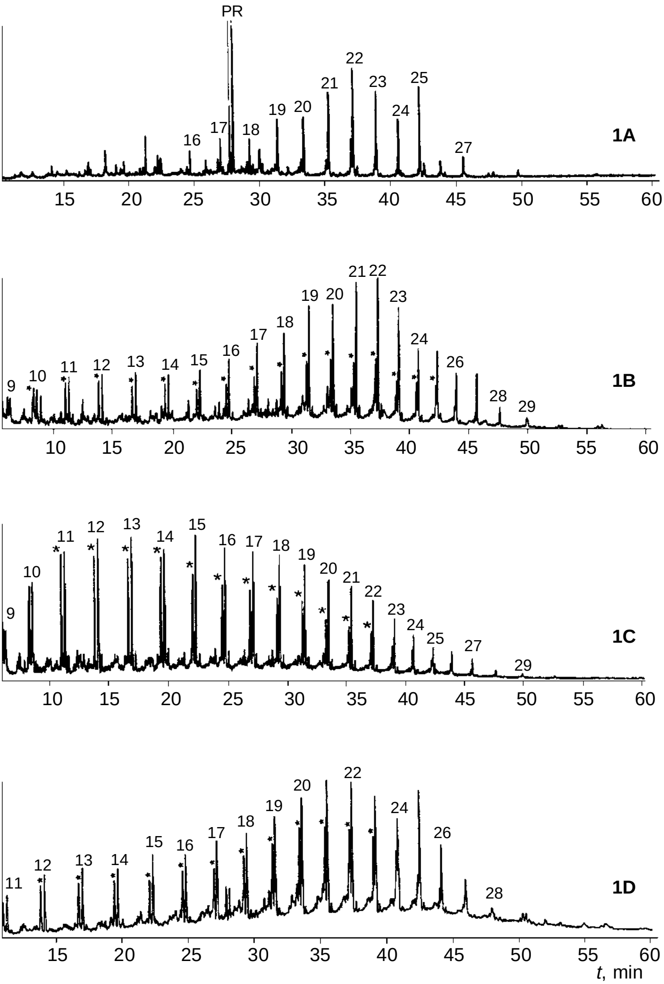

FIG. 1

Chromatograms of samples (**1A**–**1D**, **2**–**5**) obtained at different pyrolysis temperatures and durations (cf. Table I). The numbers refer to the chain length of n-alkanes, the corresponding 1-alkenes are denoted by asterisks. A alkylaromates, AN anthracene, AZ ethyl- and methylazulenes, C cresols, DMN dimethylnaphthalenes, MN methylnaphthalenes, P phenol, PR 1- and 2-pristene, X xylenols, N naphthalene, TMN trimethylnaphthalenes vestigated. This is in agreement with the results by Moliner and co-workers[15], showing that especially at temperatures above 600 °C, long-chain alkanes are dehydrogenated and cracked. Hence, if the pyrolysis is performed at temperatures higher than 600 °C, the resulting chromatograms consist mainly of products of various subsequent reactions starting with alkane cracking including dehydrogenation, cyclization, isomerization and aromatization reactions. It seems that higher temperatures can be used for pyrolysis of fossil organic matter rich in aromatic or polyaromatic hydrocarbons, because these compounds are much more stable with respect to dehydrogenation and cracking reactions.

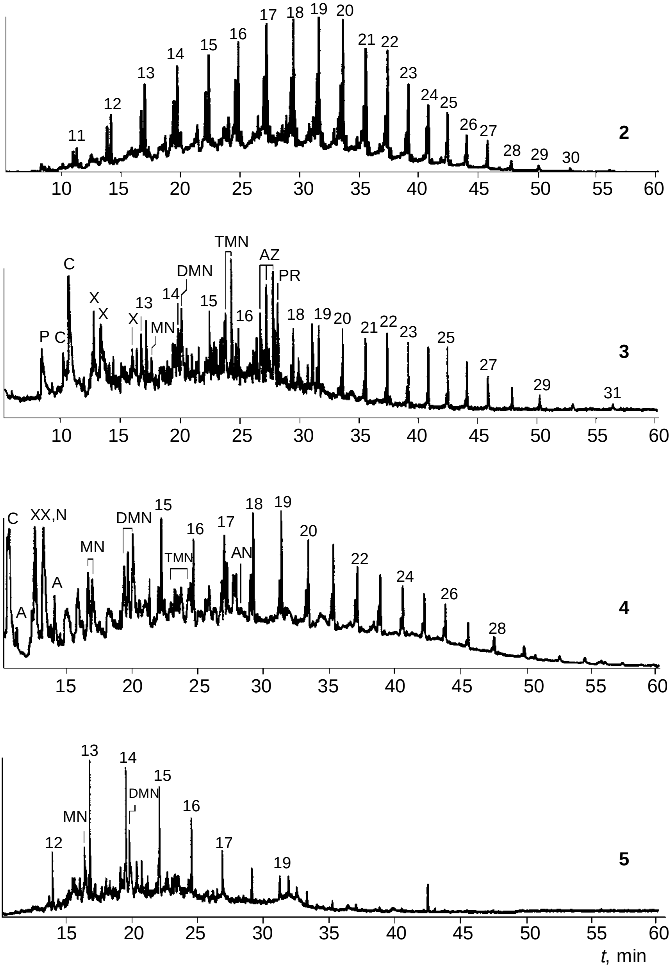

FIG. 1
(*Continued*)

The role of the inorganic material which is always present in the fossil organic matter in various concentrations is not clear. Perhaps, this material can act as a catalyst increasing, e.g. the rates of various transformations of organic matter enabling the hydrogen transfer.

Pyrolysate Yields as a Function of Origin and Thermal Maturation of the Organic Matter

The pyrolysate yields obtained from the individual samples can be related to the *IH* values determined by the Rock–Eval method (Table I, Fig. 2). As the *IH* values correspond to the atomic H/C ratio in the organic matter[16], the amount of pyrolysate obtained probably depends on this ratio as well. The H/C ratio in fossil organic matter is a function of both the organic matter source and degree of its thermal maturation[16]. Organic matter of algal type is usually rich in hydrogen, owing to the high amount of lipids present in the bodies of algae, whereas organic matter which originated from cellulose- and lignine-rich continental vascular plants is usually hydrogen deficient. Thus, it corresponds to the higher amount of pyrolysate obtained from claystones from the Sokolov Coal Basin (containing organic matter of the algal type) and the much lower amount of pyrolysate in comparison with the high-ash coal (where organic matter formed from vascular plants) from the same site (samples **2** and **3**, Table I).

The differences between the sources of organic matter are clearly reflected by the different profiles of the gas chromatograms (Fig. 1). While the GC-MS profile of the pyrolysate obtained from the algae-dominated Cypris Formation claystone displays mainly aliphatic hydrocarbons (Fig. 1, sample **2**), the profiles of the Miocene high-ash coal pyrolysate exhibits a considerably higher abundance of aromatic hydrocarbons, their oxygen derivatives (xylenes, phenols, cresols, xylenols), alkylnaphthalenes and azulenes (Fig. 1, sample **3**). The presence of mineral waxes or non-saponifiable cuticles[21] is inferred from the presence of some alkanes in the pyrolysate. Similar features are found in the chromatographic profiles of black coal pyrolysate from the Plzen Basin. However, due to the higher degree of thermal maturation of this organic matter,

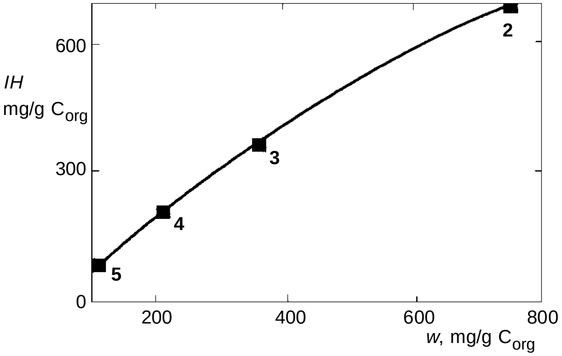

FIG. 2
Plot of the variation of pyrolysate yield *w* vs Rock–Eval *IH* values of samples **2** to **5**

the resulting composition of the pyrolysis products is less complex than that from the Miocene high-ash coal. Dimethylnaphthalenes are less abundant and pristene and azulenes, which are present in the Miocene coal, are absent from the coal from the Plzen Basin (Fig. 1, sample **4**).

The chromatographic profile of the pyrolysate obtained from the Silurian black shale is typical of organic matter which has been subjected to a high degree of thermal maturation (Fig. 1, sample **5**). In this case it is very difficult to recognize the original character of the organic matter source which has undergone cracking reactions to a large extent.

CONCLUSIONS

The results of this investigation show that, if carried out in appropriate conditions, "off-line" pyrolysis-GC-MS can serve as an efficient tool for a rapid and effective determination of the type and maturation history of fossil organic matter. The optimum pyrolysis temperature for this type of fossil organic matter is between 400–450 °C. At higher temperatures, the original composition of the individual organic compounds is strongly changed by secondary reactions (cracking, dehydrogenation, cyclization, aromatization) bringing about gradual shortening of the long-chain n-alkanes and, in more severe conditions (over 650 °C), formation of polyalkyl aromatic hydrocarbons including annelated aromatic hydrocarbons. Based on a comparison of the pyrolysis products of different samples of fossil organic matter from sediments and coals it can be concluded that the composition of pyrolysate is mainly determined by the source of organic matter. While a largely aliphatic character of pyrolysate indicates a lipid-rich algal source, aromatic character is characteristic especially of land-derived, lignin- and cellulose-rich sources. In highly matured sediments the distribution of organic molecules in pyrolysate reflects the thermal history of the individual sample, irrespective of the source of organic matter.

This study was supported by a grant from the Grant Agency of the Czech Republic (No. 205/95/0151).

REFERENCES

1. Meuzellar H. L. C., Harper A. M., Pugmire P. J., Karas J.: Int. J. Coal Geol. *4*, 143 (1984).
2. Boon J. J., Powels A. D., Eijkel G. B. in: *Peat and Water Aspects of Water Retention and Dewatering in Peat* (C. Fuchsmann, Ed.), p. 215. Oxford Press, Oxford 1986.
3. Tromp P. J. J., Moulijn J. A., Boom J. J.: Fuel *65*, 960 (1986).
4. Galleti G. C., Bocchini P.: Rapid Commun. Mass Spectrom. *9*, 815 (1995).
5. Galleti G. C., Antonelli A.: Rapid Commun. Mass Spectrom. *7*, 656 (1993).
6. Galleti G. C., Reeves III J. B., Blomfield J., Vogt K. A., Vogt D. J.: J. Anal. Appl. Pyrolysis *27*, 1 (1993).
7. Galleti G. C., Chiavari C., Duale Kahie Y.: Rapid Commun. Mass Spectrom. *7*, 651 (1993).

8. Evans J. R., Milne A. T., Soltys N. M.: J. Anal. Appl. Pyrolysis *9*, 207 (1986).
9. Boon J. J., Powels A. D., Eijkel G. B.: Biochem. Soc. Trans. *15*, 170 (1987).
10. del Rio J. C., Czechowski F., Gonzales-Vila F. J., Martin F. in: *Coal Science* (J. A. Bajares and J. M. D. Pascon, Eds), p. 99. Elsevier, Amsterdam 1995.
11. Blanco C. G., Blanco J., Bernard P., Guillen M. D.: J. Chromatogr. *539*, 157 (1991).
12. Aceves M., Grimalt J. O.: J. Chromatogr. *607*, 261 (1992).
13. Canton L., Grimalt J. O.: J. Chromatogr. *607*, 279 (1992).
14. Martin F., Erdejo T., Gonzalez-Vila F. J.: J. Chromatogr. *607*, 377 (1992).
15. Moliner R., Lazaro M., Fernandez A., Ibarra J., Comellas L.: J. Chromatogr. *655*, 155 (1993).
16. Espitalie J., Laporte J. L., Madec M., Marquis P., Laplat P., Paulet J., Boutefeu A.: Rev. Inst. Fr. Pet. *32*, 23 (1977).
17. Tissot B., Welte D. H.: *Petroleum Formation and Occurrence*, p. 328. Springer, Berlin 1978.
18. Teichmuller M., Teichmuller R., Weber K.: Fortschr. Geol. Rhein. Westph. *27*, 201 (1979).
19. Borkovcova I.: *Physical and Chemical Methods for the Determination of Organic Matter in Soils, Sediments and Waters*, p. 120. Czech Geological Survey, Prague 1986.
20. Goossens H., De Leeuw J. W., Schenck P. A., Brassell S. C.: Nature *312*, 440 (1984).
21. Nip M., Tegellar E. W., Brinkhnis H., De Leeuw J. W., Schenck P. A., Holloway P. J.: Org. Geochem. *10*, 769 (1986).