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ANALYSIS OF HYDROCARBONS IN COALS BY MEANS OF A MICRO-THERMODESORPTION–CAPILLARY GAS CHROMATOGRAPHY COMBINATION

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SUMMARY

Gas chromatographic analysis of hydrocarbons with a commercial thermo-desorption unit as injection device and intermediate trapping is applied to a series of coal samples. Nine coals of different rank (vitrinite reflectance R_m = 0.54 to 1.44%) and maceral composition are selected for this purpose. Only a few milligrams of finely powdered coal are required to determine the volatile hydrocarbons of a wide molecular-weight range up to C_{33}. Both the repeatability of the method and the influence of the thermodesorption temperature (200°C to 350°C) on the hydrocarbon yields are studied. Pertinent data are compared with those obtained from solvent extraction, liquid chromatography and gas chromatography of aliquots of the same coals. Finally, organic geochemical parameters, such as the pristane–phytane concentration ratio, methylphenanthrene index (MPI1), occurrence of norprimarane and retene in a resinite-rich coal and the abundance of biphenyl in a medium-volatile bituminous coal are discussed.

INTRODUCTION

Organic geochemical studies of the bituminous constituents of coals usually require solvent extraction, followed by liquid chromatography (LC) and gas chromatography (GC) for separation. However, due to evaporation losses during the various analytical steps, the quantitative determination of hydrocarbons is generally restricted to the higher-molecular-weight compounds with more than *ca.* 15 carbon atoms for saturated and more than *ca.* 11 carbon atoms for aromatic hydrocarbons. Thermal mobilization of hydrocarbons from solid matrices in a gas flow, combined with capillary GC, represents an alternative and simple approach to the analysis of hydrocarbons of a wide molecular-weight range in sedimentary rocks[1–7]. The present contribution describes the analysis of the volatile hydrocarbon content in a series of coal samples by a combination of micro-scale thermodesorption and capillary GC

TABLE I

CHARACTERIZATION OF COAL SAMPLES ANALYSED

Coal	Location	Seam	Vitrinite reflectance (% $R_{m_{oil}}$)	Organic carbon content (%)	Data from solvent extraction, LC and GC analysis				
					Yield (ppm)	Saturated hydrocarbons (%)	Aromatics (%)	CPI***	Pristane– phytane
A	Fushun (China)	–	0.54	60.5	31 230	12.3	23.6	1.4	7.2
B*	Ruhr District (F.R.G.)	Baldur	0.60	67.0	23 960	10.4	21.5	1.2	4.0
C*	Ruhr District (F.R.G.)	Hagen	0.73	76.4	26 520	8.7	21.1	1.3§	8.7
D	Ruhr District (F.R.G.)	Chriemhilt	0.73	76.9	63 000**	2.4**	5.8**	1.3§	9.5
E	Upper Silesia (Poland)	–	0.76	72.7	24 020	12.9	33.6	1.2	8.5
F	Rio Grande do Sul (Brasil)	–	≈0.8§§	39.2	5730	7.7	34.2	1.4	3.6
G*	Ruhr District (F.R.G.)	Q1	0.91	75.3	7830	9.9	16.1	1.0	6.6
H	Saar District (F.R.G.)	–	0.93	79.5	8570	6.7	25.5	1.0	2.3
I	Ruhr District (F.R.G.)	Hugo	1.44	82.7	2210	7.3	53.2	1.0	2.7

* Sapropelic coal.
** After Radke (personal communication).
*** CPI_{17-31}.
§ CPI_{27-29}.
§§ Derived from spectral fluorescence measurements.

using a commercial thermodesorption unit as the injection device. This method was initially designed for environmental studies, such as the determination of atmospheric organic pollutants concentrated in adsorbent traps, *e.g.* filled with charcoal.

EXPERIMENTAL

Thermodesorption

A thermodesorption–cold-trap injection unit (TCT injector, Chrompack, Middelburg, The Netherlands) attached to a capillary gas chromatograph (Model 4160, Carlo Erba, Milan, Italy) is used for this study. Hydrocarbons from coal samples (1–5 mg sample weight requirement) are thermodesorbed in a 160 × 3 mm I.D. glass tube. The cold trap consists of a 330 × 0.53 mm I.D. fused-silica capillary (100 mm cooled section) coated with CP Sil-5 CB silicone of 5-μm film thickness. The finely ground coal sample (mainly 0.06–0.2 mm grain size) is placed in the desorption tube between plugs of glass wool. Thermodesorption, generally at 300°C, and trapping at −120°C ± 4°C is performed in a helium flow of 6.5 ml/min for 12 min. The trapped compounds are subsequently desorbed by heating the cold-trap to about 250°C for 15 min.

Gas chromatography

The gas chromatograph is equipped with a 50 m × 0.33 mm I.D. fused-silica capillary, coated with SE-54 silicone (0.2 μm film thickness) as the stationary phase. The oven temperature is programmed from 30°C to 280°C at a rate of 3°C/min. The initial column temperature of 30°C causes an additional thermal focussing of the less volatile compounds. Splitless introduction of the trapped compounds into the capillary ensures maximum sensitivity of the system using flame ionization detection (FID). Quantitative results are obtained with *n*-butane as external standard using a chromatography data system (Multichrom, VG Laboratory Systems, Altrincham, U.K.). Different response factors for the various compounds are not considered due to the lack of reliable data[8]. In this respect, the yield data shown below represent *n*-butane weight equivalents in microgram per gram of organic carbon content of the coals. We can assume that this simplification is acceptable for the kind of data discussed here. The identification of aromatic hydrocarbons is verified by gas chromatography–mass spectroscopy (GC–MS) measurements of the aromatics fraction of the coal extracts.

Coal extracts

Details of extraction of coal samples (except for sample D) and subsequent LC and GC analysis are described elsewhere[9]. Coal sample D is extracted with the ternary azeotrope of chloroform, acetone, and methanol and then fractionated by medium-pressure LC prior to GC analysis[10].

Samples

The coal samples studied (Table I) comprise a wide range in terms of rank (*i.e.*, from sub-bituminous B to medium-volatile bituminous stages) and maceral composition. The mean vitrinite reflectance, which is a common rank parameter (vitrinite is a prominent constituent of most coals), varies from 0.54% (brown coal

TABLE II

THERMODESORPTION YIELDS (μg/g C_{org}) AT 300°C OF SELECTED HYDROCARBONS FOR A SERIES OF COAL SAMPLES (SEE TABLE I) DATA FOR SAMPLE D INCLUDE THE STANDARD DEVIATION OF FOUR MEASUREMENTS

– = Not specified (near detection limit); n = not specified (peak overlapping); ( ) = merged peak; [c] = value uncertain (contamination?).

Hydrocarbon	Coal sample								
	A	B	C	D	E	F	G	H	I
a Benzene	25.3	9.7	4.7	24.9 ± 5.7	n	9.0	104.7	210.0	382.4
7 n-Heptane	5.7	2.4	2.2	68.4[c] ± 20.9	4.1	3.3	457.2[c]	33.6	30.5
b Methylcyclohexane	15.8	1.4	–	5.3 ± 1.4	16.2	10.0	8.5	152.2	119.3
c Toluene	75.6	2.5	1.1	3.7 ± 0.3	n	7.9	14.5	334.9	84.0
8 n-Octane	6.1	3.0	1.0	2.7 ± 0.8	4.5	5.3	8.3	27.3	20.6
d m-, p-Xylene	55.0	2.2	0.8	19.6 ± 5.2	(2.9)	15.7	100.6	263.5	216.4
e o-Xylene	28.2	1.2	0.6	1.3 ± 0.4	(1.5)	9.0	6.4	79.5	48.2
9 n-Nonane	4.9	3.8	(1.0)	5.3 ± 1.1	5.0	9.2	12.7	27.2	17.5
10 n-Decane	4.2	4.2	n	(20.9) ± 2.1	6.5	17.9	5.2	24.6	14.6
11 n-Undecane	5.4	5.1	1.4	6.9 ± 0.5	13.1	22.6	9.2	24.5	10.7
f Naphthalene	16.6	2.4	–	–	(10.0)	70.0	2.6	73.8	38.4
12 n-Dodecane	(7.3)	5.8	1.6	6.1 ± 0.6	19.6	15.1	(20.7)	22.3	11.0
g 2-Methylnaphthalene	24.3	4.2	–	3.6 ± 0.4	(23.8)	47.9	6.8	114.0	108.6
13 n-Tridecane	5.7	6.1	1.4	5.8 ± 0.7	22.2	14.1	8.1	13.2	9.7
h 1-Methylnaphthalene	18.0	1.9	–	4.4 ± 0.5	25.3	26.3	3.7	70.0	30.0
i Biphenyl	n	1.0	–	–	n	1.4	–	9.3	34.2
14 n-Tetradecane	(10.5)	7.5	3.0	7.9 ± 1.1	35.4	15.5	6.4	17.2	4.7
15 n-Pentadecane	(13.5)	(11.3)	(4.3)	9.1 ± 0.9	(45.9)	(12.2)	(7.8)	(12.6)	(25.4)

16 n-Hexadecane	9.3	10.8	4.4	7.9 ± 1.2	36.9	9.0	5.2	10.5	3.0
17 n-Heptadecane	(16.0)	16.2	9.4	7.0 ± 1.0	37.6	8.2	5.1	(8.9)	1.7
j Pristane	53.0	28.8	58.6	28.6 ± 2.4	98.5	8.4	26.6	(4.6)	n
k C_4-Naphthalene	35.3	9.8	9.3	19.2 ± 2.0	57.2	14.9	20.8	13.3	3.6
l Phenanthrene	2.6	16.3	n	9.4 ± 1.4	25.1	17.1	11.3	17.6	26.6
18 n-Octadecane	13.2	24.4	13.2	10.3 ± 3.6	42.8	(12.9)	7.8	8.6	1.5
m Phytane	8.7	8.8	7.1	4.5 ± 1.2	17.8	2.2	7.3	2.2	1.0
19 n-Nonadecane	(24.1)	21.4	21.4	8.6 ± 1.2	42.7	4.3	7.7	7.9	1.4
n 3-Methylphenanthrene	n	4.1	—	4.4 ± 0.8	(11.5)	(4.1)	(12.8)	8.1	14.6
o 2-Methylphenanthrene	n	5.8	—	6.0 ± 1.7	(15.4)	(4.1)	14.9	13.1	21.1
p Norpimarane	81.7	n	—	—	n	n	n	n	—
q 9-Methylphenanthrene	n	n	—	(8.8) ± 1.3	(28.4)	(8.6)	(12.1)	9.8	5.9
r 1-Methylphenanthrene	n	8.2	—	5.5 ± 1.0	(19.0)	(3.0)	10.4	8.6	5.7
20 n-Eicosane	20.5	24.6	30.4	11.2 ± 1.3	43.7	3.8	(10.7)	7.4	n
21 n-Heneicosane	21.7	(32.4)	40.6	10.5 ± 1.2	45.0	3.8	10.0	(8.7)	n
22 n-Docosane	30.2	31.9	33.5	7.9 ± 0.9	38.7	5.1	8.2	5.4	n
s Retene	(100.8)	(20.9)	n	n	n	n	n	n	n
23 n-Tricosane	41.5	34.8	(45.2)	8.8 ± 2.4	41.4	4.1	(8.8)	4.2	n
24 n-Tetracosane	39.1	33.0	31.0	8.8 ± 0.4	42.0	2.5	(7.5)	(10.6)	n
25 n-Pentacosane	53.5	35.0	33.9	6.2 ± 0.8	39.0	(3.3)	5.8	3.4	n
26 n-Hexacosane	36.8	30.1	20.6	7.3 ± 0.8	34.3	1.0	(7.8)	(4.3)	n
27 n-Heptacosane	51.4	31.4	29.1	5.7 ± 0.5	36.6	1.4	4.5	2.2	n
28 n-Octacosane	29.5	27.1	18.2	6.2 ± 0.8	35.7	n	(5.4)	(2.5)	n
29 n-Nonacosane	44.3	24.1	19.0	3.5 ± 0.4	26.6	n	2.9	1.2	n
30 n-Triacontane	14.4	14.2	9.0	1.4 ± 0.2	16.7	—	1.9	0.8	n
31 n-Hentriacontane	19.4	13.3	10.9	1.6 ± 0.4	12.4	—	2.0	n	—
32 n-Dotriacontane	n	8.2	3.6	0.7 ± 0.2	n	—	0.8	—	—
33 n-Tritriacontane	n	3.1	3.8	—	n	—	0.6	—	—

from Fushun, China) to 1.44% (coking coal from the Ruhr district) in this series[9]. The rank of coal sample F is derived from spectral fluorescence measurements[11]. Besides normal humic coals, some coals with a high content of special liptinite macerals[9], such as resinite (sample A) and alginite (samples B, F, H), are selected for this study.

RESULTS AND DISCUSSION

Significance of data

Yields of selected hydrocarbons, obtained by thermodesorption at 300°C of the nine coal samples, are listed in Table II. The repeatability of the method is exemplified for coal sample D in terms of averaged yields and standard deviations (four measurements). It is assumed that most of the scatter in the data is due to inhomogeneities in the samples, since only a few milligrams of powdered coal are used in the analysis.

The influence of the thermodesorption temperature was studied for coal sample D with respect to selected compounds at various temperatures between 200°C and 350°C (Table III). As expected, there is a considerable yield increase with increasing temperature, even for the relatively volatile *n*-undecane (a factor of 3.1). For *n*-eicosane the thermodesorption yield at 350°C is higher by a factor of almost 40 than at 200°C in this example. Comparison of thermodesorption data with corresponding data from solvent extraction, LC and GC analysis of an aliquot of the same coal sample (Table III) leads to the conclusion that the pore structure of the coal prevents a considerable proportion of the hydrocarbons from being thermodesorbed, even at 350°C, at the flow conditions applied in these measurements. Whereas for *n*-pentadecane exactly the same amount of extracted and thermodesorbed material was found (12.2 μg/g C_{org}), for *n*-eicosane (26.6 *vs.* 15.5) and *n*-pentacosane (28.5 *vs.* 11.4) the difference is evident. It is emphasized, therefore, that the thermodesorption method

TABLE III

AVERAGED THERMODESORPTION YIELDS (μg/g C_{org}) OF SELECTED HYDROCARBONS FROM COAL SAMPLE D AS A FUNCTION OF TEMPERATURE, COMPARED TO THE RESPECTIVE DATA FROM SOLVENT EXTRACTION, LC AND GC ANALYSIS

n.d. = not determined. *n* = number of determinations.

Hydrocarbon	Thermodesorption temperature (°C)				Data from solvent extraction, LC and GC analysis
	200 (n = 3)	250 (n = 3)	300 (n = 4)	350 (n = 3)	
n-Undecane	2.8	4 2	6.9	8.7	n.d.
1-Methylnaphthalene	0.4	1.6	4.4	5.9	n.d.
n-Pentadecane	1.1	3.1	9.1	12.2	12.2
n-Heptadecane	0.8	2.6	7.0	10.6	14.5
Pristane	1.8	8.4	28.6	43.0	111
Phytane	0.2	1.0	4.5	4.1	11.6
n-Eicosane	0.4	2.2	11.2	15.5	26.6
n-Pentacosane	<0.2	1.4	6.2	11.4	28.5

described here produces, at best, semi-quantitative data for the higher-molecular-weight compounds. From the geochemical point of view, the major benefit of the method arises from the quantitative determination of the lower-molecular-weight hydrocarbons and geochemical parameters based on relative quantities of individual compounds.

Organic geochemical aspects

The investigation of coal extracts was initially focused on normal alkanes and branched, saturated hydrocarbons. The shape of the *n*-alkane distribution turned out to be rank-related[12]. Also, the pristane–phytane concentration ratio in the extracts varies systematically with the rank of the coals as do their organic carbon content[13] or vitrinite reflectance[14]. Thermodesorption of the bitumen from coals, as described here, provides sufficient separation of pristane (peak j in Fig. 1) and phytane (m) from adjacent peaks in the gas chromatograms only for some of the coals investigated. The pristane–phytane concentration ratios, calculated from Table II, are as follows (sample in parentheses): 6.1 (A), 3.3 (B), 8.3 (C), 6.4 (D), 5.5 (E), 3.8 (F), 3.6 (G), <2.1 (H). Comparing these values with those of Table I reveals, in terms of their geochemical significance, a satisfactory agreement for coals A, B, C, F and H. However, for samples D, E, and G the deviations between pristane–phytane concentration ratios derived from extract data and thermodesorption are considerable indicating that the separation efficiency of the GC column is insufficient.

Recently, the aromatic compounds in coal extracts have been subjected to geochemical studies. The relative intensities of phenanthrene and four methylphenanthrene isomers (*i.e.*, 1-, 2-, 3-, 9-methylphenanthrene) were used to create the so-called methylphenanthrene index (MPI1), which in humic coals turned out to be strongly dependent on rank[10]. When the thermodesorption method is used, phenanthrene (l) and its methyl derivatives (n, o, q, r) are partly superimposed on aliphatic compounds in the gas chromatograms (see, *e.g.*, Fig. 1d). Due to the loss of long-chain alkanes in higher-rank coals ($R_m > 1\%$) phenanthrene and its derivatives appear to be sufficiently separated. In those cases (see, *e.g.*, Fig. 1i), the evaluation of the MPI1 on the basis of thermodesorption yields is reasonable. For instance, one can calculate for coal sample I (measured vitrinite reflectance $R_m = 1.44\%$) an MPI1 value of 1.40 corresponding to a calculated vitrinite reflectance[15] $R_c = 1.46\%$. Even for coal sample H (vitrinite reflectance $R_m = 0.93\%$) the calculated values from thermodesorption are perfectly accurate (MPI1 = 0.88; $R_c = 0.93\%$).

Another geochemical parameter which, particularly for coals from the Saar district, turned out to represent a conclusive rank indicator, is the C_4-naphthalene (k)–phenanthrene (l) concentration ratio[9]. For instance, for coal sample H the concentration ratio (0.76) is not much different from the corresponding value obtained by solvent extraction, LC, and GC (0.86).

A further geochemical characteristic of higher-rank coals is the occurrence of biphenyl in the desorbed bitumen. This compound is present in remarkable amounts in medium- and low-volatile bituminous coals (see peak i in Fig. 1i).

Besides rank determination, the kind of organic matter input in coals can also be derived from molecular features of the bitumen. This is exemplified for coal sample A by the occurrence of norpimarane (p) and retene (s) —both compounds were identified by their mass spectra— which are known to be major constituents in the
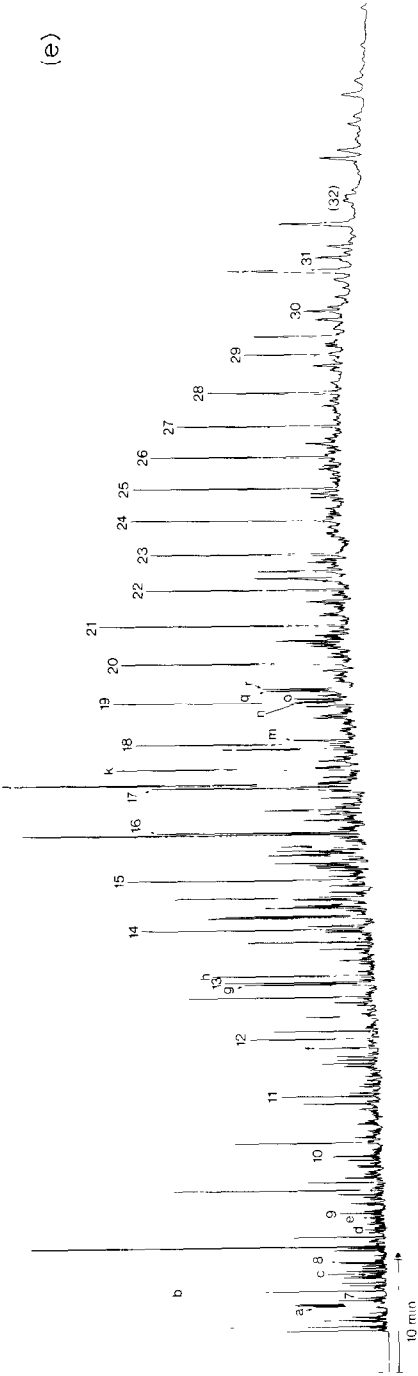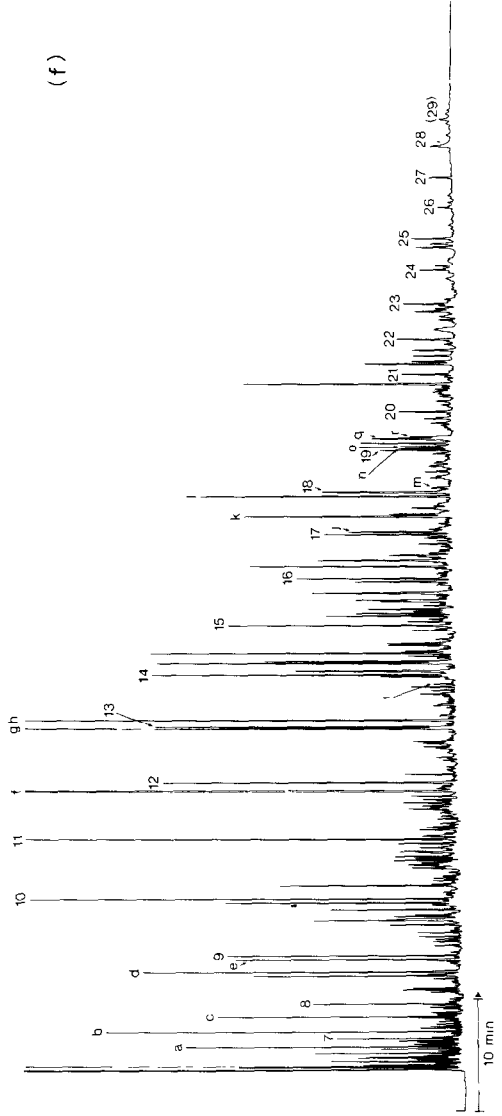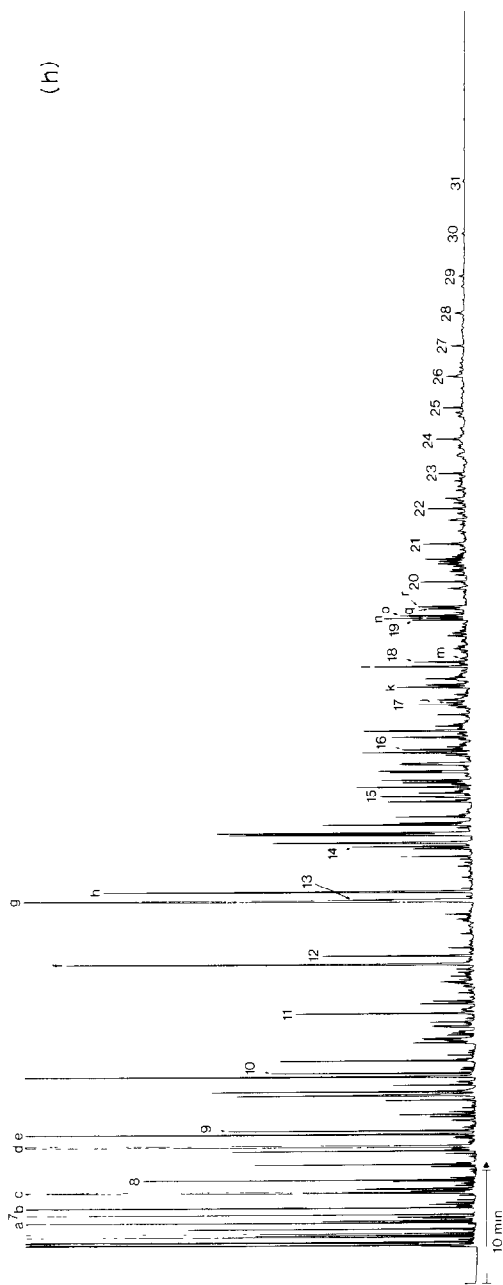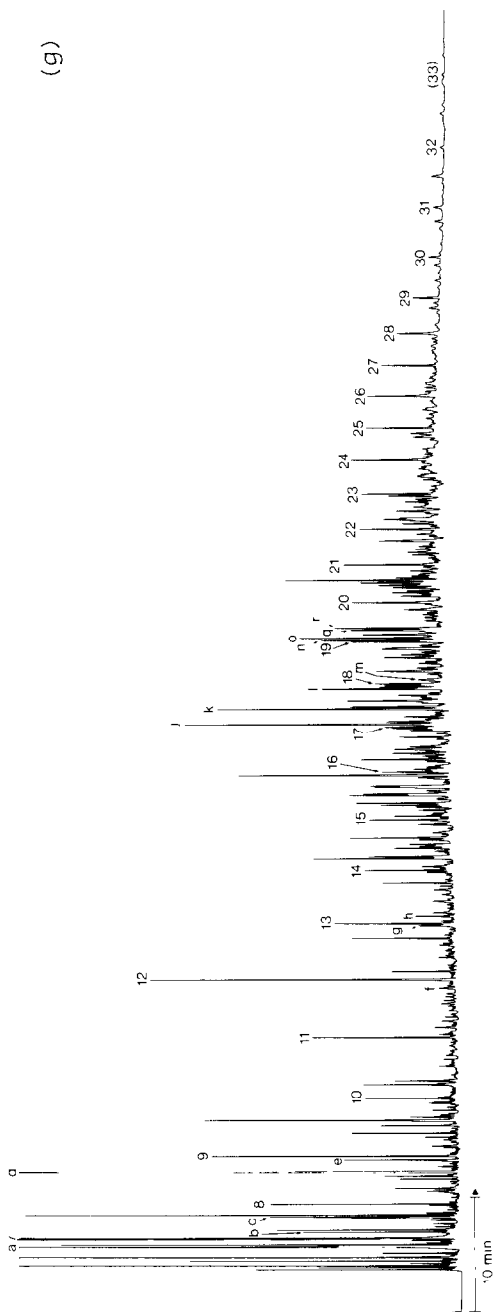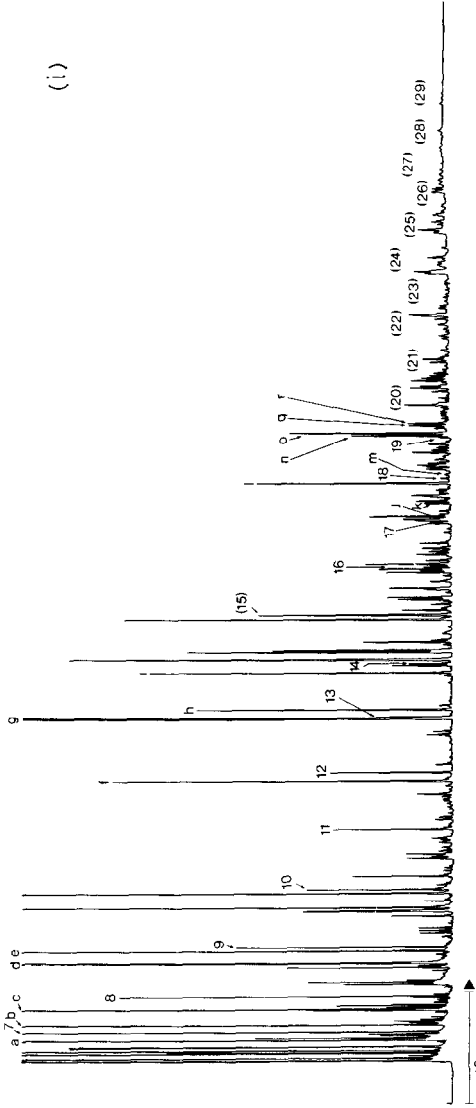
Fig. 1.

(e)

(f)

10 min

10 min

Fig. 1.

(i)
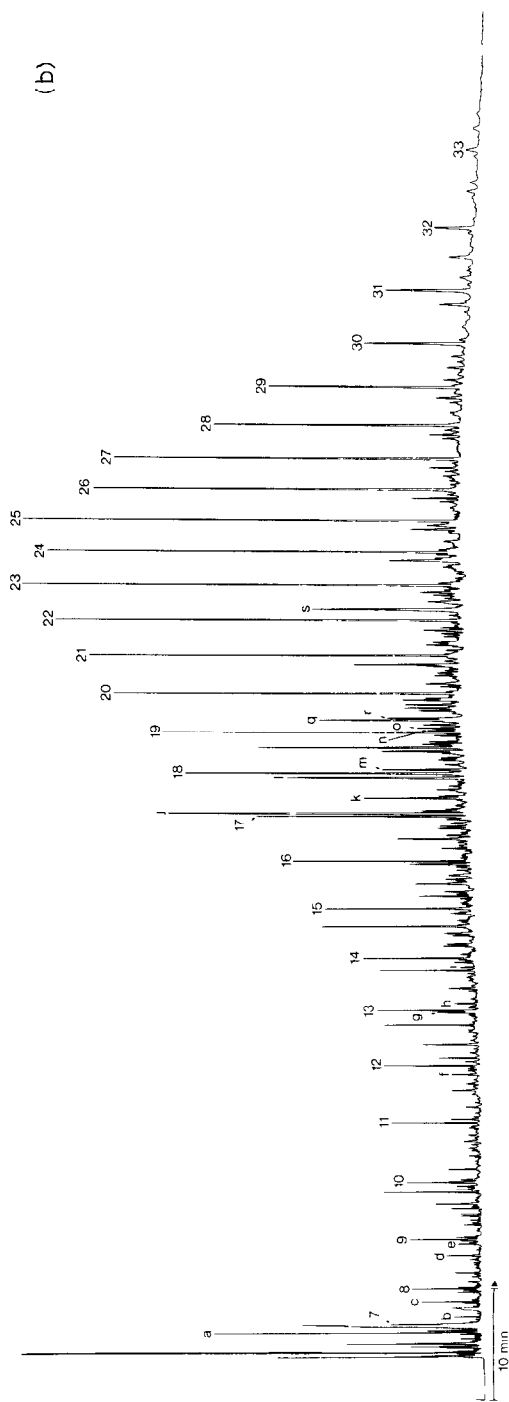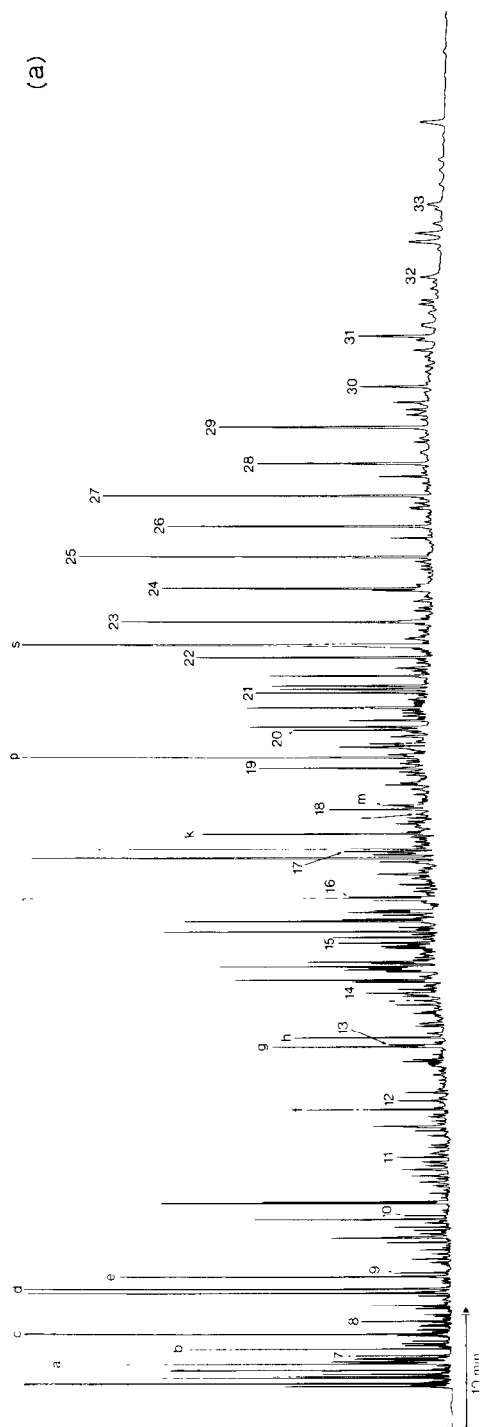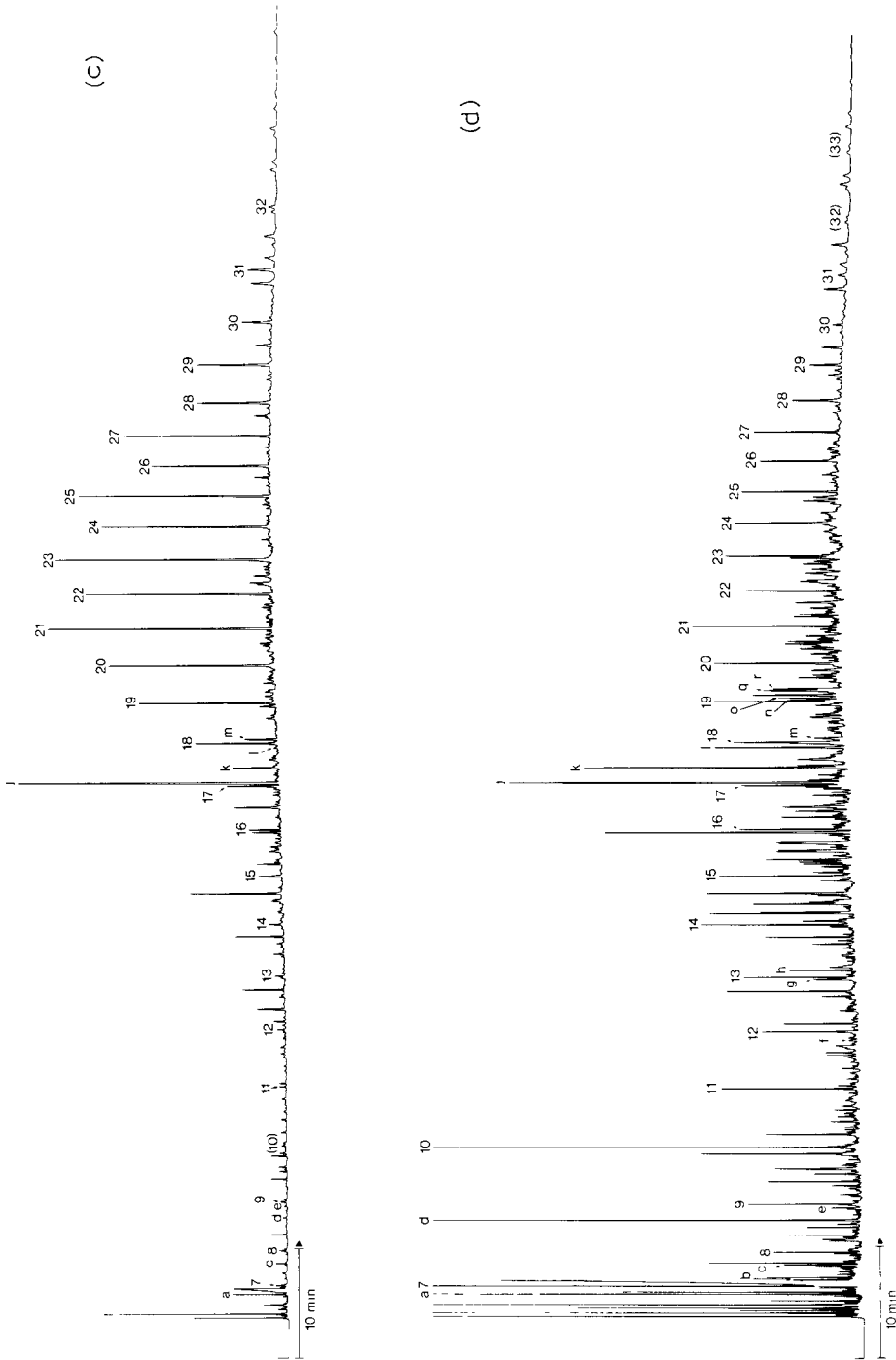
Fig. 1. Capillary gas chromatograms of hydrocarbons, thermodesorbed from coal samples A–I (see Table I) in a helium flow at 300°C. Peak identification according to Table II.

diagenetic products of terrestrial resins[16,17]. The presence of resinous components in sample A was confirmed by microscopical analysis[9].

CONCLUSIONS

In view of the complexity of the hydrocarbon composition of coals the use of a single GC column is, admittedly, problematic. For future applications, the installation of at least one additional capillary applied in parallel, i.e. with a different polarity, or the use of two-dimensional gas chromatography techniques ("selective sampling"[18], "multi-chromatography"[19]) will be necessary. However, despite the limited separation efficiency in the present examples the method turned out to provide various data of geochemical interest that are usually only obtained by elaborate solvent extraction, LC, and GC procedures.

The use of sample amounts in the milligram weight range, as in this study, appears possible. Therefore, the method offers an opportunity to study hydrocarbon distributions in the coal matrix and adjacent rocks on a very small scale. For instance, in a detailed investigation of solvent extracts from carboniferous coals it was found that the distribution of extractable hydrocarbons within a coal seam is largely homogeneous, due to a process of spreading the mobile organic compounds throughout the whole seam[20]. Micro-scale thermodesorption of coals, combined with capillary GC, could contribute to knowledge of the degree of homogenization effects in the coal matrix.

REFERENCES

1 D. Jonathan, G. L'Hôte and J. du Rouchet, Rev. Inst. Fr. Pét., 30 (1975) 65.
2 J. K. Whelan, J. M. Hunt and A. Y. Huc, J. Anal. Appl. Pyrol., 2 (1980) 79.
3 C. Saint-Paul, J.-C. Monin and B. Durand, Rev. Inst. Fr. Pét., 35 (1980) 1065.
4 R. Miller and W. Bertsch, in R. E. Kaiser (Editor), Proceedings of the 4th International Symposium on Capillary Chromatography, Hindelang 1981, Institute of Chromatography, Bad Dürkheim, 1981, p. 267.
5 R. G. Schaefer, J. High Resolut. Chromatogr. Chromatogr. Commun., 8 (1985) 267.
6 M. Bjorøy, H. Solli, K. Hall and P. Leplat, in A. G. Doré, S. S. Eggen, P. C. Home, R. M. Larsen and B. M. Thomas (Editors), Petroleum Geochemistry in Exploration of the Norwegian Shelf, Graham and Trotman, London, 1985, p. 327.
7 P. T. Crisp, J. Ellis, J. W. de Leeuw and P. A. Schenck, Anal. Chem., 58 (1986) 258.
8 H. Y. Tong and F. W. Karasek, Anal. Chem., 56 (1984) 2124.

9 W. Püttmann, M. Wolf and E. Wolff-Fischer, in D. Leythaeuser and J. Rullkötter (Editors), *Adv. Org. Geochem. 1985*, Pergamon Press, Oxford, 1986, p. 625.
10 M. Radke, H. Willsch, D. Leythaeuser and M. Teichmüller, *Geochim. Cosmochim. Acta*, 46 (1982) 1831.
11 Z. C. Corrêa da Silva, H. W. Hagemann, W. Püttmann and M. Wolf, *Zentralbl. Geol. Palaeontol., Teil 1*, (1985) 1565.
12 D. Leythaeuser and D. H. Welte, in P. A. Schenck and I. Havenaar (Editors), *Adv. Org. Geochem. 1968*, Pergamon Press, Oxford, 1969, p. 429.
13 J. D. Brooks, K. Gould and J. W. Smith, *Nature (London)*, 222 (1969) 257.
14 M. Radke, R. G. Schaefer, D. Leythaeuser and M. Teichmüller, *Geochim. Cosmochim. Acta*, 44 (1980) 1787.
15 M. Radke, D. H. Welte, in M. Bjorøy (Editor), *Adv. Org. Geochem. 1981*, Wiley, Chichester, 1983, p. 504.
16 B. R. T. Simoneit, *Geochim. Cosmochim. Acta*, 41 (1977) 463.
17 A. Livsey, A. G. Douglas and J. Connan, in P. A. Schenck, J. W. de Leeuw and G. W. M. Lijmbach (Editors), *Adv. Org. Geochem. 1983*, Pergamon Press, Oxford, 1984, p. 73.
18 G. Schomburg, F. Weeke and R. G. Schaefer, *J. High Resolut. Chromatogr. Chromatogr. Commun.*, 8 (1985) 388.
19 R. E. Kaiser and R. I. Rieder, *Labor Praxis*, 9 (1985) 1130.
20 J. Allan, S. R. Larter, in M. Bjorøy (Editor), *Adv. Org. Geochem. 1981*, Wiley, Chichester, 1983, p. 534.