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Molecular analysis of sulphur-rich brown coals by flash pyrolysis–gas chromatography–mass spectrometry

The Type III-S kerogen[☆]

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ABSTRACT

The molecular composition of five brown coals from three different basins (Maestrazgo, Mequinenza and Rubielos) in Spain was investigated by flash pyrolysis–gas chromatography and flash pyrolysis–gas chromatography–mass spectrometry. In these techniques, the macromolecular material is thermally degraded in an inert atmosphere and the compounds formed are on-line separated, identified and quantified. This information provided insight into the macromolecular structure of the coals which was inaccessible by other means. The composition of the pyrolysates is described in detail with emphasis on the distributions and relative abundance of *n*-alkanes, *n*-1-alkanes, (alkyl)phenols, sulphur compounds [(alkyl)thiophenes and (alkyl)benzothiophenes], (alkyl)benzenes and (alkyl)naphthalenes. These compound classes represent the major pyrolysis products of the samples analysed and were used to assess the contributions of specific biomacromolecules mainly originating from higher plants. One of the five brown coal samples investigated is so rich in organic sulphur (one sulphur atom for every 9–15 carbon atoms as determined by elemental analysis) that a new kerogen type (Type III-S) describing the kerogen contained in this coal is defined. Type III-S kerogen is defined as a kerogen with high atomic $S_{org.}/C$ (> 0.04) and O/C (> 0.20) ratios. Two of the five brown coals samples investigated contain a series of long-chain alkylbenzenes with an unprecedented carbon number distribution pattern with a second maximum at C_{18} . This unusual distribution pattern is thought to originate from the presence of long-chain alkylbenzene moieties bound via a heteroatom (presumably an ether bond) to the macromolecular coal matrix preferentially at position 12 in the alkyl side-chain of these moieties.

INTRODUCTION

Coal is predominantly a macromolecular organic substance mainly derived from specific tissues of higher plants such as woody tissue, cuticles, spores, pollen, seeds and corkified cell walls which have undergone chemical alterations by the coalification process [1]. To some extent remains of these tissues can still be recognized by light microscopic investigation of coal. This type of recognition has led to the maceral concept: macerals are defined as micro-

scopically recognizable entities in the coal matrix and shed light on the composition of coal and its original precursors.

Apart from this microscopic approach coal has also been analysed chemically for more than a century [2]. Elemental analysis and other bulk chemical analyses have been and still are important analytical techniques for characterizing coals. There is, however, increasing interest in the characterization of the structure of coal at the molecular level. Because of the macromolecular, insoluble nature of coal such a molecular characterization is more difficult than that of the other major fossil fuels, petroleum and natural gas. Spectroscopic techniques such as Fourier transform infrared and solid-state ^{13}C NMR spectroscopy have been used but do not

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provide information on the arrangement of atoms. Specific chemical degradation reactions have also been applied to coals to identify the structures of released moieties (*e.g.*, [3,4]). However, the yields are relatively low or the information is limited owing to less specific chemical reagents. Analytical pyrolysis (controlled thermal degradation in an inert atmosphere) in combination with gas chromatography, mass spectrometry and gas chromatography-mass spectrometry can supply detailed molecular information on coal [5–8] and isolated maceral fractions [9–11]. These pyrolysis approaches in combination with spectroscopy have led to the recognition of resistant, selectively enriched biomacromolecules in coal derived from plant cuticles (cutan [12–15]), corkified cell walls (suberan [16]), spores and pollen (sporopollenin [17,18]), seed coats [19], woody tissues [20] and resins [21].

Organic sulphur in coal is not derived from the biomacromolecules present in plant tissues. It is formed by syndeositional incorporation of reduced inorganic sulphur species formed by microbial reduction of sulphate into the organic matrix (for reviews see [22,23]) which leads to the formation of organically bound sulphur. It is therefore that marine-influenced depositional environments generate coals which generally have a higher sulphur content. Since the presence of organic sulphur is of major environmental concern in the utilization of this fossil fuel resource, a better understanding of the formation, forms and distribution of organic sulphur in coal is required [22–24].

In this paper, the results of analysis by flash pyrolysis–gas chromatography (Py–GC) and flash pyrolysis–gas chromatography–mass spectrometry (Py–GC–MS) of five sulphur-rich brown coals from Spain are reported. The results indicate that under specific conditions the organic sulphur content can become so high (one sulphur atom for every 9–14 carbon atoms) that it is appropriate to define a new type of kerogen, Type III-S.

EXPERIMENTAL

Coal samples

Five brown coal samples were selected from three different sedimentary basins in Spain. Three samples were taken from the Maestrazgo basin, which is located in the Iberian mountain chain and the

southern sector of the Catalan coastal range in NE Spain. Two of these samples (Estercuel and Portalrubio) are from the Utrillas formation and were both deposited in proximal areas of a delta estuary during the middle Albian (upper Lower Cretaceous, *ca.* 105 Ma). These coals have high sulphur contents (see Table I). This is possibly due to an influx of sulphate resulting from weathering of gypsum of the evaporitic Keuper formation in the catchment area into the delta estuary [25]. This resulted in significant sulphate reduction which, in turn, led to reaction of organic matter with reduced forms of inorganic sulphur. It is noteworthy that these conditions have led to a higher sulphur content of the coals deposited in proximal areas than in coals from the same basin derived from marine influenced depositional environments [25]. The Paula lignite was collected from sediments of the same basin and is thought to be of Tertiary age.

One sample was taken from the Mequinenza sub-basin which is located in the SE margin of the large Catalan Ebre (Ebro) basin. The Mequinenza basin is mainly filled with carbonate sediments deposited in an extensive, shallow, open palaeolake. The coal-bearing carbonate sequences were deposited in the open lacustrine zones closer to marginal evaporitic and marsh environments in the Oligocene (*ca.* 35 Ma) [26,27].

The Rubielos coal is from a basin located in the SE part of the Iberian mountain chain (NE Spain), which belongs to a Miocene (*ca.* 14 Ma) lacustrine system where lignites were deposited in the middle unit and are interbedded with lacustrine limestones which contain significant amounts of immature organic matter [28,29].

Sample treatment

Two coal samples (Mequinenza and Rubielos) were Soxhlet extracted with dichloromethane–methanol (2:1, v/v) for 36 h. The other three were analysed as such.

Elemental analysis

Elemental analysis (C, H, N, S_{tot.}) were performed on Carlo Erba Model 1106 and 1500 elemental analysers. Duplicate analyses indicated good reproducibility. Ash contents were determined gravimetrically by heating the sample at 900°C for 2 h. Pyrite and S_{org.} were determined according to ASTM methods.

Curie-point pyrolysis-gas chromatography

The brown coals were thermally degraded using a non-commercial Curie-point pyrolyser and ferromagnetic wires with a Curie temperature of 610°C. The brown coals were applied to the wire by pressing the samples on the wire [30]. The pyrolyser was mounted on the injection port of a Varian Model 3700 gas chromatograph. On-line separation of the flash pyrolysate was accomplished by using a fused-silica capillary column (25 m \times 0.32 mm I.D.) coated with CP Sil-5 CB (film thickness 0.40 μ m) (Chrompack, Middelburg, Netherlands). The oven of the gas chromatograph was temperature programmed from 0°C to 300°C at 3°C min⁻¹ using a cryogenic unit. The oven was first held at 0°C for 5 min and finally at 300°C for 15 min. Helium was used as the carrier gas. Pyrolysis products were detected by simultaneous flame ionization detection (FID) and sulphur-selective flame photometric detection (FPD) using a stream splitter (SGE) at the end of the capillary column.

Curie-point pyrolysis-gas chromatography-mass spectrometry

The coal samples were thermally degraded using a Curie-point pyrolyser (FOM-3LX [31]) and ferromagnetic wires with a Curie temperature of 610°C. The pyrolyser was connected directly to a gas chromatograph (Hewlett-Packard Model 5890) in tandem with a magnetic sector mass spectrometer (VG-70S) by direct insertion of the capillary column into the ion source. The gas chromatograph was fitted with a fused-silica capillary column (25 m \times 0.32 mm I.D.) coated with CP Sil-5 CB (film thickness 0.40 μ m) in an oven that was temperature programmed from 0°C to 300°C at 3°C min⁻¹. The oven was first held at 0°C for 5 min and finally at 300°C for 15 min. Helium was used as the carrier gas. The mass spectrometer was set at an ionizing voltage of 70 eV and operated at a cycle time of 1.8 s over the mass range m/z 40–800 at a resolution of 1000. Data acquisition was started 1 min after pyrolysis.

RESULTS AND DISCUSSION

The five selected coal samples were thermally degraded using ferromagnetic wires with a Curie temperature of 610°C. The pyrolysates of the coals were

analysed on-line by GC-MS. Compounds were identified by comparison of mass spectral and relative retention time data with literature data [32–36]. The total ion currents (TICs; Figs. 1A–5A) reveal the general composition of the pyrolysates. Although (alkyl)phenols, (alkyl)benzenes, (alkyl)naphthalenes, 1-pristene and *n*-alkanes and *n*-1-alkenes are major components in all pyrolysates, significant differences between the coals are observed. Large variations in the relative amounts of sulphur compounds (mainly alkylated thiophenes and benzo[*b*]thiophenes) are also noted. Hopanes and a series of higher-molecular-mass alkylbenzenes are only present in significant amounts in the Estercuel

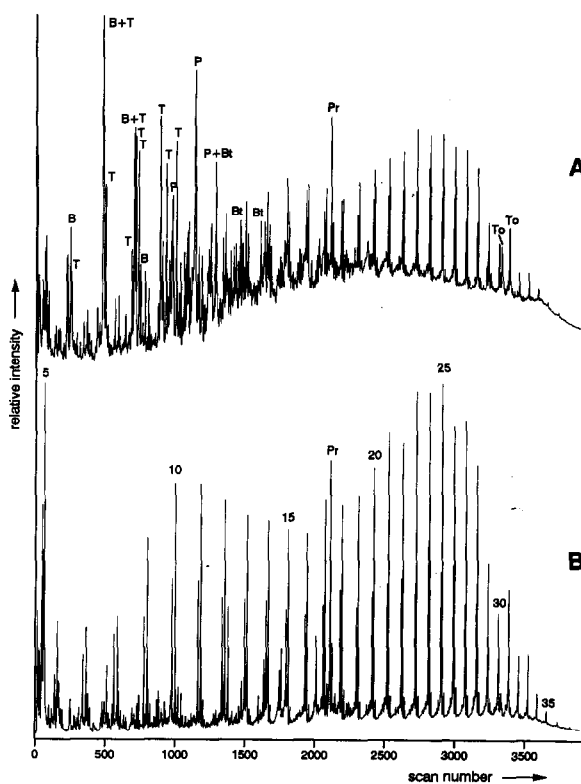


Fig. 1. (A) Total ion current (TIC) trace and (B) summed mass chromatogram of m/z 55 + 57 of the flash pyrolysate (Curie temperature 610°C) of the Mequinenza coal. Key for the TIC: B = (alkyl)benzenes; T = (alkyl)thiophenes; P = (alkyl)phenols; N = (alkyl)naphthalenes; Bt = (alkyl)benzothiophenes; D = 1,2-dihydroxybenzene; Pr = 1-pristene; To = tocopherols; H = hopanes. The number of carbon atoms of several members of the homologous series of *n*-1-alkenes and *n*-alkanes (series of doublets) in the m/z 55 + 57 mass chromatogram are indicated.

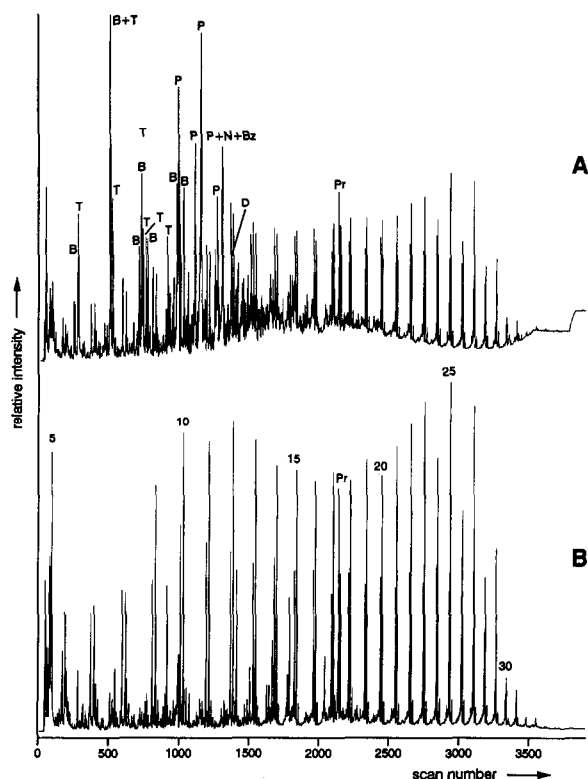


Fig. 4. (A) Total ion current (TIC) trace and (B) summed mass chromatogram of m/z 55 + 57 of the flash pyrolysate (Curie temperature 610°C) of the Paula coal. For the key to the symbols and numbers, see Fig. 1.

highly resistant biomacromolecule is selectively preserved during diagenesis and is, in case of coal formation, concentrated in the coal maceral cutinite [9–11]. In extant cuticles and in immature sediments these series of n -alkanes and n -1-alkenes are accompanied by a series of mainly long-chain methyl ketones [14]. The latter were found in the pyrolysate of the Paula coal but were below the detection limit in the other coal pyrolysates.

Other highly aliphatic biomacromolecular fractions which can be present in coal are suberan [16] and algaenan [40–45]. Suberan is a highly aliphatic biomacromolecule present in the outer bark tissue and explains the liptinitic nature of the coal maceral suberinite [16]. Algaenan is also a highly aliphatic biomacromolecule and is a major constituent of the outer cell walls of certain types of freshwater algae [40–45]. Alginite-rich coals probably contain these

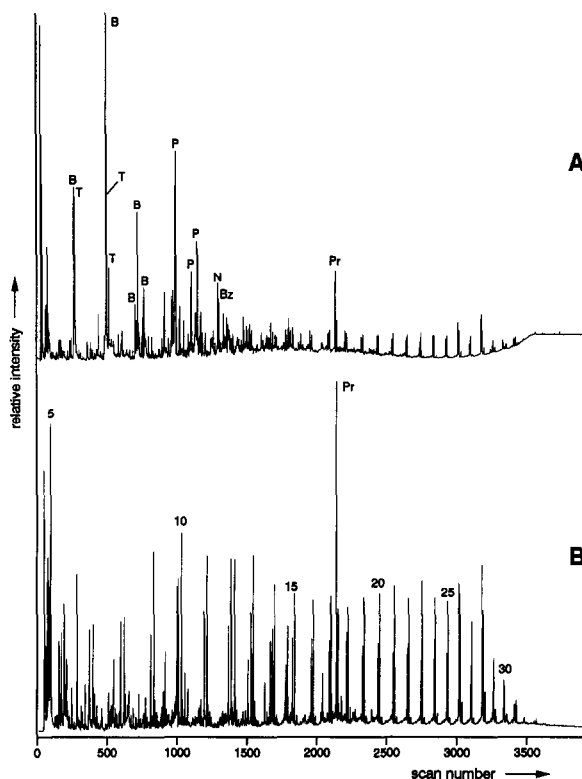


Fig. 5. (A) Total ion current (TIC) trace and (B) summed mass chromatogram of m/z 55 + 57 of the flash pyrolysate (Curie temperature 610°C) of the Rubielos coal. For the key to the symbols and numbers, see Fig. 1.

highly resistant algaenans. Recently, two other highly aliphatic biomacromolecules have been described in fossil spore walls (massulae) of water ferns [40] and in the inner coat (tegmen) of seeds of water plants [46]. These biomacromolecules can also explain, at least in part, the series of n -alkanes and n -1-alkenes in coal pyrolysates. Since all these different types of highly aliphatic biomacromolecules generate the same suite of compounds with distribution patterns depending on actual precursor organisms and stage of diagenesis, it is at present not possible to relate more specifically the series of n -alkanes and n -1-alkenes to one or more of the above-mentioned plant organs.

1-Pristene is a major component in all coal pyrolysates indicating the low stage of thermal maturity of the coals [47]. In the three unextracted coal samples it was possible to determine the pristane forma-

TABLE I
ELEMENTAL ANALYSIS, OPTICAL MEASUREMENT AND PYROLYSIS DATA FOR THE BROWN COALS STUDIED

Coal	Elemental analysis ^a							Pyrolysis								
	C (%)	H (%)	N (%)	S _{org.} (%)	O ^b (%)	H/C	S _{org.} /C	O/C	Ash (%)	S _{tot} (%)	Pyrite (%)	R _o ^J (%)	TR ^c	S _{org.} /C (estimated)	PFI ^d	R _o (%) ^f (estimated)
Mequinenza	60.6	5.3	1.0	10.1	23.0	1.05	0.062	0.28	13.9	11.5	1.2	0.31	1.60	0.11	nd	nd
Esteruel	73.2	5.8	0.7	3.2	17.1	0.95	0.016	0.18	19.2	4.4	2.3	0.39	0.44	0.03	0.19	0.42
Portlirubio	73.5	4.4	0.8	1.3	20.0	0.72	0.007	0.20	17.4	3.0	1.7	0.47	0.13	0.01	0.32	0.46
Paula	51.8	5.3	1.2	5.2	36.5 ^e	1.23	0.037	0.53 ^e	40.0	10.3	5.0	0.35	0.57	0.04	0.09	<0.04
Rubielos	45.6	3.8	1.5	3.2	45.9 ^e	1.00	0.026	0.75 ^e	15.4	4.2	0.8	0.34	0.24	0.02	nd	nd

^a On a dry and ash-free basis except for ash, total sulphur and pyrite contents, which are on a dry weight basis.

^b By difference.

^c TR = Thiophene ratio = (2,3-dimethylthiophene)/[(1,2-dimethylbenzene) + (n-1-nonene)].

^d PFI = Pristane formation index = (pristane)/[(pristane) + (prist-1-ene) + (prist-2-ene)].

^e These values are extremely high and probably erratic. Interpretation of these values should be performed with great caution.

^f R_o = Mean random vitrinite reflectance (oil).

tion index (PFI), which is defined as $[\text{pristane}] / \{[\text{pristane}] + [1\text{-pristene}] + [2\text{-pristene}]\}$ [47] and was measured from peak-height data in the m/z 55 + 57 mass chromatograms (Table I). Comparison with literature data of the Mahakam coal sequence [47] led to an estimate of the thermal maturity level in terms of vitrinite reflectance values (Table I). In the Estercuel, Portalrubio and Paula coals the calculated values agree surprisingly well with the measured values of vitrinite reflectance. These data confirmed the relatively low level of thermal maturity. Interestingly, the coals which yielded very similar pyrolysates (Estercuel and Portalrubio; *cf.*, Figs. 2A and 3A; see also later) do not have the same level of thermal maturity; the Portalrubio coal is more mature than the Estercuel coal.

It is thought that 1-pristene (and 2-pristene) are derived from thermal breakdown of macromolecularly bound tocopherols [48]. The abundance of tocopherols in the extracted Mequinenza coal (Figs. 1A and 6) support this idea. It is not completely understood why in the other coal pyrolysates tocopherols are much lower whereas 1-pristene is still a significant pyrolysis product (Figs. 2A–5A).

Hopanes are significantly present in the pyrolysates of the Estercuel and Portalrubio coals (Figs. 2A and 3A). Fig. 7 shows a partial accurate mass

chromatogram of m/z 191 revealing the distribution of the triterpanes in the Portalrubio coal pyrolysate. The distribution in the Estercuel coal pyrolysate is very similar to that shown in Fig. 7. All identified triterpanes belong to the hopane family; no triterpanes characteristic of higher land plants, such as oleananes or ursanes, were found. The abundance of hopanes relates to a contribution from bacteria to the coals.

Phenols and benzenediols

All pyrolysates contain abundant phenol and C_1 – C_3 alkylated phenols. No major differences in their distribution patterns were observed with the exception of the Rubielos coal pyrolysate where phenol is the most abundant component whereas in the other pyrolysates 3- and 4-methylphenol (which co-elute on the stationary phase used) are the most abundant. In addition 1,2-benzenediol and C_1 -alkylated 1,2-benzenediols are important pyrolysis products in the pyrolysates. The well known pyrolysis products of lignin, 4-alkyl-2-methoxyphenols and 4-alkyl-2,6-dimethoxyphenols [49], are not important pyrolysis products in these brown coals.

Similar distributions of phenols and benzenediols have been reported for pyrolysates of fossil outer seed walls (testae) of water plants and the Beulah

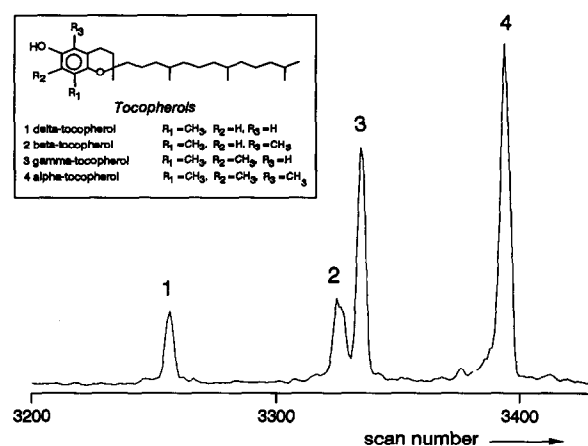


Fig. 6. Partial, summed mass chromatogram of m/z 137 + 151 + 165 + 402 + 416 + 430 showing the distribution of the tocopherols in the flash pyrolysate (Curie temperature 610°C) of the Mequinenza coal. The inset shows the structures of the tocopherols.

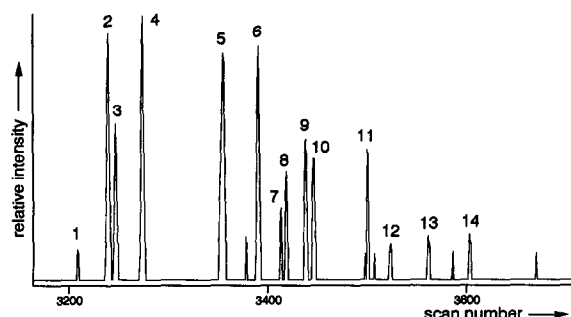


Fig. 7. Partial, accurate (mass window 0.04 dalton) mass chromatogram of m/z 191.22 revealing the distribution of the hopanes in the flash pyrolysate of the Portalrubio coal. Key: 1 = trisnorhopene; 2 = 22,29,30-trisnorhop-17,21-ene; 3 = 17 α (H)-22,29,30-trisnorhopane; 4 = 17 β (H)-22,29,30-trisnorhopane; 5 = 17 α (H),21 β (H)-30-norhopane; 6 = 17 β (H),21 α (H)-30-norhopane; 7 = hopene; 8 = 17 α (H),21 β (H)-hopane; 9 = 17 β (H),21 β (H)-30-norhopane; 10 = 17 β (H),21 α (H)-hopane; 11 = 17 α (H),21 β (H)-homohopane; 12 = 17 β (H),21 α (H)-homohopane; 13 = unknown hopane; 14 = 17 β (H),21 β (H)-homohopane.

Zap lignite [19]. At present, it is not clear whether the phenols encountered are derived from highly degraded lignin [20] or from a novel biomacromolecule, a polyphenol [19]. The first hypothesis is deemed unlikely by Van Bergen *et al.* [19] since the morphology of the testae of the fossil seeds is perfectly preserved. Such a preservation is unlikely if the underlying chemistry has been modified considerably. On the other hand, pyrolysates of recent angiosperm or gymnosperm wood, the major source of lignin-like materials in coal, contain only low relative amounts of phenols, which weakens the second hypothesis. Therefore, a straightforward interpretation of the origin of phenols in lignites and more mature coal pyrolysates cannot be made.

Sulphur compounds

The sulphur compounds present in the pyrolysates of the coals studied are dominated by hydrogen sulphide (as revealed by the FPD chromatograms) and (alkyl)thiophenes, although (alkyl)benzothiophenes were also present in all pyrolysates. Hydrogen sulphide is formed by thermal degradation of (poly)sulphide linkages in the macromolecular coal matrix whilst alkylthiophenes and -benzothiophenes are produced from sulphur-containing aromatic units [50].

The dominance of alkylthiophenes over alkylbenzothiophenes is consistent with the low level of thermal maturity of the brown coal samples [51]. The distribution patterns of the C₁–C₄ alkylthiophenes in the pyrolysates are relatively similar (Fig. 8). 2-Methylthiophene is in all cases the most abundant thiophene present. A difference is observed in the abundance of the C₂+ alkylthiophenes relative to 2-methylthiophene: in the pyrolysate of the Mequinenza coal the C₂+ alkylthiophenes are more abundant than in the pyrolysate of the Rubielos coal (*cf.*, Fig. 8A and C). In the latter pyrolysate C₄ alkylthiophenes are difficult to identify because of their low concentrations. In the C₂-cluster 2,4-dimethylthiophene is the most dominant component. This is a characteristic pattern for coal pyrolysates [23,50–53]. In kerogen pyrolysates 2,5- and 2,3-dimethylthiophene (compounds 4 and 6 in Fig. 8) are always more abundant than 2,4-dimethylthiophene [50–53]. The abundance of 3-isopropyl-2-methylthiophene (compound 14 in Fig. 8), especially in the Mequinenza coal pyrolysate, is noteworthy. This is

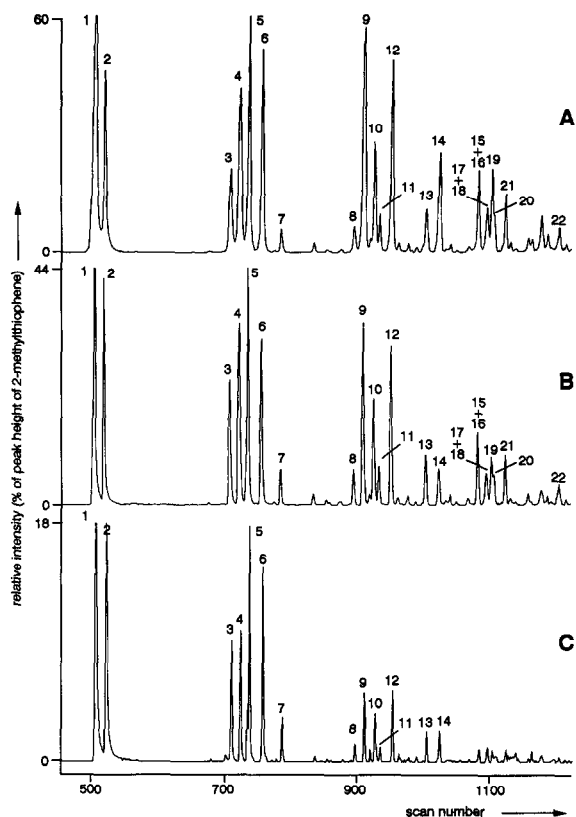


Fig. 8. Partial, accurate (mass window 0.02) summed mass chromatogram of m/z 97.01 + 98.01 + 111.03 + 112.03 + 125.03 + 126.03 + 139.03 + 140.03 illustrating the distribution of the C₁–C₄ alkylated thiophenes in the flash pyrolysates of the (A) Mequinenza, (B) Estercuel and (C) Rubielos coals. Key: 1 = 2-methylthiophene; 2 = 3-methylthiophene; 3 = 2-ethylthiophene; 4 = 2,5-dimethylthiophene; 5 = 2,4-dimethylthiophene; 6 = 2,3-dimethylthiophene; 7 = 3,4-dimethylthiophene; 8 = 2-propylthiophene; 9 = 2-ethyl-5-methylthiophene; 10 = 2-ethyl-4-methylthiophene; 11 = ethylmethylthiophene; 12 = 2,3,5-trimethylthiophene; 13 = 2,3,4-trimethylthiophene; 14 = 3-isopropyl-2-methylthiophene; 15 = 2-methyl-5-propylthiophene; 16 = 2,5-diethylthiophene; 17 = 2-butylthiophene; 18 = methylpropylthiophene; 19 = 2-ethyl-3,5-dimethylthiophene; 20 = ethyldimethylthiophene; 21 = 5-ethyl-2,3-dimethylthiophene; 22 = 2,3,4,5-tetramethylthiophene. Mass chromatograms are normalized on peak 5.

the first coal sample in which this compound is the most abundant C₄ alkylthiophene. 3-Isopropyl-2-methylthiophene has also been encountered as a major compound in flash pyrolysates of kerogens from the Monterey Formation [54]. The structure of 3-isopropyl-2-methylthiophene suggests that it is

formed during pyrolysis via β -cleavage of macromolecular moieties in the coal matrix which were formed by incorporation of sulphur into 24-ethyl steroids [51]. The predominance of this compound in all coal pyrolysates can be rationalized by the fact that the major steroids biosynthesized by higher plants are compounds with an ethyl at C₂₄ [55].

Although qualitatively no major differences were observed in thiophene composition, large variations in abundance relative to other pyrolysis products are evident (Figs. 1A–5A). The Mequinenza coal pyrolysate (Fig. 1) contains the highest amounts of alkylthiophenes relative to the other pyrolysis products. This is also reflected by the very high thiophene ratio (1.60, Table I), which is defined as $[2,3\text{-dimethylthiophene}]/\{[1,2\text{-dimethylbenzene}] + [n\text{-1-nonene}]\}$ [52]. This ratio is obtained by integration of the appropriate peaks in the FID chromatogram of the pyrolysate. The thiophene ratio can be used to obtain an idea of the organic sulphur content of the samples pyrolysed [52]. Using the plot of the thiophene ratio *versus* atomic $S_{\text{org.}}/C$ ratios determined for a whole suite of samples as reported by Eglinton *et al.* [52], the $S_{\text{org.}}/C$ ratio of the Mequinenza coal can be estimated to be 0.11. Elemental analysis indicates an atomic $S_{\text{org.}}/C$ ratio of 0.062 (Table I), which suggests that the concentration of organic sulphur is overestimated by this approach. However, these measurements both indicate that this coal is extremely rich in organic sulphur (for every 9–14 carbon atoms it contains one sulphur atom). In this context, it should be noted that Orr [56] has defined organic sulphur-rich Type II kerogens as Type II-S kerogens when their atomic $S_{\text{org.}}/C$ ratios were larger than 0.04. Following the same definition, we propose here to classify the Mequinenza coal as a Type III-S kerogen characterized by a low atomic H/C and a high atomic $S_{\text{org.}}/C$ (>0.04) and O/C (>0.20) ratios. The other coal pyrolysates contain less abundant sulphur compounds (Figs. 2A–5A) as is also evident from their thiophene ratios (Table I). The Paula coal is, however, still fairly sulphur-rich and its estimated $S_{\text{org.}}/C$ ratio (Table I) indicate that it has a composition close to that of a Type III-S kerogen, as confirmed by the elemental analysis data (Table I). The organic sulphur data obtained by Py-GC-MS show the same trends as the elemental composition data (Table I), although some discrepancies exist in absolute values.

An interesting observation is the significant difference in the abundance of alkylthiophenes in the pyrolysates of the Estercuel and Portalrubio coals, whereas the distribution of other pyrolysis products is very similar (see also the later discussion of extended alkylbenzenes), suggesting a very similar contribution of organic matter to these coals. This can be explained by the availability of inorganic sulphur species which are capable of reacting with the organic matter to form thiophene moieties in the coal matrix in the palaeodepositional environment. In the case of the depositional environment of the Portalrubio coal less inorganic sulphur species were available than in the case of the Estercuel depositional environment. A second explanation is the slightly higher level of thermal maturity of the Portalrubio coal; it is known that on increasing thermal stress organic sulphur is preferentially removed [51,57].

In the Rubielos coal pyrolysate a series of as yet unrecognized sulphur compounds were identified. Their presence was evident from the FPD chromatogram of the pyrolysate (Fig. 9), which contains a large peak not previously noted in other analyses of coal and kerogen samples [50–52]. The mass spectrum of this component (Fig. 9, inset) indicates that it is dimethyl tetrasulphide. The presence of four sulphur atoms in this molecule explains why the presence of this component in the pyrolysate leads to such a large peak in the FPD chromatogram (note also that the FPD instrument has a quadratic response). Dimethyl trisulphide and dimethyl disulphide were also identified in the pyrolysate. It was not possible to determine whether dimethyl sulphide was also present in the pyrolysate since the acquisition of mass spectra starts 1 min after pyrolysis. The geochemical significance of these dimethyl polysulphides in pyrolysates is as yet unknown but their formation by secondary reactions is unlikely because primary pyrolysis products are removed very rapidly from the heated zone. The presence of these dimethyl polysulphides may explain the discrepancy between the $S_{\text{org.}}/C$ ratio as estimated by the thiophene ratio and the higher atomic $S_{\text{org.}}/C$ ratio as determined by elemental analysis because the former determination takes only relative thiophene abundance into consideration which in case of the Rubielos coal will lead to an underestimation owing to the presence of dimethyl polysulphides in the pyrolysate.

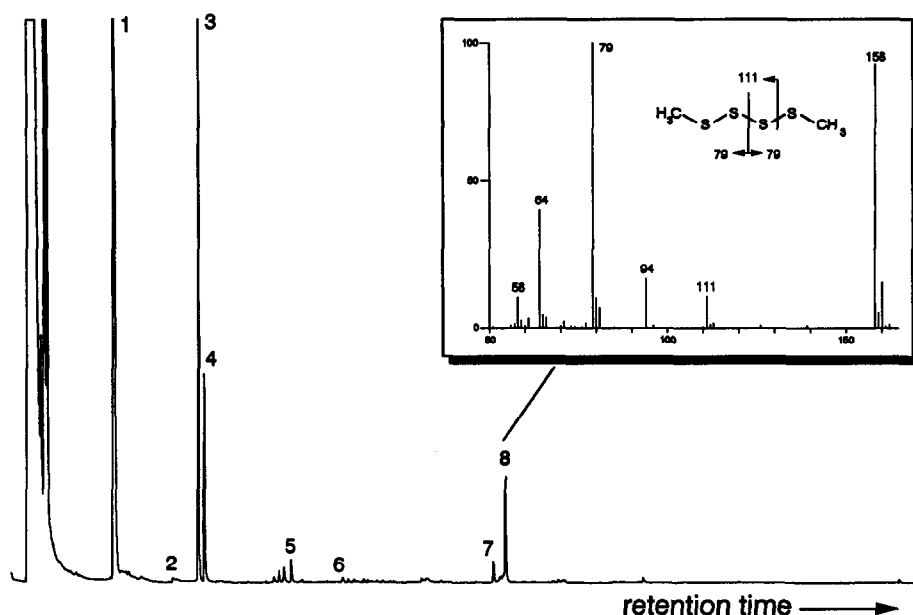


Fig. 9. Partial (0–90 min) FPD chromatogram (normalized on compound 3) of the pyrolysate of the Rubielos coal. Key: 1 = thiophene; 2 = dimethyl disulphide; 3 = 2-methylthiophene; 4 = 3-methylthiophene; 5 = 2,3-dimethylthiophene; 6 = dimethyl trisulphide; 7 = benzo[*b*]thiophene; 8 = dimethyl tetrasulphide. The inset shows the mass spectrum (corrected for background) of dimethyl tetrasulphide.

Alkylbenzenes

The C₁–C₄ alkylated benzenes are dominant pyrolysis products in all coal pyrolysates but no major differences were observed in their distribution patterns. Fig. 10 illustrates this statement; it shows the distributions in two coal pyrolysates in which some variation can be observed. For example, ethylbenzene (compound 2 in Fig. 10), propylbenzene (compound 7) and butylbenzene (compound 21) are relatively higher in the Portalrubio coal pyrolysate than in the Paula coal pyrolysate. In general, the alkylbenzene distributions are typical for those observed in coal pyrolysates [58]. The relatively low amounts of 1,2,3,4-tetramethylbenzene reveals that photosynthetic sulphur bacteria are not major contributors of organic matter to these coals [58–61]. In case of the Rubielos coal pyrolysate a substantial reduction in the abundance of C₂–C₄ alkylbenzenes relative to toluene is observed, an observation also made in case of the alkylthiophenes.

Striking differences between the coal pyrolysates were observed in the distributions of long-chain alkylbenzenes. In most samples these compounds are

dominated by monoalkylbenzenes; only the pyrolysates of Paula and Rubielos coals contain a series of 2-alkyltoluenes with a concentration of the same order of magnitude as the monoalkylbenzenes. The distributions of the monoalkylbenzenes in three representative pyrolysates are shown by partial mass chromatograms of *m/z* 91 + 92, the two most abundant ions in the mass spectra of monoalkylbenzenes (Fig. 11). In case of the Mequinenza and Rubielos coal pyrolysates (Fig. 11B and C), the concentration of the higher members of this series of compounds is only a few percent of the first member (*i.e.*, toluene). However, in case of the Estercuel (Fig. 11A) and Portalrubio (not shown but identical with that of Estercuel) coal pyrolysates, a second maximum is observed at C₁₈. Further, a second series of compounds eluting just before the monoalkylbenzenes is apparent in Fig. 11A. This second series has a maximum at C₁₇ and a slight odd-over-even carbon number predominance in the C₁₆–C₂₀ range, whereas the monoalkylbenzenes possess an even-over-odd carbon number predominance in this range. Mass spectra of the C₁₇ mem-

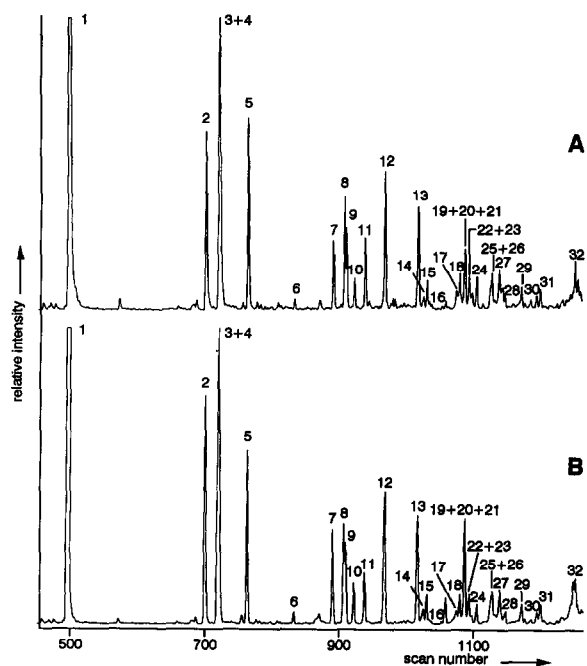


Fig. 10. Partial summed mass chromatograms of m/z 91 + 92 + 105 + 106 + 119 + 120 + 133 + 134 revealing the distributions of the C_1 – C_4 alkylated benzenes in the flash pyrolysates of the kerogens of (A) Paula and (B) Portalrubio coal. Key: 1 = toluene; 2 = ethylbenzene; 3 = *m*-xylene; 4 = *p*-xylene; 5 = *o*-xylene; 6 = isopropylbenzene; 7 = propylbenzene; 8 = 1-ethyl-3-methylbenzene; 9 = 1-ethyl-4-methylbenzene; 10 = 1,3,5-trimethylbenzene; 11 = 1-ethyl-2-methylbenzene; 12 = 1,2,4-trimethylbenzene; 13 = 1,2,3-trimethylbenzene; 14 = 1-isopropyl-3-methylbenzene; 15 = 1-isopropyl-4-methylbenzene; 16 = 1-isopropyl-2-methylbenzene; 17 = 1,3-diethylbenzene; 18 = 1-methyl-3-propylbenzene; 19 = 1-methyl-4-propylbenzene; 20 = 1,4-diethylbenzene; 21 = butylbenzene; 22 = 1,2-diethylbenzene; 23 = 1-ethyl-3,5-dimethylbenzene; 24 = 1-methyl-2-propylbenzene; 25 = 2-ethyl-1,4-dimethylbenzene; 26 = 1-ethyl-2,4-dimethylbenzene; 27 = 1-ethyl-3,4-dimethylbenzene; 28 = 2-ethyl-1,3-dimethylbenzene; 29 = 1-ethyl-2,3-dimethylbenzene; 30 = 1,2,4,5-tetramethylbenzene; 31 = 1,2,3,5-tetramethylbenzene; 32 = 1,2,3,4-tetramethylbenzene. Mass chromatograms are normalized on peak 3 + 4. Semi-quantitative determination of the alkylbenzene abundances indicated that the concentration of 1,3- and 1,4-dimethylbenzene is 30% and 8% of the toluene concentration in the pyrolysates of the Paula and Portalrubio coal, respectively.

bers of these series (Fig. 12) indicated that the second (earlier eluting) series is most likely a linear alkylbenzene with an unsaturation in the side-chain. The characteristic fragment of m/z 104, which is present in all the mass spectra of this series, indicates that the double bond is not conjugated

with the aromatic ring but reference mass spectra indicated that this fragment cannot be used to further assess the double bond position [62]. The formation of this ion is most likely induced by an α -hydrogen transfer. Mass chromatography of m/z 91 + 92, 104 and 230 of the C_{17} cluster (Fig. 13) reveals that, in addition to the major series described above, other minor components (compounds 1, 4 and 5 in Fig. 13) are present which possess similar mass spectra, suggesting that they are isomers of the major "104" component. This can be rationalized by the presence of isomers with the double bond in

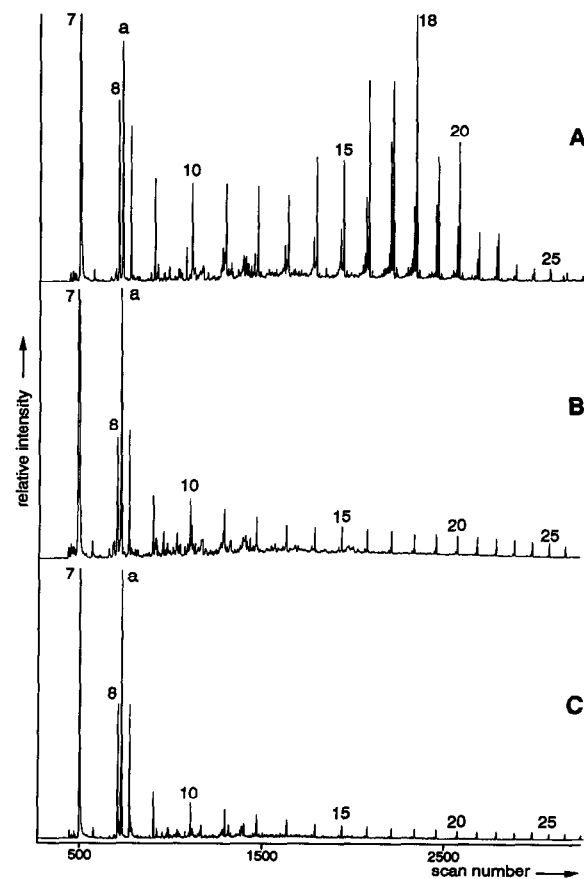


Fig. 11. Partial, summed mass chromatograms of m/z 91 + 92 revealing the distributions of alkylbenzenes in the flash pyrolysates of (A) Esterceul, (B) Mequinenza and (C) Rubielos coals. Numbers indicate total number of carbon atoms of this series of compounds. Mass chromatograms are normalized on 1,3- and 1,4-dimethylbenzene (peak a) in case of the Mequinenza and Rubielos coal pyrolysates and on dodecylbenzene in case of the Esterceul coal pyrolysate.

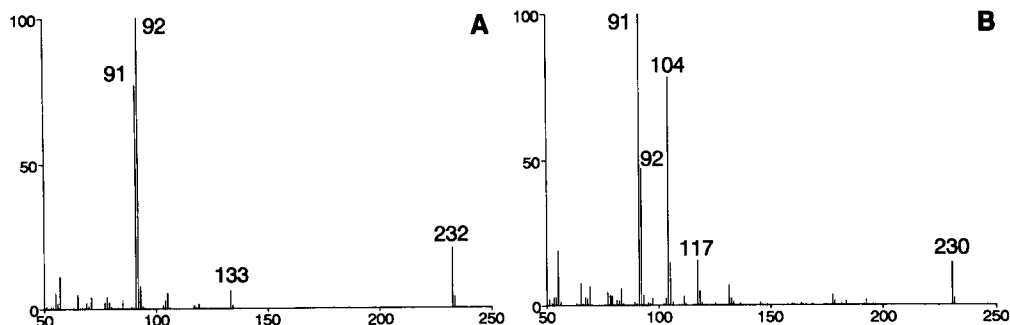


Fig. 12. Mass spectra (subtracted for background) of (A) *n*-undecylbenzene and (B) *n*-undec-11-enylbenzene obtained from the Py-GC-MS analysis of the Estercuel coal.

different positions and in different stereochemical configurations (*cis* and *trans*). By analogy with the retention behaviour of *n*-alkenes relative to *n*-alkanes [63], compound 2 in Fig. 13 is tentatively identified as undec-10-enylbenzene, compounds 3 and 4 as *cis*- and *trans*-undec-9-enylbenzene and the cluster of compounds indicated by 1 as monounsaturated undecylbenzenes with the double bond position at ω^3 – ω^9 .

To the best of our knowledge, a distribution of monoalkylbenzenes as observed in the Estercuel and Portarubio coal pyrolysates has not yet been reported. This phenomenon probably indicates that the Estercuel and Portarubio coals contain specific moieties from which these long-chain monoalkylbenzenes are generated. Similar distributions have been observed for homologous series of pyrolysis products generated from aromatic moieties (which preferentially cleave at the β -carbon-carbon bond of the alkyl side-chain): 2-alkyltoluenes, 2-alkyl-5-methylthiophenes and 2-alkyl-5-ethylthiophenes in the pyrolysate of the kerogen of the Guttenberg Oil Rock [59] and for 5-alkyl-1,3-benzenediols and mono- and dimethyl-5-alkyl-1,3-benzenediols in the pyrolysate of the kerogen of the Estonian kukersite [64]. In both studies these distributions were interpreted as caused by thermal degradation of a moiety (toluene, 2-methylthiophene, 2-ethylthiophene, 1,3-benzenediol and methylated 1,3-benzenediol) with a long alkyl chain bound to the macromolecular matrix via a heteroatom. The second maximum in the distribution can then be used to assess the position in the alkyl side-chain at which most of the moieties are bound to the macromolecular matrix. These interpretations are, to some extent, support-

ed by pyrolysis of model compounds [60]. For example, flash pyrolysis of the sodium salt of 16-(4'-methylphenyl)hexadecanoic acid generates a suite of 4-alkyltoluenes with a maximum at C₂₂. Further, unsaturated counterparts are also formed and show

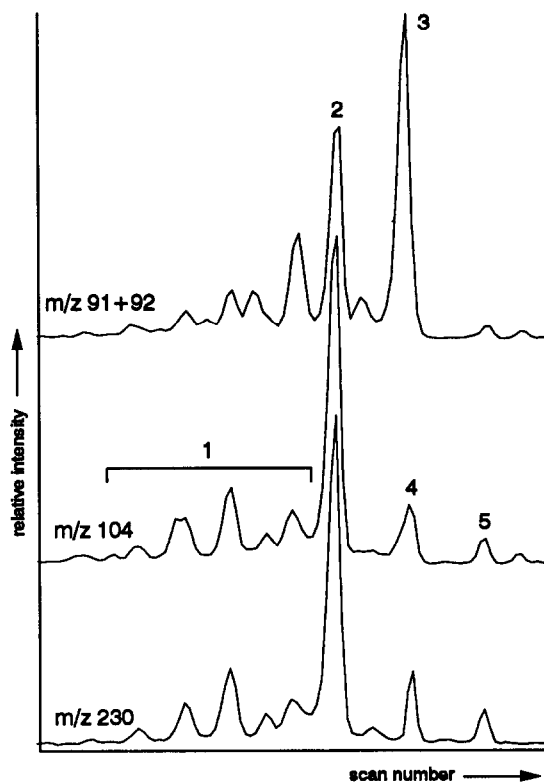


Fig. 13. Partial mass chromatograms of m/z 91 + 92, m/z 104 and m/z 230 of the pyrolysate of the Portarubio coal.

a shift in their carbon number distribution by one carbon atom [60]. These data suggest that in case of the Estercuel and Portalrubio coal long-chain alkylbenzenes are present and are preferentially bound at position 12 in the alkyl side-chain of these moieties. At present we can only speculate on the heteroatom involved in the bonding of these moieties but on basis of the significant differences in organic sulphur content between the two coals (see above) and the abundance of oxygen (Table I), ether bonds are not unlikely.

Alkyl-naphthalenes

Naphthalene and alkylated naphthalenes are important compounds in all pyrolysates, but are especially abundant in the Estercuel and Portalrubio coal pyrolysates. Fig. 14 (left panels) shows the distribution of naphthalene and its C_1 – C_3 alkylated derivatives by summed mass chromatograms of m/z 128 + 141 + 142 + 155 + 156 + 169 + 170 (the major ions in the mass spectra of these compounds) in the pyrolysates of the Mequinenza, Estercuel, Paula and Rubielos coals. The distribution of the (alkyl)naphthalenes in the Estercuel and Portalrubio coals pyrolysates is virtually identical, illustrating again the similar composition of these two samples. Substantial differences are observed in the carbon number distributions of the naphthalenes: naphthalene is the most dominant component in the Rubielos coal pyrolysate whereas the C_1 and the C_3 alkyl-naphthalenes dominate in the pyrolysates of the Mequinenza and Paula coals and Estercuel coal, respectively.

Significant differences are also observed in the internal distribution patterns. For example, the distribution of the C_2 alkylated naphthalenes (Fig. 14, middle panels) is similar for the Estercuel, Paula and Rubielos coal pyrolysates but substantially different from that of the Mequinenza coal pyrolysate. In the latter pyrolysate, 1,5-dimethylnaphthalene (compound 12 in Fig. 14) dominates whereas in the other pyrolysates 1,7-dimethylnaphthalene and/or 1,6-dimethylnaphthalene (compounds 9 and 10) are the most abundant C_2 alkyl-naphthalene(s).

The distribution of the C_3 alkyl-naphthalenes (Fig. 14, right panels) in the Estercuel, Portalrubio and Paula coal pyrolysates is similar and is dominated by 1,2,5-trimethylnaphthalene (compound 27). In case of the Estercuel and Portalrubio pyroly-

sates this compound is prominent in the TIC. The C_3 alkyl-naphthalene distributions in the pyrolysates of the other two coals are not dominated by a specific isomer. It is worth noting that although the C_2 alkyl-naphthalene distribution of the pyrolysate of the Rubielos coal is similar to that observed in the Paula and Estercuel coal pyrolysates, the C_3 alkyl-naphthalene distribution is completely different (Fig. 14). In the pyrolysates where the C_3 alkyl-naphthalenes are dominated by 1,2,5-trimethylnaphthalene the C_4 alkyl-naphthalenes are also dominated by one specific isomer, 1,2,5,6-tetramethylnaphthalene (not shown). The concentration of this component is *ca.* 50% of the concentration of 1,2,5-trimethylnaphthalene. The co-occurrence of 1,2,5-trimethylnaphthalene and 1,2,5,6-tetramethylnaphthalene as major alkyl-naphthalenes has been described before in extracts of coal and shale samples [65]. Püttmann and Villar [65] and De las Heras [66] attributed the predominance of these two specific polymethylnaphthalenes in the coal extracts to their diagenetic derivation from pentacyclic triterpenoids via 8,14-*seco*-triterpenoids. Such a derivation is in agreement with the abundance of hopanes in two of the three samples (*i.e.*, Estercuel and Portalrubio) with these characteristics. The coal samples examined by Püttmann and Villar [65] had a slightly higher level of thermal maturity (random vitrinite reflectance 0.58–0.83%) than the brown coals studied in this work. In the case of the brown coals these specific naphthalenes are probably generated mainly via thermal breakdown of the macromolecular matrix, suggesting that macromolecularly bound aromatized 8,14-*seco*-triterpenoids are the precursors of these compounds.

In the pyrolysates of the Estercuel and Portalrubio coals cadalene (4-isopropyl-1,6-dimethylnaphthalene) is an important component and the dominant C_5 alkyl-naphthalene. Its co-occurrence with 1,6-dimethylnaphthalene as a major C_2 alkyl-naphthalene can be ascribed to the presence of resin-derived material (resinite) in the coal samples [67].

CONCLUSIONS

The pyrolysates of the five brown coals all contain abundant *n*-alkanes, *n*-1-alkenes, (alkyl)phenols and alkyl(benzenes). The *n*-alkanes and *n*-1-

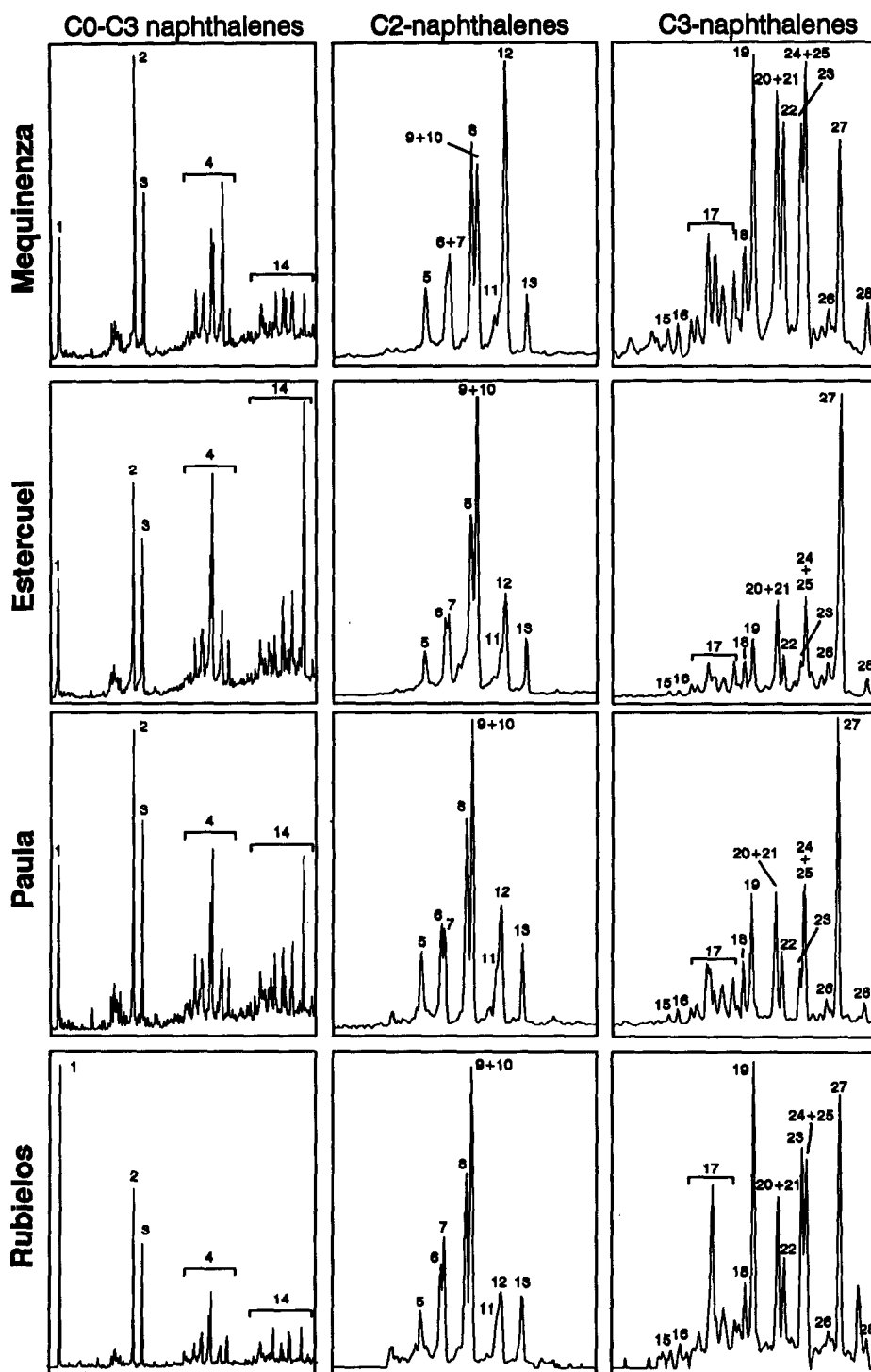


Fig. 14. Partial summed mass chromatograms of m/z 128 + 141 + 142 + 155 + 156 + 169 + 170 and m/z 156 and 170 illustrating the distribution of naphthalene and C_1 – C_3 alkylated naphthalenes and the C_2 and C_3 naphthalenes, respectively, in the pyrolysates of the Mequinenza, Esteruel, Paula and Rubielos coals. Keys: 1 = naphthalene; 2 = 2-methylnaphthalene; 3 = 1-methylnaphthalene; 4 = C_2 naphthalenes; 5 = 2-ethylnaphthalene; 6 = 2,5-dimethylnaphthalene; 7 = 2,7-dimethylnaphthalene; 8 = 1,3-dimethylnaphthalene; 9 = 1,7-dimethylnaphthalene; 10 = 1,6-dimethylnaphthalene; 11 = 2,3- and 1,4-dimethylnaphthalene; 12 = 1,5-dimethylnaphthalene; 13 = 1,2-dimethylnaphthalene; 14 = C_4 -naphthalenes; 15 = 2-propylnaphthalene; 16 = 1-propylnaphthalene; 17 = ethylmethylnaphthalenes; 18 = 1,3,7-trimethylnaphthalene; 19 = 1,3,6-trimethylnaphthalene; 20 = 1,4,6-trimethylnaphthalene; 21 = 1,3,5-trimethylnaphthalene; 22 = 2,3,6-trimethylnaphthalene; 23 = 1,2,7-trimethylnaphthalene; 24 = 1,6,7-trimethylnaphthalene; 25 = 1,2,6-trimethylnaphthalene; 26 = 1,2,4-trimethylnaphthalene; 27 = 1,2,5-trimethylnaphthalene; 28 = 1,2,3-trimethylnaphthalene.

alkenes are derived from thermal breakdown of aliphatic biomacromolecules such as cutan, algaenan and/or suberan whereas the (alkyl)phenols reflect the presence of highly degraded lignin or a polyphenol biomacromolecule. The short-chain alkylbenzenes cannot be ascribed to a specific source material in the brown coals. All pyrolysates contain 1-pristene as a major pyrolysis product. This probably reflects the presence of macromolecularly bound tocopherols. This was confirmed by the presence of significant amounts of a series of tocopherols in the pyrolysate in one extracted brown coal.

One of the five brown coal samples investigated is so rich in organic sulphur (one sulphur atom for every 9–14 carbon atoms) that it is appropriate to define a new kerogen type describing the kerogen contained in this coal. Type III-S kerogen is defined as a kerogen with high atomic $S_{org.}/C$ (>0.04) and O/C ratios (>0.20). The flash pyrolysates of such samples are dominated by sulphur compounds [mainly (alkyl)thiophenes and (alkyl)benzothiophenes] and (alkyl)phenols.

Two of the five brown samples investigated contain a series of long-chain alkylbenzenes with an unprecedented carbon number distribution pattern with a second maximum at C_{18} . This unusual distribution pattern is thought to originate from the presence of long-chain alkylbenzene moieties bound via a heteroatom (presumably an ether bond) to the macromolecular coal matrix preferentially at position 12 in the alkyl side-chain of these moieties. The origin of such moieties is unknown.

The (alkyl)naphthalene distributions in the pyrolysates of the brown coals show a large variation both in carbon number distribution and in predominance of specific isomers. The predominance of 1,2,5-trimethylnaphthalene together with 1,2,5,6-tetramethylnaphthalene is ascribed to the presence of macromolecularly bound, aromatized 8,14-secotriterpenoids. The co-occurrence of 1,6-dimethylnaphthalene and cadalene as major naphthalene reveals the contribution of resin-derived material in some of the brown coals.

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