PHILOSOPHICAL TRANSACTIONS OF THE ROYAL SOCIETY A MATHEMATICAL, PHYSICAL & ENGINEERING SCIENCES

Structural Studies of Coal Extracts [and Discussion]

A. A. Herod, W. R. Ladner, C. E. Snape and W. Watt

Phil. Trans. R. Soc. Lond. A 1981 **300**, 3-14
doi: 10.1098/rsta.1981.0044

Phil. Trans. R. Soc. Lond. A **300**, 3–14 (1981)
Printed in Great Britain

CHEMICAL AND PHYSICAL STRUCTURE OF COAL

Structural studies of coal extracts

By A. A. Herod, W. R. Ladner and C. E. Snape
The National Coal Board, Coal Research Establishment,
Stoke Orchard, Cheltenham, Gloucestershire GL52 4RZ, U.K.

The production of liquids from coal by extraction followed by catalytic hydrocracking gives rise to complex extract intermediates and liquid products. Structural studies on these materials with n.m.r., mass spectrometry and other techniques lead to an understanding of the processes occurring and to more effective use of the products. The extract intermediates are characterized by ^{1}H and ^{13}C n.m.r., molecular mass and ultimate analyses. Average structures are derived to represent these complex materials. The volatile hydrocracked liquids are analysed by mass spectrometry and chromatography.

1. Introduction

The Coal Research Establishment of the National Coal Board is currently developing two coal liquefaction processes. These processes involve the extraction of coal with either a supercritical gas or with a hydrogen-donor solvent and hydrocracking the coal extracts produced (Whitehead & Williams 1975; Maddocks & Gibson 1977; Davies 1978) and are discussed in detail by Martin & Williams (this symposium). The production of liquids from coal gives rise to complex high molecular mass intermediate extracts as well as a wide range of liquid products. To help to understand the processes occurring and to make effective use of the products, it is important to carry out adequate chemical analyses.

This paper describes some of the methods being used for the analysis of coal extracts and distillates, dealing mainly with the structural analyses of extracts and with hydrocarbon type analysis of distillate products. The methods are illustrated with examples that are not necessarily typical since the yield and nature of the material produced depends upon the conditions used for the extraction and upon the severity of the hydrocracking.

2. Structural analysis of coal extracts

(*a*) *Fractionation and analysis*

The extract is first divided into three fractions, namely *n*-pentane solubles, asphaltenes and benzene insolubles, by solvent separation. After the extract has been refluxed with benzene and filtered to separate the benzene insolubles, the filtrate is concentrated and 10 times its volume of *n*-pentane is added to precipitate the asphaltenes. The *n*-pentane solubles remain in solution

The *n*-pentane solubles are then further separated into paraffinic, aromatic and polar fractions by adsorption chromatography on silica gel. Approximately 95 % of the extract is recovered from the solvent and chromatographic separations. An example of the yields of the various fractions obtained from coal extract, together with their analyses, are given in table 1.

The fractions are subjected to ultimate, molecular mass and phenolic hydroxyl analyses. Number average molecular masses are determined isopiestically by using a Hitachi–Perkin–Elmer 115 instrument. Phenolic OH contents are measured by enthalpimetric titration (Vaughan & Swithenbank 1970). The benzene-insoluble fractions are silylated (Snape & Bartle 1979) or methylated to enhance their solubility in tetrahydrofuran and chloroform-*d* used in molecular mass determinations and spectroscopy respectively.

Table 1. Yields and analyses of coal extract fractions

	yield (% by mass)	ultimate analysis (% by mass) C	H	O	N	S	OH	n.p.O. (by diff.)	molec. mass	C:H
extract		83.1	6.4	8.6	1.1	0.8	5.0	3.9	400	1.1
n-pentane solubles										
paraffins	2	85.4	14.3	<0.5	<0.1	<0.1	<0.1	<0.5	310	0.5
aromatics	19	88.3	7.8	2.3	0.3	0.9	1.2	1.2	270	0.95
polars	14	80.7	7.9	9.6	0.6	0.7	7.3	2.7	250	0.9
asphaltenes	35	82.4	6.2	8.8	1.3	1.0	6.3	2.9	530	1.1
benzene insolubles	30	81.7	5.4	10.0	1.8	0.9	6.6	3.8	920	1.3

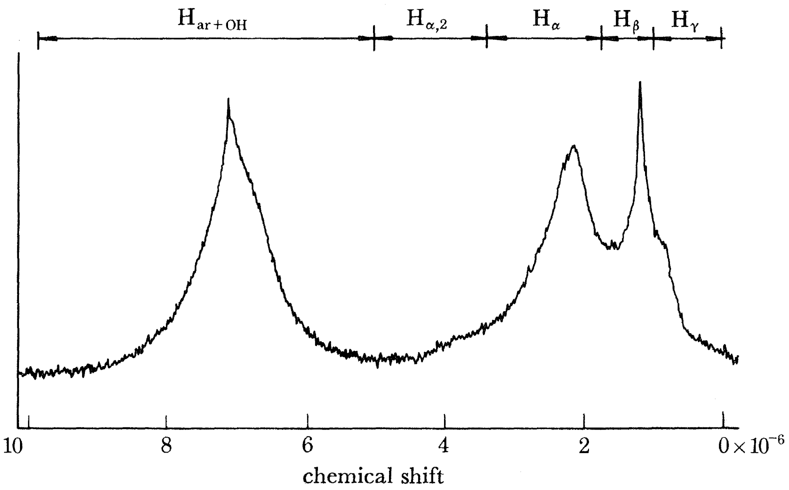


Figure 1. ^1H n.m.r. spectrum of the asphaltene fraction of a coal extract.

(*b*) ^1H *n.m.r. spectroscopy*

The example of the ^1H n.m.r. spectrum of an asphaltene fraction of an extract shown in figure 1 was obtained at 60 MHz by using a Hitachi–Perkin–Elmer R24B instrument with chloroform-*d* as solvent.

The assignments of the bands in the spectrum are shown in table 2, together with the proportions of the various forms of hydrogen. The major separation in the ^1H spectra is between the aliphatic and aromatic hydrogen resonances, aliphatic resonances occurring in the chemical shift region $0.5–5.0\times10^{-6}$ and aromatic resonances in the region $6–9\times10^{-6}$. The aliphatic resonances are further divided into four subgroups and occur further away from the aromatic resonances (i.e. at lower chemical shift values) as the influence of the aromatic ring decreases. For example, methylene adjacent to two aromatic rings ($H_{\alpha,2}$) occurs between 3.4 and 5.0×10^{-6}, methylene adjacent to one aromatic ring (H_α) between 2.0 and 3.4×10^{-6} and

TABLE 2. ASSIGNMENTS OF THE BANDS IN THE ^{1}H N.M.R. SPECTRA OF COAL EXTRACT FRACTIONS

			hydrogen distribution (%)				
			n-pentane solubles				
hydrogen type	symbol	$10^6 \times$ chemical shift	paraffins	aromatics	polars	asphaltenes	benzene insolubles
aromatic	H_{ar}	6.0–9.0	0	45.4	25.5	42.5	50.4
phenolic	H_{OH}	5.0–9.0			5.3		
ring-joining methylene	$H_{\alpha,2}$	3.4–5.0	0	2.4	3.0	4.8	6.7
CH_3, CH_2 and CH α to an aromatic ring	H_α	1.9–3.4	0	32.2	32.5	31.2	27.0
β-CH_3, CH_2 and CH β or further from an aromatic ring + paraffinic CH_2 and CH	H_β	1.0–1.9	73.2	15.1	26.3	15.8	12.0
CH_3 γ or further from an aromatic ring + paraffinic CH_3	H_γ	0.5–1.0	26.8	4.9	7.4	5.7	3.9

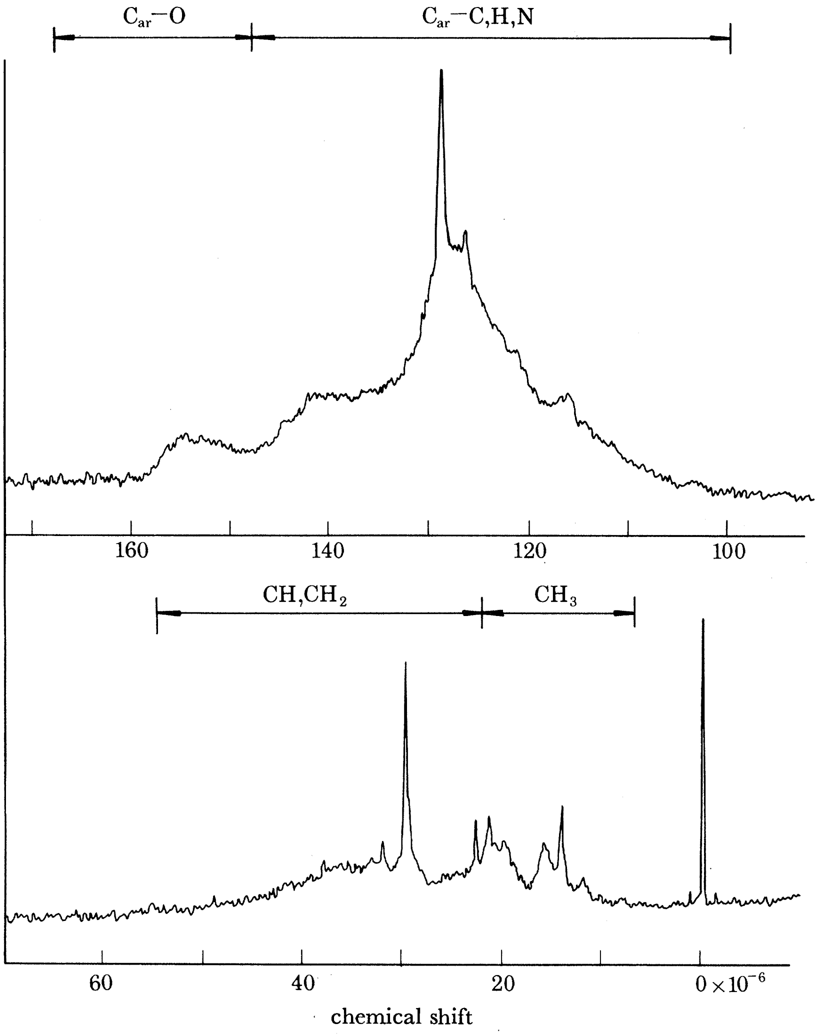


FIGURE 2. ^{13}C n.m.r. spectrum of the asphaltene fraction of a coal extract.

methylene not adjacent to an aromatic ring (H_β) between 1.0 and 2.0 × 10^{-6}. Hydrogen on carbon γ or further from an aromatic ring, together with paraffinic CH_3 (H_γ) occurs in the range 0.5–1.0 × 10^{-6}.

TABLE 3. ASSIGNMENTS OF THE BANDS IN THE ^{13}C N.M.R. SPECTRA OF COAL EXTRACT FRACTIONS

carbon type	10^6 × chemical shift	carbon distribution (%)				
		n-pentane solubles				
		paraffins	aromatics	polars	asphaltenes	benzene insolubles
carbonyl	170–210	—	—	—	—	—
aromatic C–O	148–168	—	1.6	6.9	7.6	7.5
aromatic C–C, C–H, C–N	100–148	—	69.6	56.4	68.6	75.8
methylene methine	22.5–60	91.0†	20.0	23.5	16.0	11.6
methyl	11–22.5	9.0	8.8	13.2	7.8	5.1

† Includes some CH_3 in branched paraffins.

(*c*) ^{13}C *n.m.r. spectroscopy*

The ^{13}C n.m.r. spectrum of the asphaltenes, shown in figure 2, was obtained at 20 MHz by using a Bruker WP80/WG instrument with chloroform-*d* as solvent. Chromium acetylacetonate was added to the sample and gated decoupling was employed to obtain reliable quantitative data (Ladner & Snape 1978).

The assignments of the bands of the ^{13}C spectra are given in table 3 and are based on a detailed consideration of the chemical shifts of structures that are believed to be likely to be present in coal-derived materials (Snape *et al.* 1979). As in ^1H spectra, the major separation in the ^{13}C spectra is between aromatic and aliphatic resonances. The aromatic resonances resulting from C–O groups (148–168 × 10^{-6}) are well separated from other aromatic resonances. Methyl resonances have lower chemical shift values than methylene and methine resonances.

In common with the spectra of numerous coal derivatives (see, for example, Pugmire *et al.* 1977) there is a sharp peak at 29.7 × 10^{-6}. This is attributed to CH_2 groups in alkyl chains containing at least eight carbon atoms. However, the intensity of this peak is low and it is also superimposed upon resonances from CH_2 groups in a wide variety of other structures.

Carbonyl resonances that occur in the region 170–210 × 10^{-6} are not found in the spectrum of the asphaltenes; this indicates that it is reasonable to assume that virtually all the non-phenolic oxygen is present in aromatic ether groups.

(*d*) *Structural analysis scheme*

The high molecular mass and the complex nature of the coal extract fractions makes it impossible to analyse individual components in these materials, and a structural analysis scheme has therefore been devised that enables average chemical structures to be derived for the aromatic coal extract fractions. This approach has been widely used in coal research since the 1960s (Brown & Ladner 1960; Bartle *et al.* 1979; Ouchi *et al.* 1979).

The first step in the structural analysis scheme is to calculate the numbers of the different atoms and groups in an average molecule from the hydrogen and carbon distributions, ultimate analyses, phenolic hydroxyl content and molecular mass. These are given in table 4. The second step is to derive a series of structural parameters that can be used to construct molecular structures to represent the extracts.

The fraction of aromatic carbon or aromaticity (f_a) is obtained directly from the carbon distributions

$$f_a = n_{C_{ar}}/n_C.$$

The number of alkyl and hydroaromatic groups per molecule is given by

$$n_{a.g.} = n_{H_\alpha}/a,$$

hydroaromatic groups counting as two alkyl groups. The value of a is chosen by taking account of the various groups which contribute to the H_α band in the ^1H n.m.r. spectrum. Since both methylene and methyl groups are major contributors to the H_α band, a has been chosen as 2.3.

TABLE 4. NUMBERS OF ATOMS OR GROUPS PER AVERAGE MOLECULE

atom or group	*n*-pentane solubles: aromatics	*n*-pentane solubles: polars	asphaltenes	benzene insolubles
C	19.9	16.8	36.4	62.6
H	20.9	19.6	32.6	49.3
phenolic O (p. O)	0.2	1.1	2.0	3.6
non-phenolic O (n.p.O)	0.2	0.4	0.9	2.2
N	0.06	0.1	0.5	1.2
S	0.08	0.05	0.2	0.3
H atoms				
$H_{ar,OH}$	9.6	6.0	13.8	24.9
$H_{\alpha,2}$	0.5	0.6	1.6	3.3
H_α	6.7	6.4	10.1	13.3
H_β	3.1	5.2	5.2	5.9
H_γ	1.0	1.4	1.9	1.9
C atoms				
C_{ar}	14.2	10.7	27.7	52.1
CH_2, CH } C_{al}	4.0 } 5.7	3.9 } 6.1	5.9 } 8.7	7.3 } 10.5
CH_3	1.7	2.2	2.8	3.2

The number of ring-joining groups per molecule ($n_{r.j.g.}$) is given by

$$n_{r.j.g.} = \tfrac{1}{2}n_{H_{\alpha,2}} + n_{n.p.o.} + n_N + n_S,$$

where $n_{n.p.o.}$, n_N and n_S are the numbers of non-phenolic oxygen, nitrogen and sulphur atoms per molecule respectively. The heterocyclic atoms are assumed to be in aromatic ether, carbazole and dibenzothiophene structures. Since methylene groups are the main contributors to the $H_{\alpha,2}$ band in the ^1H n.m.r. spectrum, the aliphatic H:C ratio has been chosen to be 2.

The number of peripheral aromatic carbon atoms per molecule (n_{C_p}) is given by

$$n_{C_p} = n_{H_{ar+OH}} + n_{a.g.} + 2n_{r.j.g.}.$$

The number of internal aromatic carbon atoms per molecule, $n_{C_{int}}$ is given by

$$n_{C_{int}} = n_{C_{ar}} - n_{C_p}.$$

The fraction of the sites on the aromatic skeleton occupied by alkyl and hydroaromatic and phenolic hydroxyl groups (σ') is given by

$$\sigma' = n_{a.g.} + n_{p.o.}/n_{a.g.} + n_{H_{ar+OH}}.$$

The third step is to calculate the numerical values of these parameters (table 5) and then construct by trial and error a molecular structure to fit them. An example of one such structure representing the asphaltene fraction of an extract is shown in figure 3. It must be realized that these structures are only statistical averages of the very large number of individual components present in various extract fractions. The individual compounds will vary both in size and chemical type.

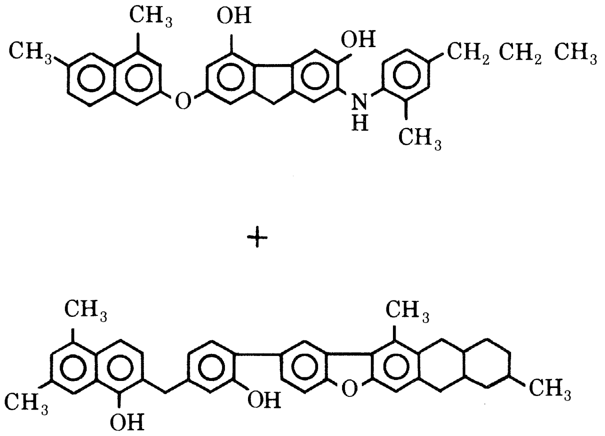


FIGURE 3. Average structure of the asphaltene fraction of a coal extract.

TABLE 5. STRUCTURAL PARAMETERS

parameter	symbol	*n*-pentane solubles aromatics	 polars	asphaltenes	benzene insolubles
aromaticity	f_a	0.71	0.63	0.76	0.83
alkyl and hydroaromatic groups	a.g.	2.9	2.8	4.4	5.8
ring-joining groups	r.j.g.	0.6	0.8	2.4	5.3
peripheral carbon	C_p	13.6	10.4	23.1	41.2
internal carbon	C_{int}	0.6	0.3	4.6	9.9
degree of substitution	σ'	0.25	0.44	0.35	0.31

3. ANALYSIS OF COAL DISTILLATES

Catalytic hydrocracking of coal extracts produces a wide range of materials of lower molecular mass, including fully hydrogenated compounds (saturates), partly hydrogenated aromatics (hydroaromatics) and aromatics, which are then separated into fractions by distillation. Distillates boiling up to 167 °C are amenable to full quantitative analysis by gas chromatography. However, those boiling above 167 °C are too complex for a detailed analysis of individual components to be attempted, but they can be divided into hydrocarbon types, for example, by mass spectrometry. This section of the paper describes the use of an MS30 double beam mass spectrometer coupled to a DS50 data system for the analysis of coal distillates of boiling ranges 167–247 °C, 247–297 °C, 297–347 °C and 347–417 °C. These relatively narrow boiling ranges are chosen to minimize fractionation effects in the glass inlet system of the mass spectrometer.

Owing to their different ionization characteristics, saturates and aromatics (including hydroaromatics) are treated separately in hydrocarbon type analysis. When the mass spectrometer is operated at high ionization energy (70 eV), ions are produced from both saturates and aromatics, while at low ionization energy (10 eV) ions are only produced from aromatics. Hydrocarbon type analysis is especially suitable for distillation fractions boiling in the range 167–417 °C.

Fractions boiling above 417 °C are more difficult to analyse by mass spectrometry because of their increased complexity and lower volatility. M.s. methods to deal with these fractions are under development (Bennett & Herod 1979).

(*a*) *Saturates*

Two matrix methods are employed with 70 eV mass spectra of a distillate fraction for determining the relative amounts of saturates and aromatics. The standard 9×9 matrix method (A.S.T.M. D2425) is used for the 167–247 °C distillate and a 19×19 matrix method for the higher boiling distillates (Gallegos *et al.* 1967). Both methods are based on the principle that when the distillates are subjected to 70 eV, the various chemical types (alkanes, cycloalkanes, alkylbenzenes, etc.) produce intense fragmentation peaks characteristic of the parent compound. However, the methods rely on calibrating the matrices by using standards representative of the distributions of hydrocarbons (paraffins, cycloparaffins and aromatics) in the sample to be analysed. These matrix methods were set up originally for the analysis of petroleum products and because the distribution of hydrocarbons in coal-based distillates is likely to be significantly different from that in petroleum-based distillates, adsorption chromatography on silica gel, following A.S.T.M. D2549 has been used as the primary standard method for the estimation of saturates in coal-based distillates. The matrix coefficients have been adjusted to allow for the differences between petroleum-based and coal-based distillates, and periodic checks are made on the saturate content of samples by liquid chromatography to ensure that the matrix results are acceptable.

(*b*) *Aromatics and hydroaromatics*

As already mentioned, at low electron energy aromatic molecules are ionized without fragmentation while saturates remain unionized. The electron energy of the sample beam is set at 10 eV and that of the reference beam at 70 eV with perfluorokerosene as the reference compound. The electron energy of the sample beam is adjusted so that the intensity of the fragment ion m/z 91 in *p*-xylene is of the order of 0.1 % of the molecular ion intensity (m/z 106).

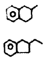
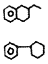
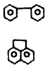
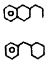
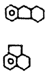
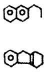
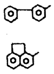
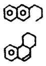
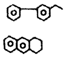
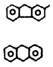
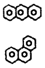
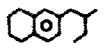
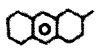
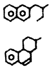
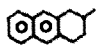
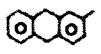
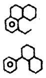
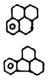
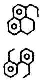
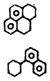
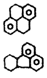
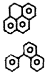
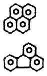
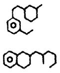
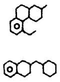
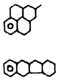
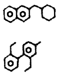
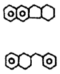
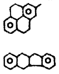
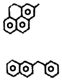
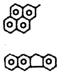
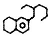
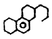
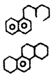
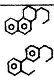
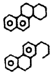
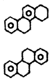
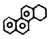
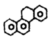
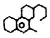
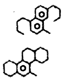
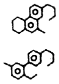
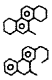
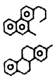
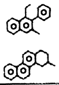
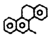
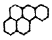
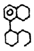
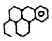
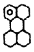
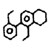
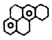
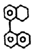
A mass spectrum of a distillate is obtained that only contains peaks corresponding to aromatic molecular ions. From determinations of relative intensities of molecular ions (peak heights) per unit mass, the low electronvolt spectrum is used to derive relative percentages by mass. For example, the concentration of species of empirical formula C_8H_{10} (xylenes and ethylbenzene) is determined as a percentage of the total aromatics, but it is not possible to determine the relative concentrations of *o*-, *m*- and *p*-xylenes and ethylbenzene. Thus, low electron energy spectra can be used to provide quantitative information about the distribution of the various aromatic hydrocarbon types, but not about individual molecules.

The results are presented as a matrix array based on carbon number and Z number defined by the general hydrocarbon formula C_NH_{2N+Z} (table 6). Table 7 shows examples of some of the possible structures corresponding to various carbon and Z numbers.

The aromatic hydrocarbon type analyses are determined for the various distillation fractions in the range 167–417 °C and then the results are summed on the basis of the relative abundance of each fraction to give the distributions shown in table 7. The aromatic distributions in the 167–417 °C distillate are compared by relative amounts in each carbon number in figure 4*a* and in each type or Z number in figure 4*b*. The carbon number distributions show that the distillate contains about 60 % of C_{14} and C_{16} components, probably hydrogenated anthracenes, phenanthrenes and pyrenes, together with about 18 % of C_{15} and C_{17} components, which may be methyl derivatives. The remainder consists mainly of components with carbon numbers that could correspond to hydrogenated naphthalenes, diphenyls, fluorenes and possibly chrysenes.

The Z number charts show that about 50% of the aromatics in the distillate (figure 4*b*) corresponds to the two Z series -8 and -10. Structures making up these series contain one aromatic ring plus either one or two cycloalkyl rings (see table 6). The Z series -12, -14 and -16, which include naphthalenes, diphenyls and fluorenes or dihydroanthracenes respectively, have similar abundances, ranging from 9.6 to 13.6%, while the amount of the $Z = -18$ series, which includes anthracenes and phenanthrenes, is quite small.

Table 6. Structures corresponding to the various carbon and Z numbers

carbon number	Z number −6	−8	−10	−12	−14	−16	−18	−20	−22
7									
8									
9									
10									
11									
12									
13									
14									
15									
16									
17									
18									
19									
20									

An alternative method of presenting the data on hydrocarbon type analysis is shown in figure 5, where the results are given as a three-dimensional histogram, showing the aromatic distribution by Z number and carbon number.

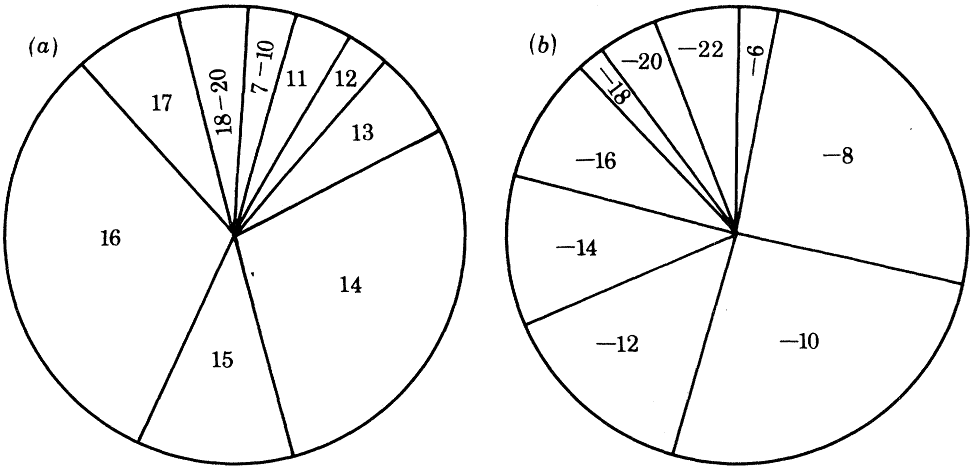


FIGURE 4. Distribution of aromatics in 167–417 °C distillate. (*a*) Carbon number; (*b*) Z number.

TABLE 7. DISTRIBUTION OF AROMATICS IN 167–417 °C DISTILLATE

carbon number	Z number −6	−8	−10	−12	−14	−16	−18	−20	−22	total
	concentration (% by mass)									
7	0.2									0.2
8	0.2	0.4								0.6
9	0.1	0.5								0.6
10	0.2	1.2	0.7	0.1						2.2
11	0.4	2.6	0.6	0.6						4.2
12	0.1	1.8	0.6	0.3	0.2					3.0
13	0.1	1.9	2.1	0.3	1.2	0.3				5.9
14	1.0	10.2	9.0	2.3	4.4	0.7	0.7			28.3
15	0.2	3.0	3.6	1.1	2.0	0.6	0.2			10.7
16		2.5	4.9	6.4	2.3	6.5	0.5	4.6	5.0	32.7
17		0.9	2.6	1.8	0.8	1.0	0.1	0.1	0.4	7.7
18		0.6	1.3	0.6	0.3	0.3	0.1			3.2
19			0.1	0.1	0.1	0.1				0.4
20			0.1	0.1	0.1					0.3
total	2.5	25.6	25.6	13.7	11.4	9.5	1.6	4.7	5.4	100.0

(*c*) *Identification of individual components*

Gas chromatography in conjunction with mass spectrometry is used to identify the structures of the major components in the distillate fractions. Separation is carried out with the use of a glass capillary column coated with a non-polar phase, the eluant from the column being transferred into the vacuum in the mass spectrometer via a jet separator which removes the bulk of the carrier gas.

The mass spectral information on the individual components of the distillates is stored in the data system and recalled in the form of computer-constructed chromatograms; an example of a chromatogram for a distillate with a nominal boiling range of 167–247 °C is shown in figure 6.

This chromatogram is relatively simple but with the higher boiling fractions it becomes increasingly more difficult to obtain detailed structural information because the many components were only partly resolved by the chromatographic separation.

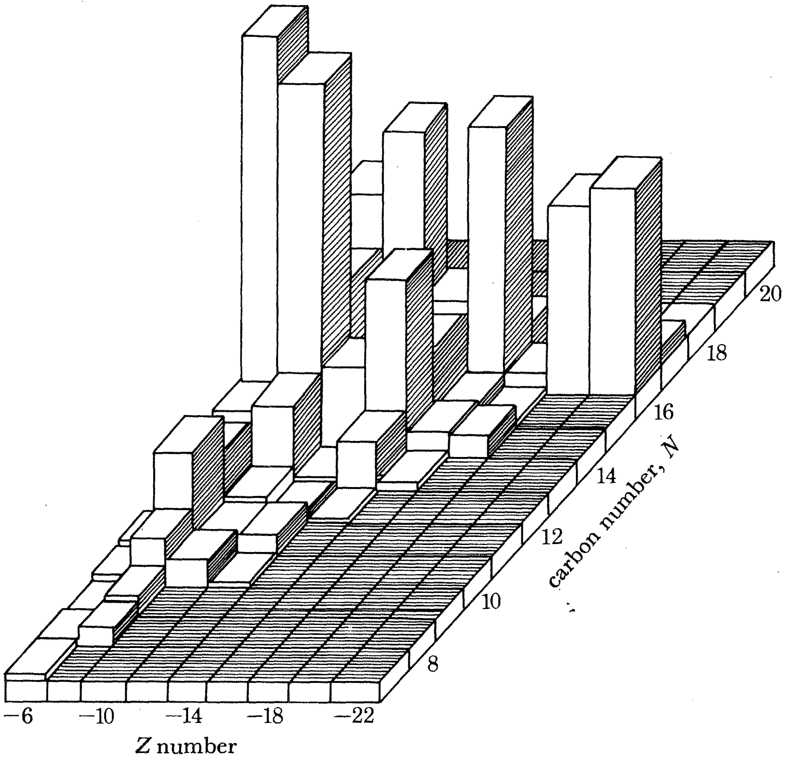


Figure 5. Three-dimensional histogram of aromatics in 167–417 °C distillate.

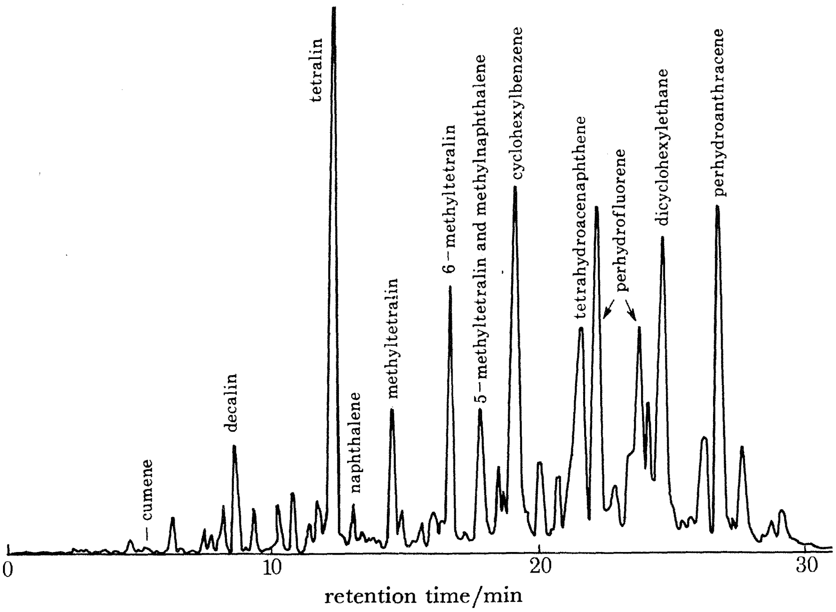


Figure 6. Chromatogram of 167–247 °C distillate.

4. CONCLUSIONS

Both supercritical gas extracts and hydrogen-donor solvent extracts of coals can be divided into *n*-pentane solubles, asphaltenes and benzene insolubles by solvent separation, and the *n*-pentane solubles can be further divided into paraffins, aromatics and polars by adsorption chromatography on silica gel. A structural analysis scheme based on elemental analysis, molecular mass and n.m.r. can then be used to provide an indication of the types of molecules present in the various aromatic fractions. From the structural parameters so obtained it is possible to construct molecular structures to represent the data.

For coal-derived distillates, estimates of the saturate content are obtained by mass spectrometry. An estimate of the relative concentrations of aromatics and hydroaromatics is obtained by a type analysis method based on mass spectrometry at low ionization energy.

Further work on the development of methods for the chemical analysis of coal extracts and their hydrocracked products is required. For example, to improve our knowledge of the groupings containing the heteroatoms (N, S and O) present in coal extracts and to extend the mass spectrometric hydrocarbon type analysis method to higher boiling distillates.

We wish to thank the National Coal Board for permission to publish this paper and the European Coal and Steel Community for financial support. The views expressed are those of the authors and not necessarily those of the Board.

REFERENCES (Herod *et al.*)

Bartle, K. D., Ladner, W. R., Martin, T. G., Snape, C. E. & Williams, D. F. 1979 *Fuel, Lond.* **58**, 413–422.
Bennett, M. & Herod, A. A. 1979 Presented at A.S.M.S. Conference, Seattle, 2–8 June.
Brown, J. K. & Ladner, W. R. 1960 *Fuel, Lond.* **39**, 87–96.
Davies, G. O. 1978 *Chemy Ind., Lond.*, pp. 560–566.
Callegos, E. J., Green, J. W., Lindemann, L. P., Le Tourneau, R. & Teeter, R. M. 1967 *Analyt. Chem.* **39**, 1833–1838.
Ladner, W. R. & Snape, C. E. 1978 *Fuel, Lond.* **57**, 658–662.
Maddocks, R. R. & Gibson, J. 1977 *Chem. Engng Prog.*, pp. 59–63.
Ouchi, K., Chicada, T. & Itoh, H. 1979 *Fuel, Lond.* **58**, 37–42.
Pugmire, R. J., Grant, D. M., Zilm, K. W., Anderson, L. L., Oblad, A. G. & Wood, R. E. 1977 *Fuel, Lond.* **56**, 295–301.
Snape, C. E. & Bartle, K. D. 1979 *Fuel, Lond.* **58**, 898–900.
Snape, C. E., Ladner, W. R. & Bartle, K. D. 1979 *Analyt. Chem.* **51**, 2189–2198.
Vaughan, G. A. & Swithenbank, S. S. 1970 *Analyst, Lond.* **95**, 890–893.
Whitehead, J. C. & Williams, D. F. 1975 *J. Inst. Fuel* **48**, 182–184.

Discussion

W. WATT, F.R.S. (*Department of Metallurgy and Materials, University of Surrey, Guildford, U.K.*). What is the justification for assigning all the nitrogen and sulphur in the coal to cross-linking groups only? The authors seem to be ignoring the strong possibility that there are nitrogen and sulphur heterocyclic groups in coal.

W. R. LADNER. When considering the structure of coal itself, as opposed to extracts of coal, it is customary to assign a proportion of the heteroatoms, especially nitrogen, to heterocyclic groups, since compounds such as pyridine, quinoline and thiophene are well known constituents of coal tar. However, in our paper on the structure of coal extracts, we have assumed that the non-phenolic oxygen, nitrogen and sulphur are in aromatic ether, carbazole and dibenzothiophene structures respectively. As the number of these atoms per molecule is relatively small, amounting in the asphaltene fraction, for example, to about 1 oxygen atom, 0.5 of a nitrogen atom and 0.2 of a sulphur atom, the omission of heterocyclic groups makes little difference to the structural analysis scheme. It would, of course, be more accurate to apportion some of the heteroatoms to cyclic structures.

Current investigations with n.m.r. methods and non-aqueous potentiometric titration have shown that 30–40% of the nitrogen in s.c.g. extracts occurs in basic environments such as pyridine and quinoline type structures.