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Fractionation by planar chromatography of a coal tar pitch for characterisation by size-exclusion chromatography, UV fluorescence and direct-probe mass spectrometry

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Abstract

A coal tar pitch, extensively studied by other techniques, has been fractionated by planar chromatography using successive development in tetrahydrofuran, chloroform–methanol (4:1, v/v), toluene and pentane. Pitch fractions were distinguished by relative retention. The fractions were characterised in solution by size-exclusion chromatography, UV-fluorescence emission spectroscopy and as the solid on silica, by direct solid-probe mass spectrometry. The method has led to structural information not readily available by direct characterisation of the original mixture itself: (i) A progressive shift of UV-fluorescence spectral maximum intensity and molecular mass with decreasing mobility of the fractions on the planar chromatographic plate, suggesting progressively larger polynuclear aromatic systems; (ii) Nitrogen containing species in the pitch separated from the polynuclear aromatic hydrocarbons which form the bulk of the sample. Neutral and basic nitrogen fractions were defined relative to standards and molecular mass numbers in probe mass spectrometry; (iii) Mass ranges of nitrogen components in these fractions exceed those found previously by GC–MS of the total pitch or its fractions. (iv) Size-exclusion chromatography of the fractions suggests that polar materials are not simply separated by size.

1. Introduction

Planar chromatography has recently experienced a renaissance in the pharmaceutical industry: the development of the technique has been aided by the availability of prepared plates with different surface materials and properties and the ability to operate with virtually any combination of solvents and solvent mixtures. One major advantage of technique is that fractions of material applied to the plate, which would normally be immobile in gas or liquid chromatographic analysis (because of extreme polarity, involatility or high molar mass), can subsequently be recovered and examined by other micro-analytical techniques. Applications of planar chromatography to coal- and oil-derived materials as well as to geochemical samples have been recently reviewed [1]. The technique has been used to distinguish bitumens in oil derived materials and to determine different chemical types (asphaltenes and preasphaltenes) in coal-derived materials. Coal tar pitch continues to be analysed by GC–MS by many

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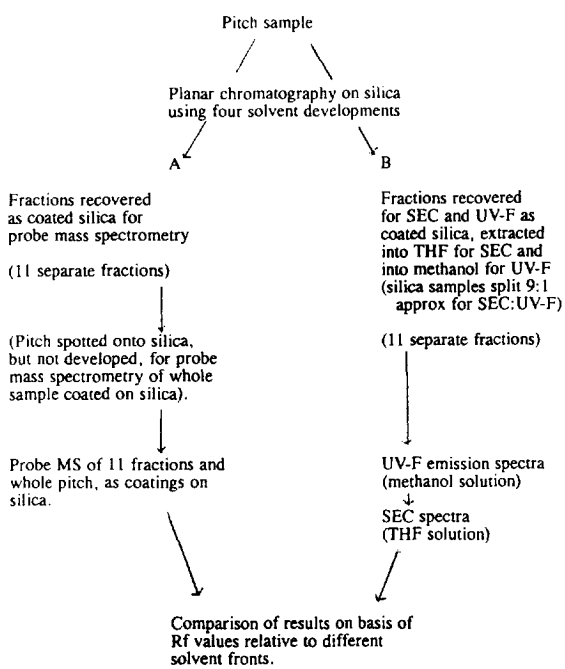
workers and for a variety of reasons; for instance, coke oven emissions and tars have been examined [2] within the context of studies in occupational health; polynuclear aromatic hydrocarbons (PAHs) in a reference tar [3] have been quantified to enable validation of analytical methods for complex materials containing these compounds; PAH have also been partitioned into water from a coal tar [4] in order to estimate and model PAH concentrations in groundwaters contacting these complex wastes; in relation to carbon fibre production, PAH in supercritical fluid extracts of pitch [5] have been examined for comparison with volatiles produced during mesophase formation; azaarenes in pitch fractions [6] taken from the site of a former coal tar distillation plant have also been analysed in some detail. Nitrogen bases of a Brazilian coal tar [7] have been characterized by GC–MS following a complex fractionation scheme to separate them from the tar. Our previous analytical work on coal liquefaction products [8], coal tar fractions and pitch [9–14], have been related to assessment of product stability and to environmental and occupational health problems.

The chemical composition of anthracene oil and pitch can be summarised as being composed mainly of polynuclear aromatic hydrocarbons with smaller quantities of aza-poly nuclear aromatics and even smaller quantities of mixed nitrogen, sulphur and oxygen substituted aromatic systems; basic (pyridinic and amino) and neutral (pyrrole and nitrile) nitrogen types have been identified. Anthracene oil is the distillate fraction of coal tar immediately before the residue, pitch, and will overlap, in terms of chemical types, with pitch. GC–MS examination of anthracene oil, of chemical class fractions in anthracene oil and of similar materials have revealed the complexity of nitrogen containing heterocyclics [9–12,14] which are not so evident from the studies on pitch itself [13,15,16]. The pitch sample used in the present study has been examined previously by GC–MS [13,15], probe mass spectrometry [16] and by laser desorption mass spectrometry [15,16]: the present results are compared with these earlier studies. GC–MS and probe mass spectrometry [13,15] have indicated the presence of aromatics up to m/z 352 (GC–MS) and up to m/z 566 (probe-MS) in the same pitch sample. Laser desorption mass spectrometric techniques indicate, however, that only a limited part of the pitch can be observed by GC–MS and probe-MS: laser desorption mass analysis (LIMA) [15,16] showed the presence of materials with molecular masses of up to 12 000 (the detection limit of the instrument); traces of material at up to 200 000 have been identified by matrix-assisted laser desorption (MALDI–MS) [16].

The work described in this paper covers the application of planar chromatography to a coal tar pitch, with examination of pitch fractions by size-exclusion chromatography (SEC), UV-fluorescence spectroscopy (UV-F) and probe-MS. (For outline of the procedure see Scheme 1.) The results indicate the power of planar chromatographic separation coupled with recovery of fractions, to lead to structural information not readily available by direct characterisation of the original mixture itself.



Scheme 1. Experimental set-up. Pitch sample planar chromatography on silica using four solvent developments. (A,B) Fractions recovered.

2. Experimental

2.1. Sample and standards

The pitch sample is a product of the high temperature coking of coal, to give coal tar which is subsequently distilled, leaving pitch as the residue. The present sample is a soft pitch, containing some light ends (anthracene oil), such as phenanthrene, below the normal distillation cut-off at a boiling point of about 450°C. The elemental composition of the sample is: C 91.4%, H 4.1%, N 1.32%, S 0.76%. Standard samples, carbazole, pyrogallol, quinoline, phenanthrene, perylene and rubrene were obtained from Aldrich and Koch-Light.

2.2. Planar chromatography

Whatman PC plates were used, in sizes of 20×10 cm or 20×20 cm, coated with K5 or K6 silica gel; particle sizes of K5 and K6 are the same (10–12 μm) but the two silica gels have different mean pore sizes (150 and 60 Å, respectively). Plates were not heat activated before use; the normal pretreatment consisted of washing the plates with the most polar solvents used for sample development, in the same flow direction as sample development. Plates were washed with THF and, after drying, with chloroform–methanol. This produced a band of yellow material along the top of the plate and reduced blank signal in subsequent experiments to a negligible level. Solvents were tetrahydrofuran (THF), (BDH unstabilised), chloroform–methanol (4:1, v/v) (BDH solvents), toluene (BDH AnalaR grade) and pentane (BDH).

Samples were applied to the plates in THF solution using disposable micropipettes of 1-μl volume (Alltech Associates) and the solvent allowed to dry. Development was achieved using four successive solvents, starting with THF, followed by chloroform–methanol, toluene and finally pentane. The solvent front for THF was allowed to move approximately 5 cm (1/4 of the available travel distance) from the sample origin; each successive solvent advanced the solvent front from the origin by approximately another 5 cm (1/4 of the available travel distance). Each solvent was allowed to equilibrate with the vapour phase for at least half an hour before the plate was inserted, to minimise evaporation from the solvent front; the solvent was dried before the next solvent system was used.

After development, the dried plates were examined under UV light at 254 and 366 nm; zones of fluorescence were marked using a soft pencil, to permit estimation of relative retention factors (R_F) and collection of sample laden silica layers for further study. Relative retention factors were calculated based on the pentane solvent front (i.e. total available) distance. The surface was scraped onto aluminium foil using a spatula and stored in a freezer until required. Parallel but separate developments were carried out for the pitch to produce fractions for (i) mass spectrometry and for (ii) use in size-exclusion chromatography and UV-fluorescence spectroscopy.

2.3. Size-exclusion chromatography

Molecular mass (MM) distributions of samples were determined by size-exclusion chromatography (SEC) using polystyrene–polydivinylbenzene packed columns (PL gel, 3 μm mixed-E; Polymer Laboratories) in unstabilised tetrahydrofuran with the UV absorption detector set at 254 nm; no corrections were applied to detector response. Data in the form of elution time profiles were collected using a Perkin-Elmer 2010 data station. Profiles for different fractions were superimposed using Microsoft Exel software. Sample laden silica gel from the thin-layer plates, held in 5-ml volume bottles, were extracted for several minutes in an ultrasonic bath using 1 or 2 ml of tetrahydrofuran (also used as eluent in SEC); the silica was allowed to settle. A sample of clear liquid was injected into the SEC chromatograph and analysed using the UV detector set at 254 nm; the full scale signal of the detector was 1000 mV and the most dilute of the samples gave signal strengths of about 3 to 4 mV. A background sample gave a signal less than 1 mV; the background signal of an unwashed plate

could completely mask any sample signal. Sample concentrations were too dilute for use with the evaporative analyser detector.

SEC profiles of samples were compared on an elution time basis, since conversion to a molar mass distribution requires assumptions of molecular shape and selection of an appropriate standard. There is not yet any basis for making selection of a suitable polymer since the shapes of large molecules of pitch are not known. The elution times for polystyrene standards, carbazole and polynuclear aromatic hydrocarbons were determined.

2.4. UV-fluorescence spectrometry

UV-fluorescence emission spectra of tars were recorded for excitation at 254 nm with a Perkin-Elmer LS 50 luminescence spectrometer (excitation and synchronous spectra were not obtained for these fractions). The spectrometer features automatic correction for changes in source intensity as a function of wavelength. Emission spectra were not further corrected for other factors, e.g. changes in emission photomultiplier response as a function of wavelength. A quartz cell of 1-cm light pathlength was used, with emission being detected perpendicular to excitation (90°). A scan speed of 240 nm min^{-1} and a spectral bandwidth of 2.5 nm were used. The standard procedure used in these experiments has been presented in greater detail elsewhere [17].

Sample fractions extracted from silica gel scrapings from the PC plates were characterised by UV-fluorescence spectroscopy as well as size-exclusion chromatography; only about 10% of the scraped silica was needed for the fluorescence work. To extract sample from the scrapings kept in 5-ml bottles, methanol (BDH Spectrosol grade) was added to fill the volume; extraction was carried out in an ultrasonic bath for several minutes. The silica was allowed to settle and clear liquid pipetted into the fluorescence cell of the spectrometer. The wavelength used for excitation was 254 nm; fluorescence emission spectra were recorded for pitch fractions and standards over the 300–500 nm range. The background spectrum (not shown) was very weak and quite different from the spectra of the pitch fractions.

2.5. Probe mass spectrometry

Material from the PC plates was examined using a Jeol JMS-AX505W double-focusing mass spectrometer equipped with a standard solids injection probe and electron-impact ionization. Sample was inserted into the glass sample tip and heated in the ion source vacuum to 350°C. Mass spectra in nominal mass were collected during the pressure pulse caused by evaporation of volatiles from the silica gel, using an ionizing voltage of 70 eV. Mass spectra of each fraction were examined in the light of relative retention data on the PC plate for standards and the mass numbers generated for the pitch components. For reference, the whole pitch was examined from a dried spot deposited on silica gel and introduced into the probe in the same manner as the separated pitch fractions.

3. Results and discussion

3.1. Planar chromatography

Table 1 presents (i) fractional elution distances for the four solvents, compared with the total distance moved by the pentane front, taken as 1.0, (ii) retention factor ranges for standard single compounds and the separated pitch fractions and (iii) R_F values and labels of bands of sample laden silica removed for characterisation by size-exclusion chromatography (SEC), UV-fluorescence spectroscopy (UV-F) and probe-MS. Although two separate developments were carried out, one for MS and one for UV-F and SEC, the separations are related in terms of the R_F values relative to the different solvent fronts as listed in the table. The most advanced spot of the pitch was observed to have migrated further than perylene and about as far as phenanthrene, with rubrene (tetraphenyl naphthacene) indicating a much lower relative retention value. The visible fluorescence colours of the pitch-aromat-

Table 1
Retention values of pitch fractions and standards for MS, UV-F and size exclusion

Sample	R_F of spot or range of R_F for fraction			
	MS experiments		UV-F and SEC experiment	
	Fraction	R_F range	Fraction	R_F range
Pyrogallol		0.31		0.27
Perylene		0.71		0.77
Rubrene		0.64		0.64
Quinoline		0.50		0.38
Carbazole		0.60		0.57
Pentane front		1.0		1.0
Pitch	1	0.77–0.72	a	0.80–0.77
			b	0.77–0.73
			c	0.73–0.70
Toluene front		0.74		0.72
Pitch	2	0.72–0.68	d	0.70–0.65
Pitch	3	0.68–0.64	e	0.65–0.62
Pitch	4	0.64–0.62	f	0.62–0.58
Pitch	5	0.62–0.58	g	0.58–0.55
Pitch	6	0.58–0.55	h	0.55–0.51
Pitch	7	0.55–0.51	i	0.51–0.47
			j	0.47–0.39
Chloroform–methanol front		0.52		0.40
Pitch	8	0.51–0.47	k	0.39–0.32
Pitch	9	0.47–0.44		
Pitch	10	0.44–0.40		
Pitch	11	0.40–0.30		
THF front		0.27	0.23	
Blank			0.87	
Solvent fronts				
Pentane solvent		1.0	1.0	
Toluene solvent		0.74	0.72	
Chloroform–methanol solvent		0.52	0.40	
THF solvent		0.27	0.23	

ics region ranged from blue, through green to red or brown, suggesting the presence of increasingly complex mixtures of condensed aromatic ring structures. The region of pitch at shorter relative retention distances, corresponding to little or no movement in toluene, is thought to contain more polar species, although specific chemical functionalities are not immediately apparent. The predominant visible fluorescence colour in this region was white. Comparison with R_F data for pyrogallol (trihydroxy benzene), carbazole and quinoline in Table 1 indicate that components of pitch detected by visible fluorescence had larger R_F values than pyrogallol and encompassed the R_F range of the neutral and basic nitrogen compounds, carbazole and quinoline, respectively. No significant material remained at the sample origin or in the THF solvent region, indicating that the black colour of the pitch solution (dissolved in THF) was not

due to free carbon. Clearly components of the pitch not soluble in THF could not be examined.

3.2. UV-fluorescence spectroscopy

UV-fluorescence emission spectra of the set of samples are shown in Fig. 1(a–e). The background spectrum (not shown) of the washed silica gel was very different from the standards and pitch fractions, corresponding to low intensity noise and similar to the spectrum obtained with "pure" methanol, itself transparent in this UV range. The UV fluorescence spectra of some of the standards are shown in Fig. 1a, pitch fractions recovered in the toluene zone (a–e) in Figs. 1b and 1c and the apparently more polar fractions f–k in Figs. 1c, 1d and 1e, respectively. The profiles in Fig. 1 were normalised to full scale.

In Fig. 1a, the fluorescence emission maximum of perylene (curve 3), a five-ringed system, is observed to occur at longer wavelengths than that of rubrene (tetraphenyl naphthacene: curve 1), in which the active condensed aromatic system is naphthacene (linear four-ringed system) with the pendant phenyl groups not giving separate fluorescence, but "pumping" the naphthacene fluorescence by energy transfer. Structures such as rubrene with pendant phenyl groups are probably not present in the pitch, having been destroyed during the high temperature preparation in the coke oven; therefore shifts in the emission maximum to longer wavelengths in pitch fractions may be interpreted to indicate shifts to larger aromatic clusters. Curve 2 of Fig. 1a shows the emission spectrum of an impurity in the rubrene sample, with a smaller R_F value on the silica gel than rubrene itself, which was more abundant and gave a much more intense spectrum with much better definition; on the TLC plate the impurity gave a red colour compared to the yellow colour of rubrene.

In Figs. 1b and 1c, emission maxima of aromatic fractions (i.e. fractions which moved in toluene–curves for samples a–e in Table 1) were observed to shift to longer wavelengths with decreasing R_F value, from about 360 nm for sample a, to about 460 nm for sample e, with samples b and c showing more than one maximum of intensity. As will be shown below, this shift to larger wavelengths correlated with apparent increases in molecular masses of these fractions. Fractions a and b eluted within the pentane band, beyond the toluene front; as the lightest fractions in the pitch, these two could be expected to have characteristics similar to those of anthracene oil. Fractions c, d and e, which did not migrate beyond the toluene front, appear to contain more complex aromatic mixtures with R_F values in the range between perylene to (R_F) smaller than rubrene. With decreasing R_F values, increasingly broad and featureless bands were observed in the UV-F emission spectra, reflecting the progressively more complex nature of mixtures of fused-ring aromatic structures.

At the low wavelength end, the initial rising edge (320–360 nm) for each of fractions a–c developed in nearly coincident manner (Fig. 1b). This observation provides evidence that the size-range of smaller aromatic ring systems within the three fractions did not change significantly, although their different mobilities on the PC plates suggest differences in chemical functionalities and polarities. By contrast, the slopes of rising edges in the spectra of fractions d and e may be clearly observed to decrease sharply with decreasing R_F value (Fig. 1c).

Two exceptions have been observed to the trend of emission maxima shifting to higher wavelengths with increasing R_F value:

(i) In Fig. 1c, the maximum of fraction f was observed to shift to shorter wavelengths compared with fractions d and e; fractions d–f had all moved well beyond the chloroform–methanol (R_F 0.4) solvent front into the toluene zone, corresponding to R_F values of neutral nitrogen compounds, which follow the PAH up the plate. The increase in slope of the rising edge of the spectrum (fraction f), against the trend signalled above suggests the presence of smaller aromatic ring systems in this fraction compared to fractions d and e.

(ii) Similarly, the emission spectrum of fraction k was observed to appear at shorter wavelengths than expected by the general trend; Fig. 1e suggests the predominance of smaller fused-

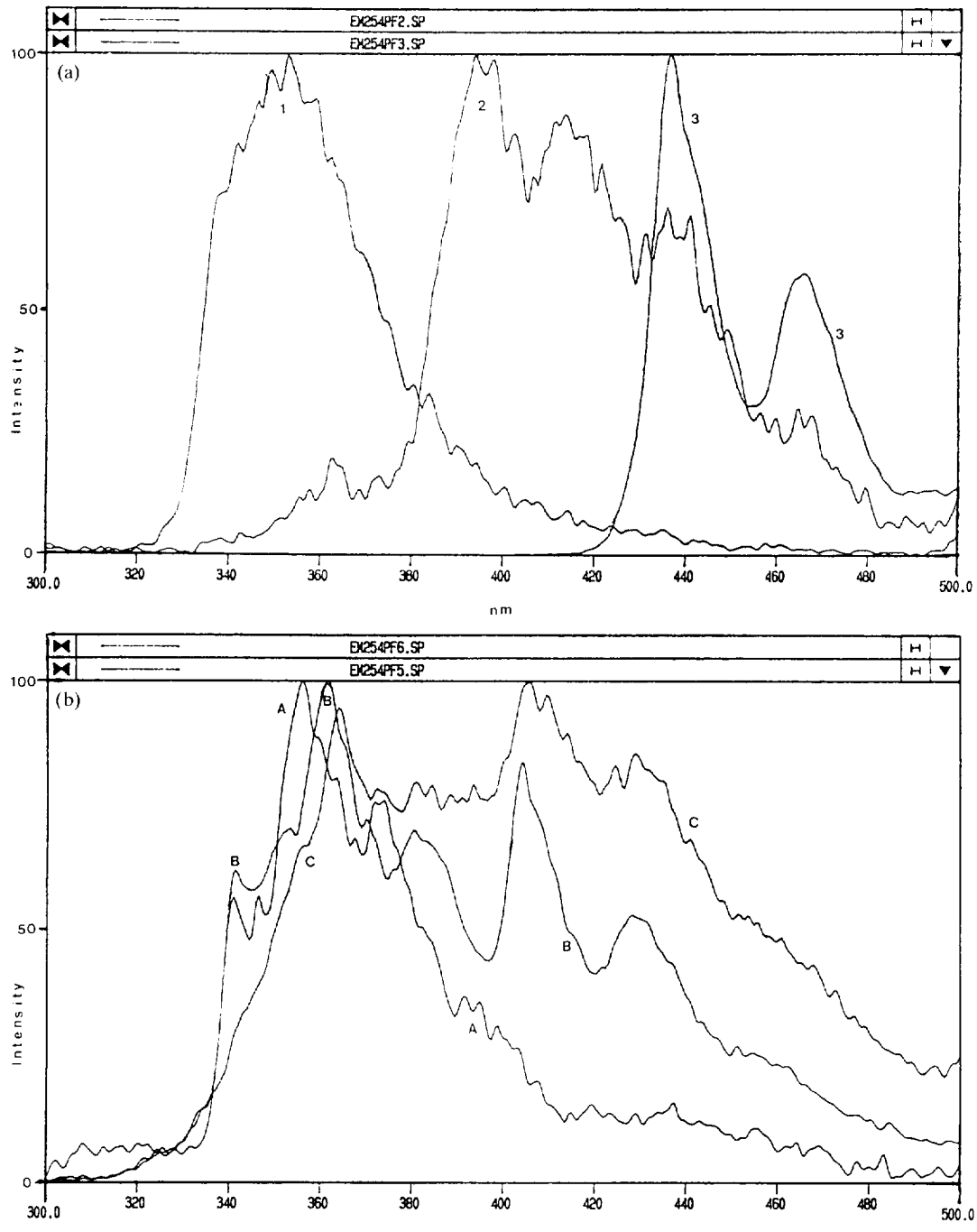


Fig. 1. UV-F emission spectra with excitation at 254 nm of fractions of pitch recovered from a PC plate; graphs are normalised intensity vs. wavelength (nm). (a) rubrene, curve 1; an impurity in rubrene, curve 2; and perylene curve 3; (b) pitch fractions a, b and c; (c) pitch fractions d, e and f; (d) pitch fractions g, h and i; (e) pitch fractions j and k.

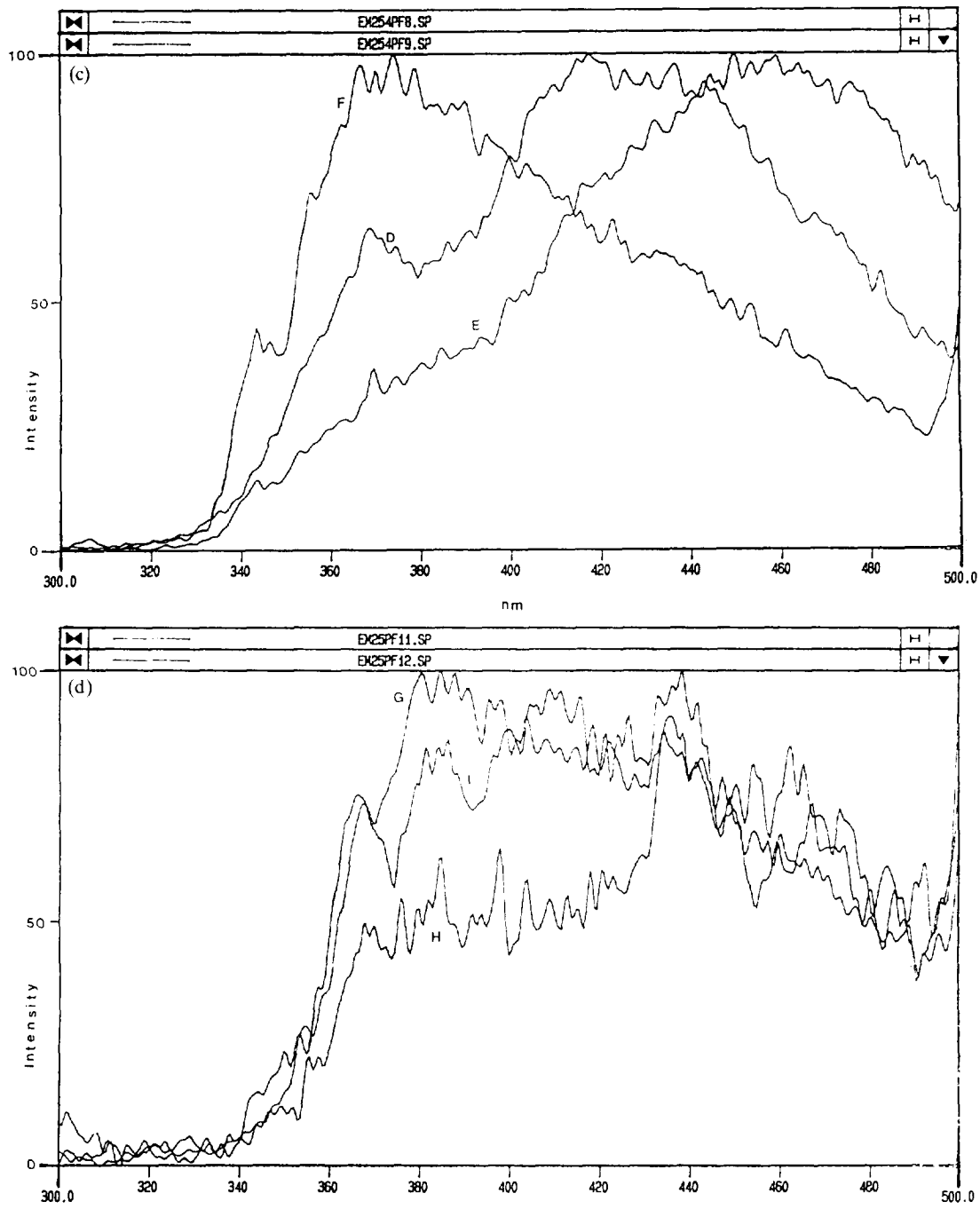


Fig. 1. (*continued*)

ring aromatic structures in fraction k compared to the more mobile fractions g–j.

Apart from fraction k, all fractions were found to be mobile in toluene, having migrated beyond the chloroform–methanol solvent front (Table 1); their relative R_F values correspond to nitro-

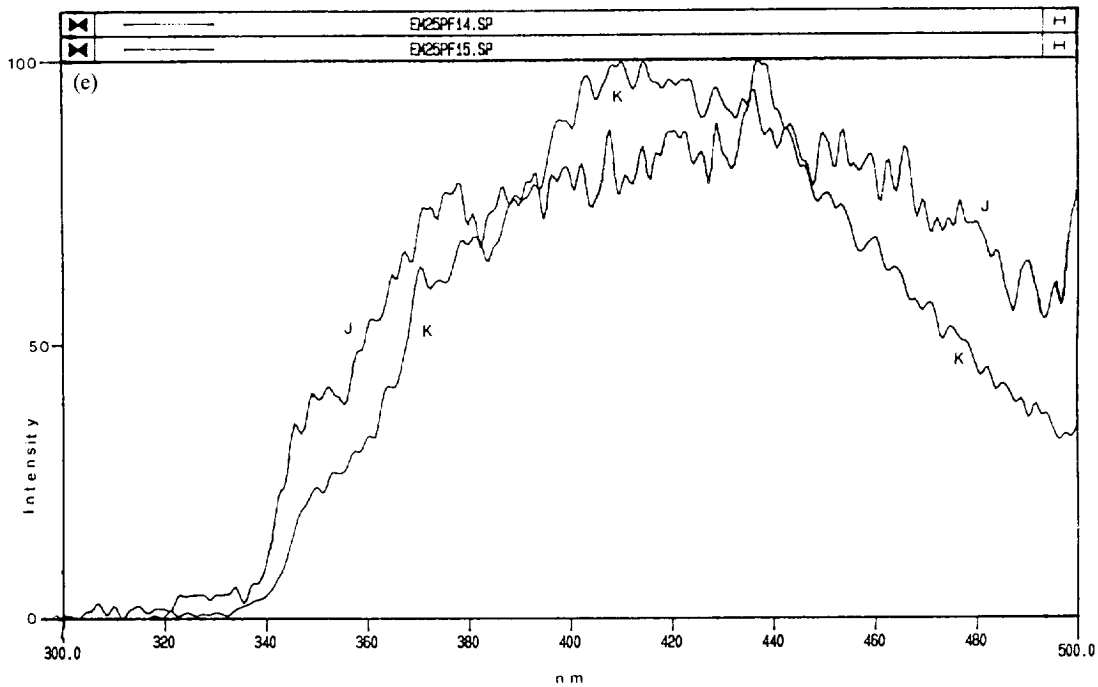


Fig. 1. (*continued*)

gen containing less polar compounds, viz. pyrroles and aromatic nitriles. However, fraction k represents material not mobile in toluene, but mobile in the more polar chloroform–methanol solution. On the basis of R_F values comparable with quinoline and pyrogallol, this fraction is thought likely to contain pyridines or aza heterocyclics and oxygenated molecules.

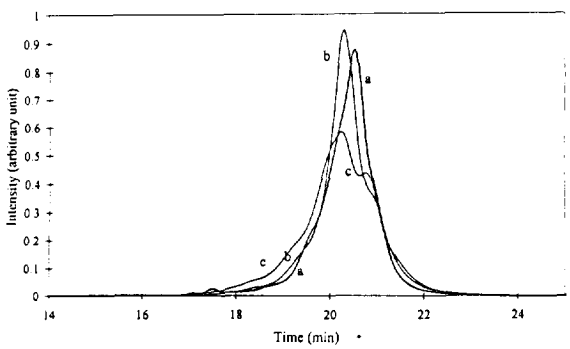
3.3. Size-exclusion chromatography

SEC profiles for the pitch fractions separated by planar chromatography are shown in Figs. 2(a–d). The SEC traces have been presented on an elution time basis; elution times for polystyrene standards and some standard aromatic compounds and the SEC profile of the whole pitch are shown for comparison in Fig. 2e. Significant features of SEC-derived distributions of the pitch fractions are as follows:

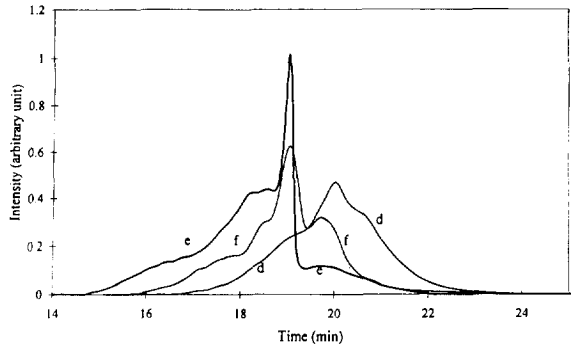
(i) In the first three fractions (a, b and c) corresponding to material mobile in pentane and fractions immobile in pentane but close to the toluene–pentane front, relatively narrow single peaks were observed, broadening at the base and showing a range of elution times, 19 to 22 min, corresponding to relatively small molecular masses. In terms of standards, this range includes perylene at 21.5 min, toluene at 20.2 min and benzo[*ghi*]perylene at 20.2 min. The molecular mass range identified by probe-MS for these fractions ranges from less than 200 to over 600 (c.f. Ref. [15] and below).

(ii) Fractions d and e are aromatic fractions less mobile than fraction c in toluene. Fraction d shows a significantly wider base width, but the overall shape of the profile resembles those of the earlier fractions. Fraction e however shows a very different profile with a base width from the start of the whole pitch profile at 15 min. This low elution time value is thought to correspond to the largest molecular mass material found in the present work in the whole sample, i.e. that part of the whole pitch sample soluble in THF.

(iii) For the more polar fractions f to k, the base widths of the SEC profiles were observed to increase significantly in comparison with fractions a to c. Peaks of greater intensity and better



(a)



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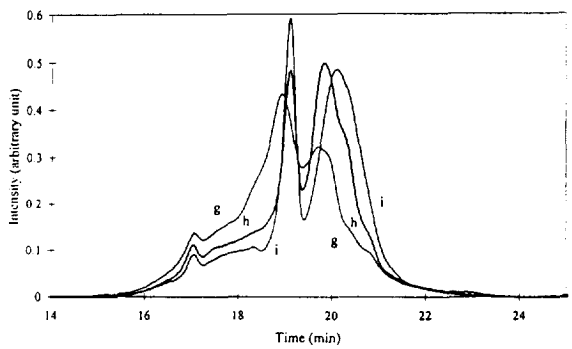
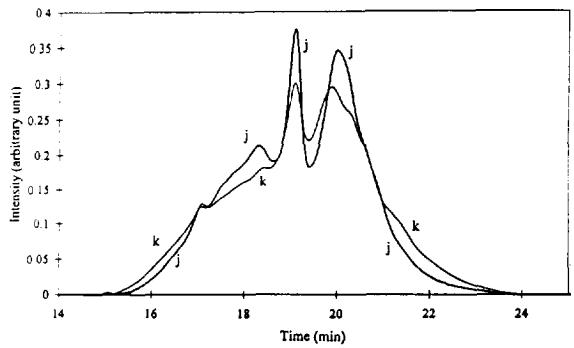
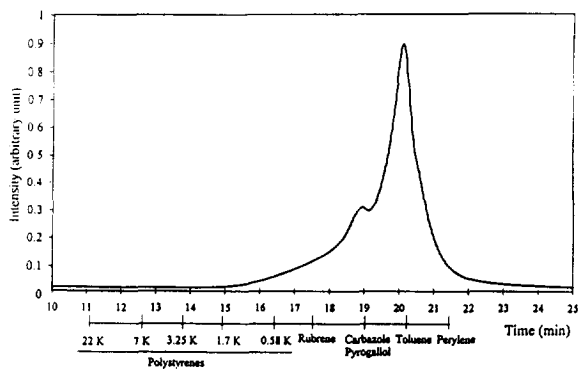


(c)



(d)



(e)

Fig. 2. Size-exclusion chromatograms of fractions and pitch; plots show intensity of UV absorbance at 254 nm vs. elution time (min). (a) pitch fractions a, b and c; (b) pitch fractions d, e and f; (c) pitch fractions g, h and i; (d) pitch fractions j and k; (e) whole pitch profile with elution times of aromatic standards and polystyrenes.

definition were found at shorter retention times, 17 to 19 min, corresponding to increasing contents of larger molecular mass materials. However, all fractions except fraction e showed a significant peak at long elution times (between 19 and 21 min); the distributions also display a significant area between 21–24 min which becomes larger with decreasing R_F. In view of the shorter elution times for small aromatic molecules, this observation was thought likely to indicate the presence of polar materials (as identified by the PC separation), not separating on the basis of molecular size alone during SEC.

On the PC plate, the pyrogallol standard had a smaller R_F value than the trailing edge of the pitch sample, indicating that molecules as polar as pyrogallol are not present in the pitch solution. However, smaller molecular mass material of low polarity would be expected to appeared in fractions with considerably greater mobility on the PC plates. The elution times for pyrogallol, carbazole, perylene and toluene on this system are 19, 19, 21.5 and 20.2 min, respectively. Thus the material appearing at longer elution times than 19 min in the less mobile fractions would appear to be of uncertain molecular mass but of high polarity: pyridine and quinoline, both strongly polar, gave elution times between 20–21 min. It appears reasonable to infer from this data that for these highly polar species, size exclusion cannot be considered as the predominant mechanism. A probable mechanism may be adsorption of the polar molecules on the column packing.

In comparison with the whole pitch (Fig. 2e), elution time distributions of the fractions lie within the overall profile envelope with the greater intensity of the peak at 20 min rather than at about 19 min and a base width from 15 to 24 min approximately.

3.4. Mass spectrometry

The mass spectra for some of the fractions are shown in Fig. 3; Table 2 summarises molecular types found in each fraction. The first four fractions gave molecular ions for polynuclear aromatic hydrocarbons ranging from fluorene (m/z 166) as the light end up to m/z 482, corresponding to a dimethyl tetrabenzobinaphthyl type. In these four aromatics fractions, the molar mass of the major components increases, from 202 and 228 in the first fraction, to 228, 252, 276 and 302 in the second, to 302, 326 and 352 in the third and to 350, 376 and 400 in the fourth. There is clearly some overlap of individual components, but this could be explained in part by the increasing number of structural isomers possible for the higher mass components; we have not studied the separation of isomers such as the $C_{20}H_{12}$ series including perylene by planar chromatography, but using appropriate solvents such a separation appears possible [1]. In terms of R_F ranges these first four fractions correspond to fractions a–e (inclusive) in the UV-F and SEC range.

The subsequent pitch fractions corresponding to more polar components show evidence of the presence of nitrogen-containing heterocyclics; the identifications have been based on the odd mass numbers of their molecular ions. Fractions 5, 6 and 7 correspond to the range of mobility between aromatics in the toluene zone and the chloroform–methanol solvent front (samples parallel to fractions f–j). Fractions 8, 9, 10 and 11 were taken from material mobile in chloroform–methanol but not mobile in toluene, corresponding to fraction k. In terms of R_F values of known standards, this range corresponds to quinolines and similar aza heterocyclics, as well as oxygenates. Planar chromatography of standards such as carbazole and quinoline indicates that neutral nitrogen compounds (pyrroles) migrate in toluene, and elute to greater R_F values than quinoline, a basic nitrogen compound which does not migrate in toluene; nitriles are neutral nitrogen compounds and their behaviour is expected to resemble that of pyrroles.

As expected, no significant changes in molecular mass could be detected between the upper mass ranges identified within the different fractions. This is due to fractionation of the sample on the heated probe with only the most volatile components being detected at masses below the upper limit of the instrument (750 mass units). At present, molecular mass distributions of fractions separated by planar chromatography are

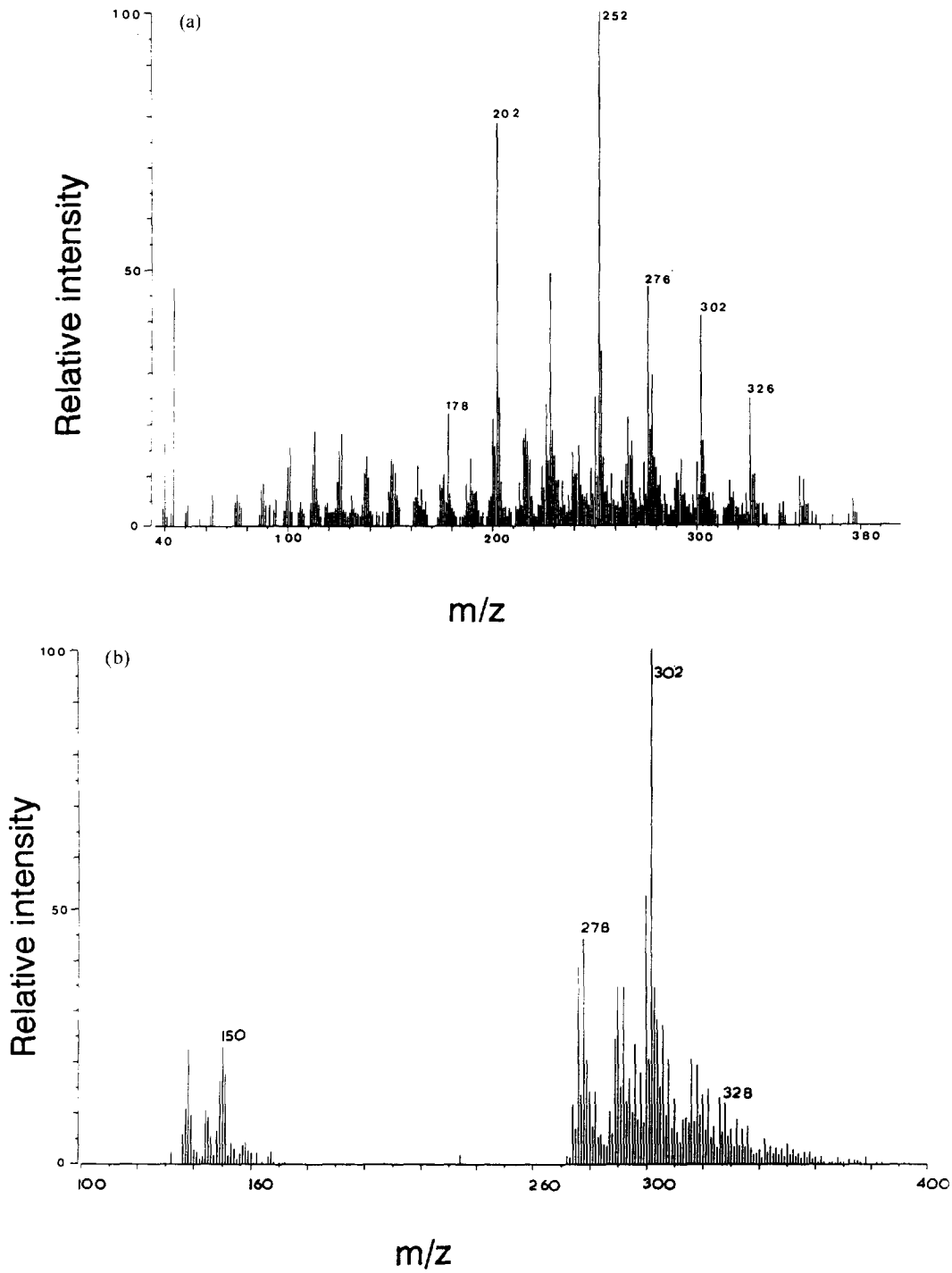


Fig. 3. Mass spectra of fractions evaporated from silica in the solids probe. Plots are of normalised intensity vs. mass number (m/z). (a) whole pitch from silica; (b) fraction 2 aromatics; (c) fraction 4 aromatics; (d) fraction 5 neutral nitrogen heterocyclic aromatics; (e) fraction 6 neutral nitrogen heterocyclic aromatics; (f) fraction 9 basic nitrogen heterocyclic aromatics.

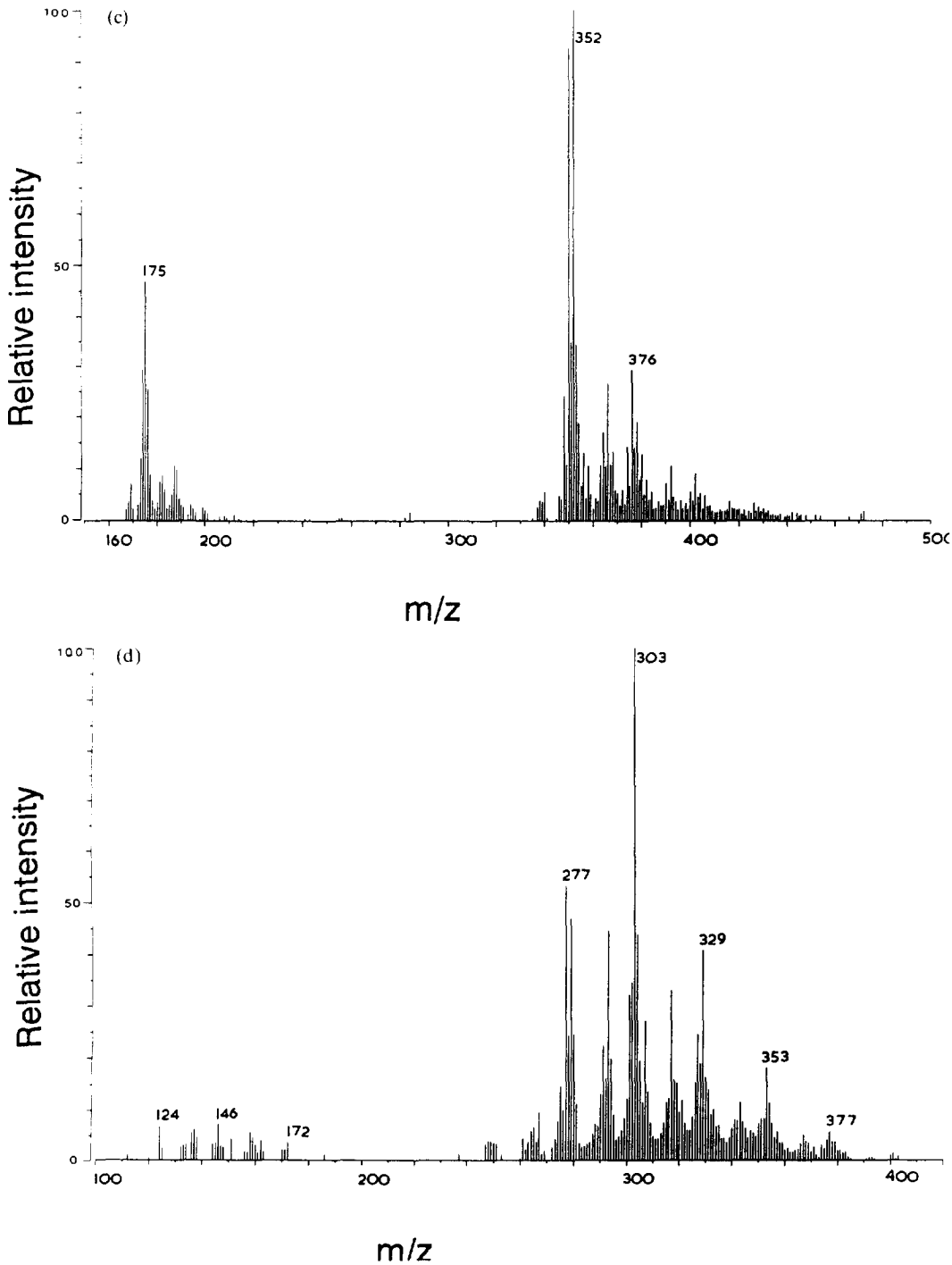
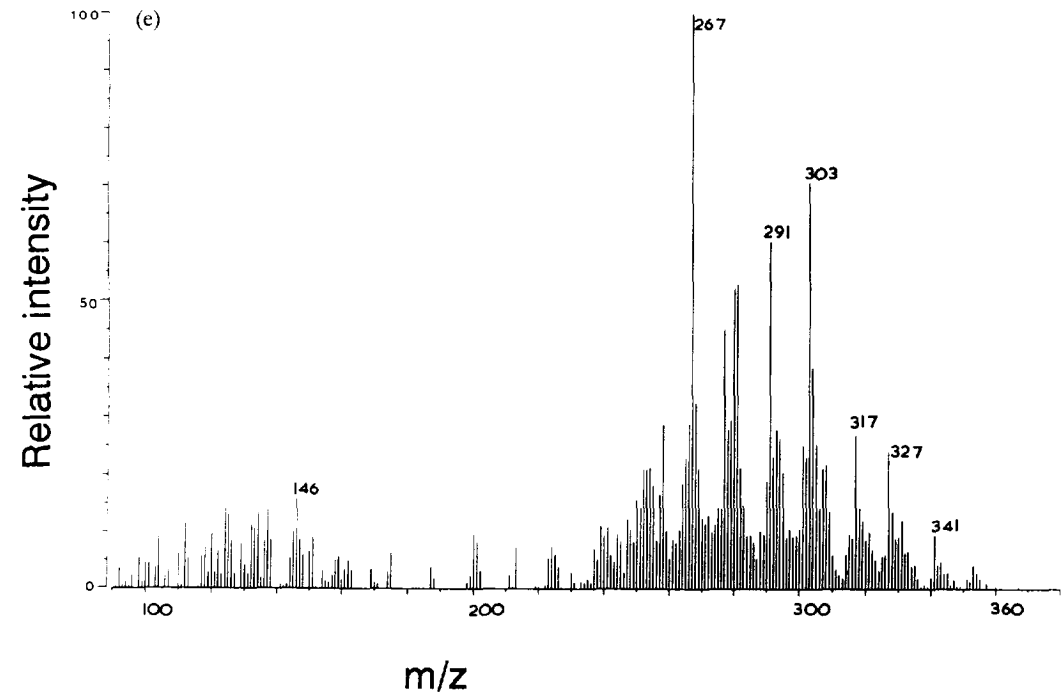


Fig. 3. (*continued*)



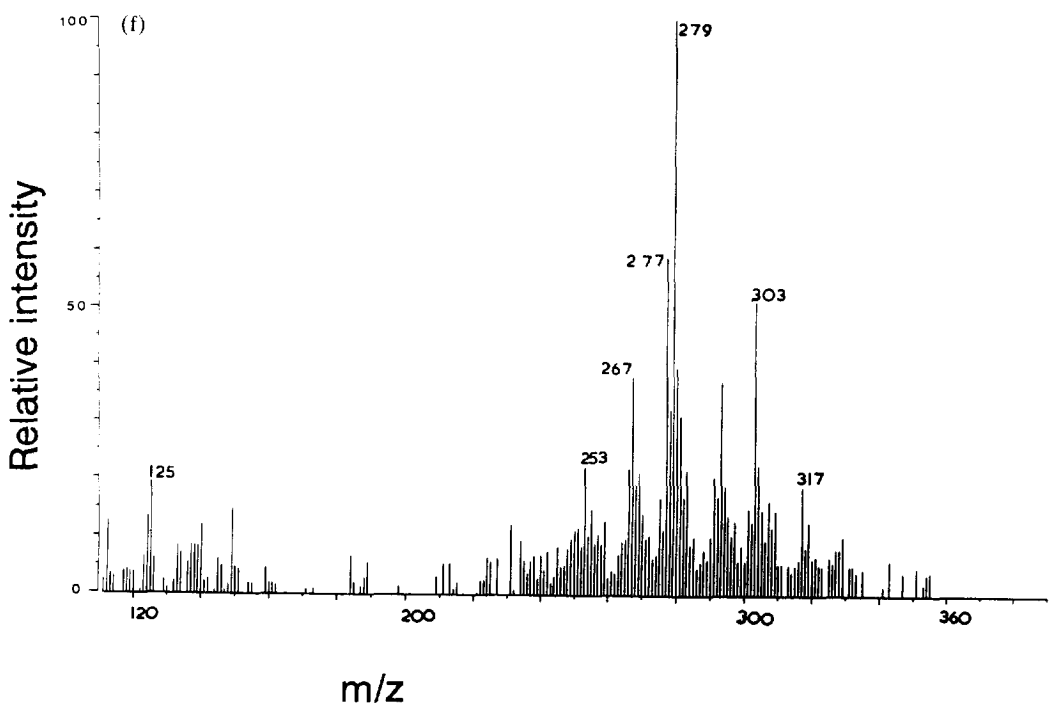


Fig. 3. (*continued*)

Table 2
Mass spectral data; major masses and types in the fractions from planar chromatography

Fraction	*m/z*	Possible types
1	166, 170, 178; 202, 216, 230, 244, 258, 272, 286; 226, 240, 254; 228, 242, 256; 252, 266; 218, 232, 246, 260; 268, 282.	Fluorene, alkyl-naphthalene, phenanthrene, pyrene, chrysene, benzopyrene, benzo[*ghi*]fluoranthene benzonaphthofuran, dinaphthofurans and homologues or alternative structures.
2	202, 216, 230, 244, 258, 272; 226, 240; 228, 242, 256; 248; 252, 266, 280, 294; 268, 282, 296, 310, 324; 276, 290, 278, 292, 306, 320, 334, 348, 362; 300, 328, 342, 356; 302, 316, 330, 344, 358, 372; 298; 318, 332, 346, 360; 308, 322, 366, 350; 326, 340, 354, 368; 352; 378;	Pyrene, benzo[*ghi*]fluoranthene, chrysene, benzonaphthothiophene, benzopyrene, dinaphthofuran, indenopyrene, pentacene, coronene, dibenzopyrene, phenanthro-naphtho-thiophene, phenanthro-naphtho-furan, dibenzanthraquinone, benzoindenopyrene, tribenzopyrene, heptacene, homologues and alternative structures.
3	226; 228; 252, 266; 268; 276, 290; 278, 292; 298; 300; 302, 316; 318, 332; 350, 364, 378, 392, 406, 420; 352, 366, 380, 394, 408, 422; 326, 340; 342, 356, 370, 384, 398; 368, 382, 396; 358, 372; 376, 390, 404, 418, 432, 446; 426, 440; 428, 442, 456; 400; 402, 416, 430, 444, 458, 472; 450, 464; 452, 466, 480; 468, 482; 448; 320; 322; 324; 374;	benzo[*ghi*]fluoranthene; chrysene; benzo-pyrene; pentacene; coronene; dibenzopyrene; benzocoronene; tribenzopyrene; rubicene; hexacene; diphenanthrofuran; naphthoacenaphthenothiophene; benzorubicene; dibenzorubicene; octacene; dibenzocoronene; tetrabenzopyrene; tribenzocoronene; pentabenzopyrene; ditetracenofuran; possibly -thiophene and -furan structures.
4	302; 326, 340; 350, 364; 352, 366, 380; 376, 390; 400, 414; 402; 392, 406; 346; 348; 374; 382; 384; 408; 424; 426;	dibenzopyrene; rubicene; benzocoronene; benzoindenopyrene, dibenzocoronene; tri-benzopyrene; heptacene; naphtho-phenan-thro-furan and -thiophene; dibenzorubicene.
5	167, 181, 195, 209; 203, 217; 227, 241; 229, 243, 257; 253, 267; 261, 275; 265, 279, 293, 307, 321, 335; 277, 291; 303, 317; 319, 333; 327; 329, 343, 357, 371; 353, 367; 361; 377; 379; 401; 403;	carbazole or naphthalene nitrile; phenanthrene nitrile; pyrene nitrile; phenyl naphthalene nitrile; chrysene nitrile; benzopyrene nitrile; pentacene nitrile, dibenzopyrene nitrile; naphtho-phenanthro-nitrile; hexacene nitrile; tribenzopyrene nitrile; diphenanthryl nitrile; tribenzoindenopyrene; heptacene nitrile
6	267, 281; 277, 291; 303, 317, 331, 345; 327, 341, 355; 353, 367; 343, 357.	dibenzocarbazole; benzopyrene nitrile; pentacene nitrile; dibenzopyrene nitrile; hexacene nitrile; benzonaphthofuran nitrile.

Table 2 (*continued*)

Fraction	*m/z*	Possible types
7	217; 220, 234, 248; 229, 243, 257; 230, 244; 253, 267; 273, 287; 275, 289; 280, 294, 308; 301, 315.	benzocarbazole; oxygenates; phenyl naphthalene nitrile; chrysene nitrile; thiophene nitriles; pyrrolo-substituted PAH
8	217; 229, 243, 257, 269; 253, 267; 277; 279; 303, 317; 341.	azabenzofluorene; azachrysene; azabenzopyrene and other aza-PAH
9	167; 179, 193, 207, 221; 203, 217; 229, 243, 257; 233, 247; 253, 267; 269, 283; 277; 279, 293; 301; 303, 317; 329, 343.	aza-PAH; -fluorene; -phenanthrene; -pyrene; -chrysene; -benzonaphthofuran; -benzopyrene; -dinaphthofuran; -indenopyrene; -pentacene; -coronene; -dibenzopyrene; -hexacene.
10	195, 209, 223, 237, 251; 203, 217; 229, 243, 257; 219, 233, 247; 245, 259; 253, 267; 269, 283; 277, 291; 293; 301; 303; 327; 353; 368, 382; 409.	aza-PAH; -fluorene; -pyrene; -chrysene; -benzonaphthofuran; -benzopyrene; -dinaphthofuran; -indenopyrene; -pentacene; -coronene; -dibenzopyrene; -rubicene; -tribenzopyrene; -diphenanthrofuran; -phenanthro-chryseno-thiophene.
11	309; 315; 341, 355; 409	Possibly aza-oxygenates.

being compared by some of the soft ionisation techniques previously shown capable of detecting much higher masses in coal and coal derived liquids [15].

4. Discussion and comparison with previous work

The probe-mass spectrum of the whole pitch produced from silica gel closely resembles that shown in Ref. [15] (as Fig. 2c) produced at low ionizing volts; the main differences are the higher upper mass limits observed when using lower ionizing voltages, compared to the 70 eV in the present study, which causes the doubly charged peaks detected in the present spectra. Thus both the lower high mass limit and the doubly charged peaks appear to result from the way in which the instrumentation was set up in the present study. Both sets of spectra (the present and that of Ref. [15]) showed that polynuclear aromatic hydrocarbons are the major components; however, nitrogen containing polynuclear aromatic hydrocarbons were not readily identifiable from the mass spectra of the whole pitch.

It is possible to identify nitrogen PAHs without fractionation [10], the preparation of basic nitrogen fractions for GC–MS making their identification unambiguous [8,9,11], but the procedure involves complex solvent extraction procedures and does not separate neutral nitrogen-substituted PAHs from basic nitrogen-substituted PAHs. Class separation methods [12] which allow collection of separate neutral and basic nitrogen fractions, based on liquid chromatography are also complex and require relatively large volumes of solvents. Typical upper limits of nitrogen PAH detected in this pitch and other coal-derived materials by GC–MS are about *m/z* 253, azabenzopyrene [8–12,18] with only one example [6] by GC–MS extending to *m/z* 301, possibly azacoronene. In contrast, the GC–MS results for PAH generally extend beyond benzopyrene (*m/z* 252) to dibenzopyrene (*m/z* 302) [2,3], the methyl derivative (*m/z* 316) [3], and to tribenzopyrenes (*m/z* 352) [15] in this pitch.

By contrast, the probe mass spectra of fractions separated on silica gel PC plates have allowed the identification of isomer classes rather than individual isomers but have extended the mass range of identified nitrogen PAH to nearly m/z 500, whilst confirming the previous identifications of major nitrogen PAH in the pitch. It appears, the identification of neutral and basic nitrogen types as well as the major PAH components can be achieved during one rapid, simple and inexpensive separation with the use of standards to define the separation using only small volumes of solvents.

Fractionation by planar chromatography followed by SEC and UV-F spectroscopy thus allows a unique and novel set of structural parameters to be correlated: we have been able to show that molecular masses of polynuclear aromatic systems increase with decreasing R_F (decreasing solubility) and increasing molecular masses of the fractions.The combination of UV-F spectroscopy (fraction k) with probe-MS has allowed the identification of a second series of compounds, nitrogen-containing PAHs, which commence with small aromatic systems and become larger (in parallel with the PAHs) as retention distance decreases.

In a recent study [17] of the UV-fluorescence emission spectroscopy of coal pyrolysis tars in methanol solution, the emission spectrum was observed to shift to higher wavelengths as the excitation wavelength was increased. This indicates a similar trend to that observed in the fractions from planar chromatography with decreasing R_F; the change is more readily observed in the planar chromatography fractions, however, presumably because, in the absence of fractionation, more intense emission from material in which smaller polynuclear aromatic systems predominate may mask weaker fluorescence intensities (due to low quantum yield) of larger polynuclear aromatic systems at the higher wavelengths.

Laser desorption MS work [15] has indicated the presence of material with molecular masses up to m/z 12 000 (the instrument limit) while matrix-assisted laser desorption MS has shown molar masses up to 200 000 in this pitch [16]. Size-exclusion chromatography of the pitch, in comparison with polystyrene standards, indicates an upper mass limit of about 2000. A recent comparison, by Sheng and co-workers [19], of matrix-assisted laser desorption MS and size-exclusion chromatography has also indicated that SEC may severely underestimate the molar mass range of a polymer. Furthermore, in the present study, it is probable that the highest molecular mass and/or most polar components of the pitch were insoluble in the chromatographic solvent, tetrahydrofuran, denying access for detection by any of the analytical techniques subsequently used.

A linear relation between molar mass (200–2500) and elution volume using Sephadex LH-20 with pyridine as the solvent for preparative size-exclusion chromatography has been reported [20] and taken to indicate that the size-exclusion mechanism operated over the entire elution range. There was evidence [20] from infra-red spectroscopy of the fractions that some very polar oxygen-containing compounds accumulated in the late-eluting fraction. In the present work, there are indications that polar oxygenates (phenols and acids as opposed to furans) would be found in the fractions of low R_F, near the THF/chloroform–methanol solvent front and appear at long elution times in the size-exclusion chromatograms.

5. Conclusions

This work was undertaken to explore the application of planar chromatography to the fractionation of a complex coal derived material with recovery of fractions based on relative retention data and subsequent examination of separated fractions by size-exclusion chromatography, UV-fluorescence spectroscopy and probe mass spectrometry. The separation is relatively rapid and inexpensive and requires only small volumes of solvents. The study has lead to structural information not readily available by direct characterisation of the original mixture itself. Some of the important findings may be summarised as follows:

(1) The general shift of UV-fluorescence emission maxima to higher wavelengths has been observed to correlate with progressively diminishing mobility on the PC plates. This finding strongly suggests the presence of increasingly larger polynuclear aromatic systems in the less mobile fractions. These changes were found to correlate with increasing molecular masses of the fractions, as observed by SEC.

(2) The combination of UV-F spectroscopy with probe-MS has allowed the identification of two series of compounds, basic and neutral nitrogen-containing PAHs, which commence with small aromatic systems and become larger (in parallel with the PAHs) as retention distance decreases. The combination of planar chromatographic separation with mass spectrometric probe methods is relatively rapid and more informative in comparison with extraction of nitrogen-specific fractions by solution techniques.

(3) The size-exclusion mechanism thought to operate in SEC has been observed to fail for components of increasing polarity, by the appearance of a prominent peak and much residual material at elution times longer than those expected for small molecular mass species.

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