Planar chromatographic separation of petroleum residues and coal-derived liquids

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Abstract

Vacuum distillation residues from two petroleum crudes, a coal liquefaction extract and a coal tar pitch have been fractionated by planar chromatography (PC) using two solvent sequences: pyridine–acetonitrile and tetrahydrofuran (THF)–toluene. Fractions recovered from PC were examined by UV-fluorescence spectroscopy (UV-F), size-exclusion chromatography (SEC). UV-F and SEC of the whole samples showed differences in aromatic cluster size and molecular mass (MM) ranges which could be related to the different origins of the samples. The MM ranges indicated by SEC were greater for the vacuum residues than for coal-derived materials. However, the UV-F spectra of the fractions indicated that the petroleum residue fractions contained similar aromatic types, whereas the fractions from coal liquids contained significantly different aromatic types. SEC profiles of the fractions indicated a separation of coal-derived samples by increasing molecular size with increasing immobility in PC, whereas for petroleum fractions, the same trend was not apparent. MALDI-mass spectra of the set of original samples showed broadly similar ranges of MM distributions but additional work is necessary to identify appropriate matrices and procedures in order to improve the MALDI spectra. © 1999 Published by Elsevier Science B.V. All rights reserved.

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1. Introduction

In an earlier paper [1], we described the fractionation of a coal tar pitch by planar chromatography (PC). The separated fractions were characterised by size-exclusion chromatography (SEC), UV-fluorescence (UV-F) and probe-mass spectrometry (MS). The characterisation of separated fractions led to structural information not readily available from the direct characterisation of the original sample itself. With increasing mobility on the analytical plates, decreasing sizes of polynuclear aromatic ring systems and shifts to smaller molecular mass (MM) distributions were observed. In this paper, the application of planar chromatographic separation prior to instrumental characterisation has been extended to complex liquid mixtures of different origins and structural characteristics: a coal liquefaction extract from the British Coal Point of Ayr liquefaction pilot-plant and two petroleum-derived vacuum residues. Data from a coal tar pitch have been retained for comparison.

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The work was performed to establish that large aromatic molecules can be detected in these different, relatively intractable materials; the definition of large molecules in the context of the experimental methods used is discussed below, but generally implies MM greater than 1000 u. An understanding of both MM ranges and differences in chemical structures of the different sample types and of the different fractions is necessary for the development of processes for their more profitable use. The thermal treatment of the coal extract differs markedly from that of the pitch sample or the vacuum residues and all four samples were expected to contain different types of large MM materials.

Information on molecular structures of these samples are only available in terms of analyses in the gas chromatography (GC) and GC–MS ranges. For coal-derived materials this range corresponds to an upper mass limit of approximately 300 u; aromatics above about mass 300 do not normally elute from high temperature columns. For petroleum-derived samples, the range is somewhat larger: aliphatics with carbon numbers at up to about C60 can be detected by high temperature GC methods [2]. However, work on coal-derived materials [3–6] and petroleum residues [7] by MALDI (matrix assisted laser desorption–ionisation)—MS and SEC provide evidence that the MM ranges of these materials extend to much higher values: MM ranging from several thousand to several tens of thousands have been identified, with an upper limit of the order of 100 000 u.

Relatively little detailed structural information is available on these very high MM materials. Extrapolation of structures from those identified by GC, GC–MS and probe-MS has been shown [8] to give incorrect C–H ratios for the structures of high mass materials. That is, aromatic structures with added benzogroups (as in benzopyrenes) or with complete shells of benzo rings (as in the difference between benzene and coronene) with mass greater than 1000 u have C–H ratios much greater than the C–H ratio of the whole sample. For coal-derived liquids, related work based on SEC [9] shows some of these materials appearing at elution times comparable to polystyrene MM standards of mass 1–1.84 million. The data strongly suggest that material appearing at the exclusion limit of the analytical columns consists of large MM material—as opposed to aggregates of smaller molecules. In UV-F spectroscopy, the 'excluded' fractions of these coal-derived samples were found to have very low quantum yields, with weak fluorescence above 450 nm [10,11].

In the present study, PC has been used to obtain fractions for examination by UV-F and SEC. Quantities of recovered fractions were insufficient for more extensive characterisation by IR, NMR and elemental analysis, in part because of the difficulty in removing the solvent (1-methyl-2-pyrrolidinone, NMP) from fractions recovered by scraping the chromatographic plates [12,13]. Recovered materials show strong IR signals for silica and NMP and although both these materials can ordinarily be removed from the sample, available techniques are not readily applicable to such small samples.

2. Experimental

2.1. Samples

'Vacuum residues' are residues of the flash vacuum distillation (at 450°C; 3.3–4.0 kPa (25–30 mmHg)) of the bottoms fraction from atmospheric pressure distillation of degassed crude oil. At the vacuum distillation stage, the 'true boiling temperature' corresponding to the actual 450°C is about 548°C. Cracking and coke formation by the residue is normally minimised by using short residence times. Heavy petroleum residues have high loadings of trace elements (principally vanadium and nickel). They are also regarded as difficult materials for further processing and refining because of high hydrogen requirements; common uses include asphalt for road making [14] or feedstock for petroleum coke production. The present samples, labelled as Samples 1 and 2 (of South American and Eastern European origins, respectively), are pre-refinery samples prepared during pilot crude oil assay tests (ASTM D 86; Ref. [15]) and are thought to have undergone relatively little thermal degradation.

Coal tar pitch is the +450°C boiling residue from the distillation of coke oven tars, which, in this case, have been produced during high temperature (~1200°C) coking. Two coal tar pitch samples were included for comparison, one of which has been

extensively examined [5,6,16] by PC, UV-F and SEC and MS. These samples are known to have undergone extensive cracking (and probably some condensation and repolymerisation) during the coking and subsequent distillation stages.

The final sample was a Point of Ayr coal liquefaction extract produced at the Point of Ayr Coal Liquefaction Facility. In the 'British Coal' pilot coal liquefaction process, the extracts are filtered to remove minerals and undissolved coal and are hydrocracked; light and medium distillates are removed and the residue recycled as process solvent [17]. The coal extract sample is expected to have undergone thermal degradation during the 1-h average residence time in the digester (420–440°C) and to contain recycle solvent—more thoroughly divested of side chains and other substituents. The

present sample has been characterised in hydrocracking studies [18–21] and examined by Mössbauer spectroscopy to detect iron complexes [22,23]. The extract may contain some aliphatic waxes, possibly up to 15% by weight [24].

The overall characterisation scheme in the present study is shown in Fig. 1, with details of individual methods presented below. Although both pitch samples have been fractionated, the results were sufficiently similar for only one set to be presented below.

2.2. PC

Whatman chromatographic plates (silica gel: K6, 10×20 cm) were used with two solvent sequences: (i) pyridine followed by acetonitrile and (ii) THF
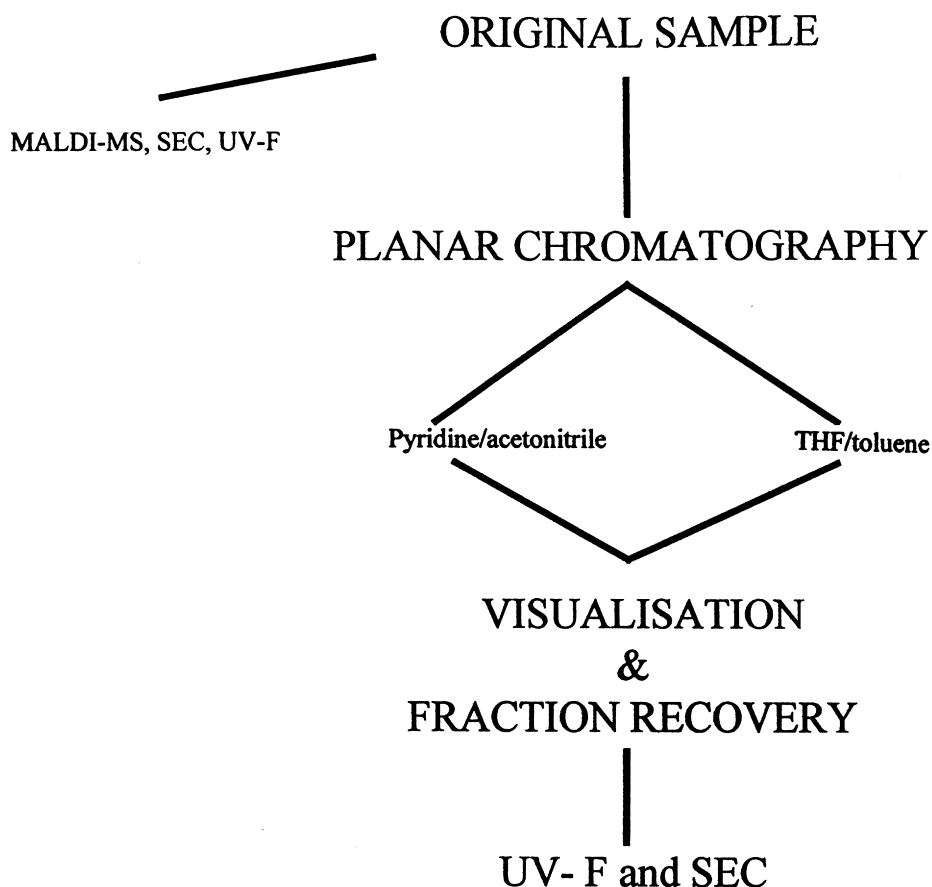

Fig. 1. The sample characterisation scheme.

followed by toluene. Before use, the plates were washed in the more polar solvent (pyridine or THF) and dried, to remove contaminants from coating materials. Whilst NMP appears to dissolve the pitch completely, it cannot be readily evaporated from the plate due to its high boiling point (over 200°C). Sample was, therefore, applied to the plates in the form of partially dissolved slurries in pyridine. Development tanks were equilibrated for half an hour to saturate the vapour phase before insertion of the plates. Sample was applied to the plates by multiple spotting on a narrow band at the origin, along a 20-cm side and dried in air before development. The first development in the more polar solvent proceeded for 4 or 5 cm; the plates were removed from the tank and dried before insertion into the second solvent for development for a further 2 or 3 cm beyond the first solvent front. Multiple development was undertaken (manually) to enhance the separation of fractions. After final drying, bands of silica were scraped from the plates representing: (i) material immobile in both solvents; (ii) material

accumulated at the first solvent front (not mobile in the second solvent); and (iii) material mobile in both solvents (advancing to the second solvent front). R_f values for the fractions and solvent fronts are given in Table 1. Individual sample fractions were recovered from the silica scrapings by dissolving at room temperature in NMP, assisted by ultrasonic agitation. Recovery of fractions from silica was semi-preparative with some sample remaining on the substrate. No attempt was made to recover quantitative fractions.

Analytical development of the five samples (at three different spot concentrations each), has also been carried out in both solvent sequences using Whatman K6 20×20 cm plates.

2.3. SEC

SEC was carried out using a polystyrene–polydivinylbenzene column ('Mixed-E', 3-µm; Polymer Laboratories). In this column polystyrene MM standards from 100 up to 30 000 u may be resolved,

Table 1
Solvent migration distances and R_f values of fractions of the samples

Sample	Solvents	Migration distance, mm (R_f)	Range of fraction recovered	
			mm	R_f
Petroleum	Pyridine	50 (0.61)	0–10	0–0.12
Residue 1	Acetonitrile	82 (1.0)	10–50	0.12–0.61
			50–82	0.61–1.0
	THF	40 (0.55)	0–10	0–0.14
	Toluene	72 (1.0)	10–40	0.14–0.55
			40–72	0.55–1.0
Petroleum	Pyridine	40 (0.49)	0–10	0–0.12
Residue 2	Acetonitrile	82 (1.0)	10–40	0.12–0.49
			40–82	0.49–1.0
	THF	45 (0.63)	0–10	0–0.14
	Toluene	72 (1.0)	10–45	0.14–0.63
			45–72	0.63–1.0
Point of Ayr digest	Pyridine	47 (0.57)	0–12	0–0.14
	Acetonitrile	83 (1.0)	12–47	0.14–0.57
			47–83	0.57–1.0
	THF	44 (0.55)	0–10	0–0.13
	Toluene	80 (1.0)	10–44	0.13–0.55
			44–80	0.55–1.0
Pitch	Pyridine	55 (0.63)	0–15	0–0.17
	Acetonitrile	88 (1.0)	15–55	0.17–0.63
			55–88	0.63–1.0
	THF	48 (0.58)	0–15	0–0.18
	Toluene	83 (1.0)	15–48	0.18–0.58
			48–83	0.58–1.0

showing a linear relationship between ($\log_{10}$ MM) and elution volume (or time). Larger MM polystyrene standards up to 2 million u elute at shorter times with a different relationship between MM and time, and are classed as excluded from the column porosity. The calibration graph has been shown elsewhere [18]. The 'whole' samples and fractions recovered from planar chromatographic separation have been examined by UV-absorbance detection at 350 nm at a column temperature of 85°C and an eluent (NMP) flow-rate of 0.45 ml min^{-1}. For all the samples and fractions examined in this work, preliminary SEC work [5,10,25] using a similar 'Mixed-E' column but with tetrahydrofuran as eluent showed high-mass materials separating by adsorption rather than by size; the THF results are not presented here.

The petroleum residues and digest are likely to contain waxes, whilst the pitch sample is expected to contain little purely aliphatic material. In this work, the use of NMP as the analytical solvent and detection by UV absorbance and fluorescence do not permit the observation of materials with purely aliphatic structures.

2.4. UV-F

The Perkin-Elmer LS50 luminescence spectrophotometer was set to scan at 240 nm min^{-1} with a slit width of 2.5 nm. Synchronous spectra were acquired at a constant wavelength difference of 20 nm, using a quartz cell with 1 cm path length. The spectrometer featured automatic correction for changes in source intensity as a function of wavelength. Emission, excitation and synchronous spectra of the samples were obtained in NMP. Due to inevitable uncertainty in the concentrations of samples recovered from the chromatographic plates, spectra have been presented in peak-normalised mode. To minimise self-absorption effects, solutions were successively diluted with NMP until the fluorescence signal intensity began to decrease with further dilution. However, it was necessary to examine the fractions immobile on the plates in relatively concentrated solutions because the fluorescence quantum yields were very low; in these cases, sample was added until the fluorescence signal was significantly greater than the background fluorescence. Details of the procedure for acquiring UV-F spectra have been given elsewhere [26–28].

2.5. MALDI-MS

A Fisons VG-TOFSPEC instrument was used in linear mode, with a 337-nm nitrogen laser and a VAX 4000-based data system with OPUS software. As samples strongly absorbed laser light at 337 nm, initially no matrix was added and the sample allowed to act as its own matrix (i.e., laser ablation). Pyridine- and tetrahydrofuran-insoluble fractions of the coal tar pitch, examined in the presence and absence of matrix [5], have been observed to give similar MALDI-spectra. Similar procedures have been used for analysis of urinary porphyrins [29]. However, NMP extracts of kerogens only gave reasonable spectra in the presence of added matrix [12]. In the present work, matrices which have been tried with the set of samples include sinapinic acid, 2,5-dihydroxybenzoic acid (DHB), α-cyano-3-hydroxycinnamic acid [α-cyano], 2-(4-hydroxyphenylazo)-benzoic acid (HABA) and 9-anthracene carboxylic acid (9-A). Sample and matrix solutions in NMP or in mixtures of chloroform–methanol were deposited onto the target stub by vacuum drying. Deposition of NMP alone produced no signal above m/z 200. An ion accelerating voltage of 28 kV was used at maximum laser power; approximately 50 spectra were summed in each case.

3. Results and discussion

Fig. 2 presents tracings of photographs (taken under UV light at 254 nm) of developed chromatographic plates, showing differences between the behaviour of the five samples in the two solvent systems and at three different sample loadings. The petroleum residues gave white 'bubble'-shapes at the pyridine front and 'spear'-shapes at the toluene front, whilst coal-derived samples simply gave discrete symmetrical spots with some red or brown fluorescence. Although, the relatively small number of samples examined does not allow generalisations, these differences suggest an inexpensive and rapid method for identification–differentiation between coal- and petroleum-derived liquids.
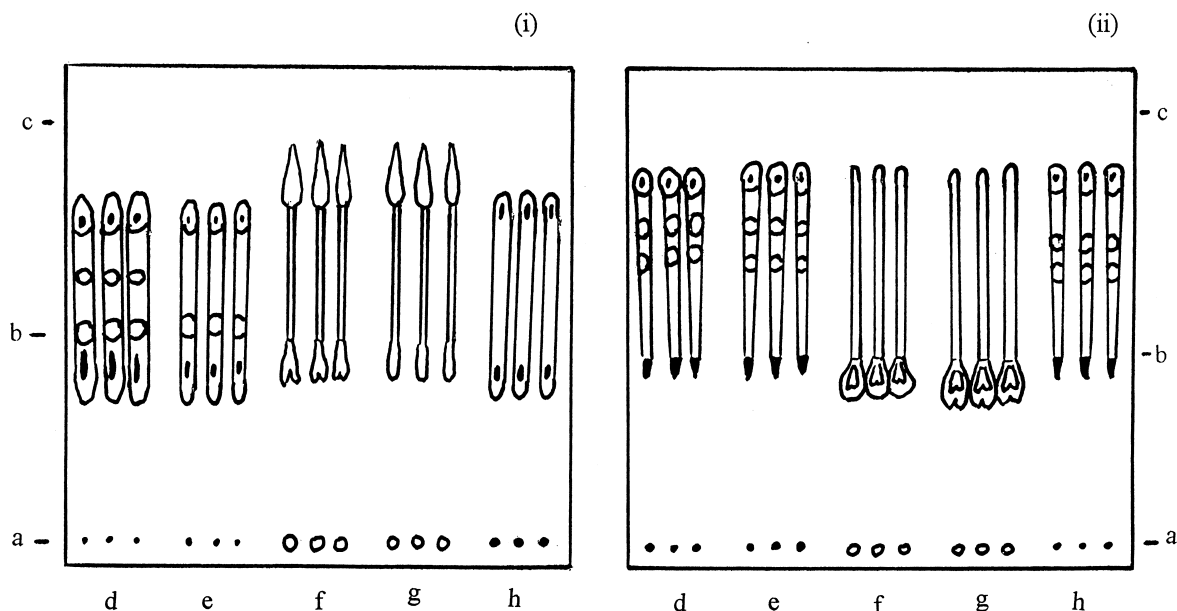
Fig. 2. Tracings of photographs of analytical developments using both solvent sets and all five samples, in UV at 254 nm; development in solvent systems toluene and tetrahydrofuran (i) and acetonitrile and pyridine (ii). The sample spotting line (origin) is shown at (a) and solvent fronts are shown as (b) THF or pyridine and (c), toluene or acetonitrile. Sample spots are (d) pitch 1, (e) pitch 2, (f) petroleum residue 1, (g) petroleum residue 2 and (h) coal extract. Fluorescence colours were white with some red–brown in the pitch and extract (black in the Figure); origin spots were white for petroleum residues and black for coal-derived samples.

3.1. Interpretation of UV-F spectra of complex coal-derived liquids

The samples considered in this study contain mixtures of components with different structural features. The nature of UV-fluorescence spectroscopy does not allow precise interpretations in terms of differences in the occurrence of these structural features. This is due to the multiplicity of possible types of structural features likely to contribute to shifts in the positions (and shapes) of the spectra. The difficulty is common to the evaluation of results from most analytical techniques applied to complex mixtures, where changes in large numbers of different structural features may contribute simultaneously to observed changes in the resulting spectrum.

With this cautionary note on the many possible exceptions, a simplified classification of structural differences likely to shift UV-F spectra of complex fossil fuel-derived liquid mixtures to *longer* wavelengths may be summarised as follows: (i) the presence of alkyl and alkoxy substituents; (ii) the presence of heteroatom containing aromatic sub-

stituent groups, with the phenolic-OH group possibly being the most abundant. Primary amines are not normally encountered in abundance in coal liquefaction extracts [30–32] or tars; with respect to the presence of heteroatomic substituents [33], the magnitudes of shifts in spectra to longer wavelengths would decrease in the order primary>secondary> tertiary amines. Shifts of UV-F spectra to longer wavelengths may also result from (iii) the presence of linearly conformed polynuclear aromatic ring systems (e.g., pentacene to tetracene) and of formally fixed double bonds—as in zethrenes [34]; (iv) presence of structures with fused five-membered rings (with no ring carbons available for substitution) found in components of pitches and extracts of coal (e.g., fluoranthene) [35–38]. Fused five-membered rings are more reactive, and their destruction is expected to shift both UV-absorbance and UV-fluorescence spectra to considerably shorter wavelengths than the loss of analogous six-membered rings.

Evaluation of spectra from complex mixtures must also take account of the much smaller quantum yields from large MM materials, particularly those

containing large polynuclear aromatic ring systems. Due to the greater fluorescence intensities of smaller polynuclear aromatic ring systems, in the characterisation of complex mixtures, signal due to larger polynuclear aromatic ring systems tends to get swamped. Fractionation has been shown to assist in acquiring data more specific to larger MM fractions [6,16]. Examples of this behaviour have also been observed in this study and are described below.

To summarise, UV-F signal at longer wavelengths may be attributed to the presence of larger polynuclear aromatic ring systems or aromatic cluster sizes (the shift to longer wavelengths being much enhanced by the presence of embedded five-membered rings), as well as that of heterocyclic structures and alkyl or heteroatom substituents. Similar comments on the interpretation of UV-F spectra in terms of extents of catalytic hydrocracking of coal liquefaction extracts may be found in Ref. [39].

3.2. Characterisation of the original ('whole') samples

Fig. 3a and b present synchronous UV-F spectra of the two petroleum residues and of the three coal-derived samples, respectively. Differences were observed between the spectra of the two petroleum residues (Fig. 3a) above 340 nm, possibly suggesting a somewhat greater concentration of larger aromatic ring systems in Sample 2 compared to Sample 1. The character of the spectra of the two vacuum residues clearly differed from those of the three coal-derived materials, with the vacuum residues showing relatively greater intensity between 300–380 nm and less intensity above 390. The spectra of the coal-derived materials extended to somewhat longer wavelengths than those of the vacuum residues.

Significant differences were observed between the spectrum of the liquefaction extract and those of the two pitch samples. Although characteristic peaks appeared at similar wavelengths—suggesting a degree of correspondence between structural features fluorescing under these conditions, greater intensities were observed in the spectrum of the liquefaction extract at all wavelengths.

We have previously observed that, prior to fractionation—by PC or solvent separation, the (more abundant) less polar and/or smaller MM material tend to dominate measured bulk characteristics (e.g.,

UV-F spectra or SEC chromatograms) of a coal tar pitch [3,11,16]. In the present case, the liquefaction extract is likely to contain a wider spectrum of smaller MM materials—and possibly smaller aromatic ring systems. The greater relative intensities observed in the spectra of the extract are, thus, consistent with the mode of its preparation, whilst the pitch samples consist of distillation residues with boiling ranges above 450°C.

Fig. 4 presents size-exclusion chromatograms for the five 'whole' original samples. No significant signal was observed after the permeation limit of the column at about 25 min. As in UV-F spectroscopy, chromatograms of the coal tar pitches were found to be different from that of the coal liquefaction extract, where two peaks are evident, one at about 21 min and a peak at 24 min, the latter probably due to the presence of recycled solvent.

SEC chromatograms of the vacuum residues in Fig. 4 showed major peaks at shorter elution times (19–22 min) than those of the coal-derived samples (22–25 min). The result probably reflects the greater average MM of the two vacuum residues, where much of the more volatile material has already been removed by distillation during successive atmospheric pressure and flash vacuum distillation steps. The latter step clearly provides more extensive removal of relatively lighter material compared to coal tar distillation (i.e., pitch preparation). Similar differences have been found between an atmospheric pressure *distillation residue* of a petroleum crude and a coke oven *tar* [7]. Structures and MM of material eluting at the exclusion limit of the column, at about 11 min, are not known; this elution time corresponds to that of the polystyrene MM standard of 1.84 million u.

In summary, the UV-F spectra of the whole samples show different relative intensities for the different sample, but over approximately the same range of wavelengths; the SEC profiles indicate that the petroleum residues were of greater average mass than the coal-derived materials.

3.3. Characterisation of fractions from preparative PC

Table 1 presents solvent migration distances and R_f values for the collected fractions, calculated from the second solvent front. Due to the similarity of
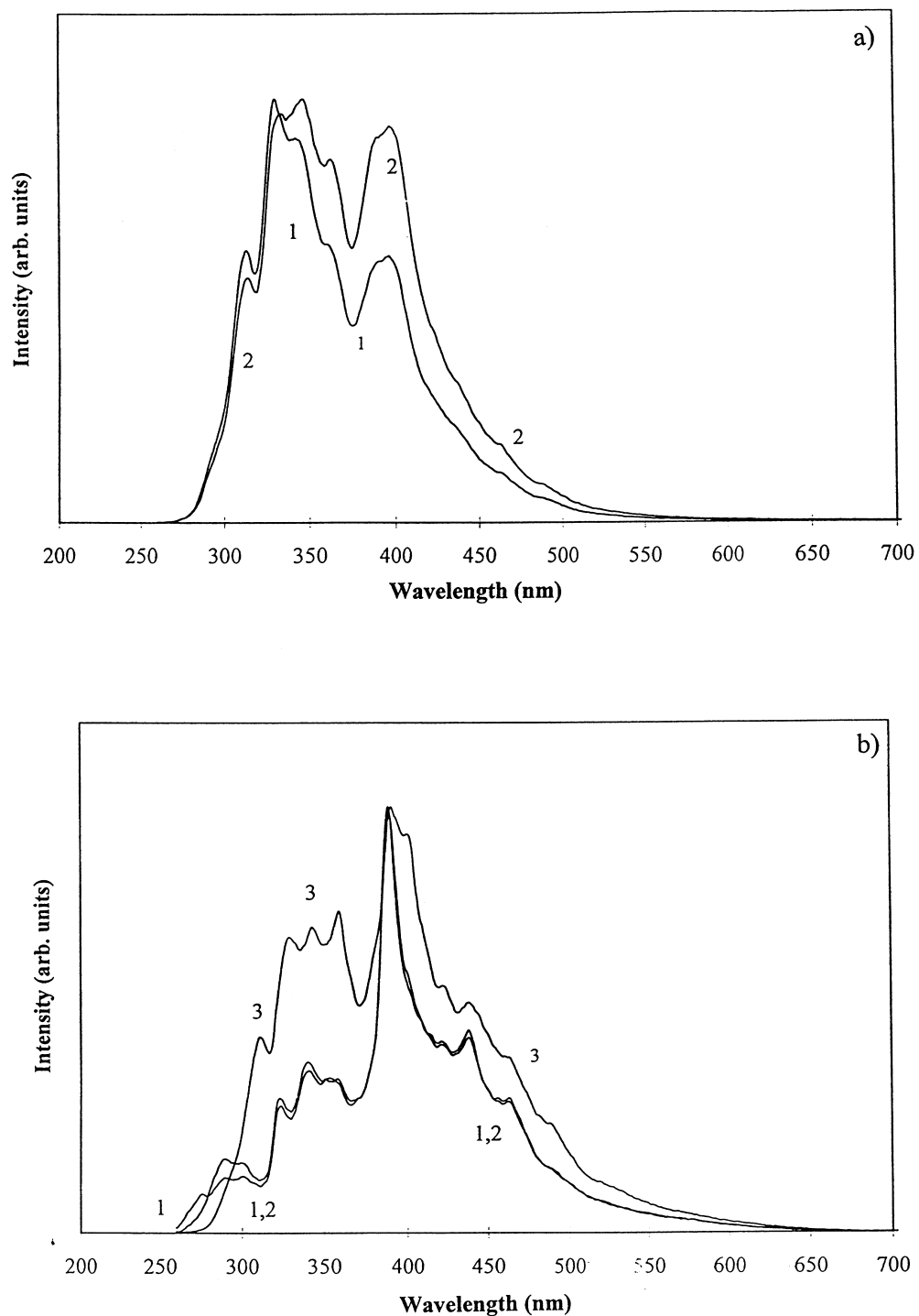
Fig. 3. Synchronous UV-fluorescence spectra with 20 nm difference between excitation and emission for (a) two petroleum residues, marked 1 and 2, respectively and (b) the pitch samples (1, pitch 1; 2, pitch 2) and the Point of Ayr digest (3).
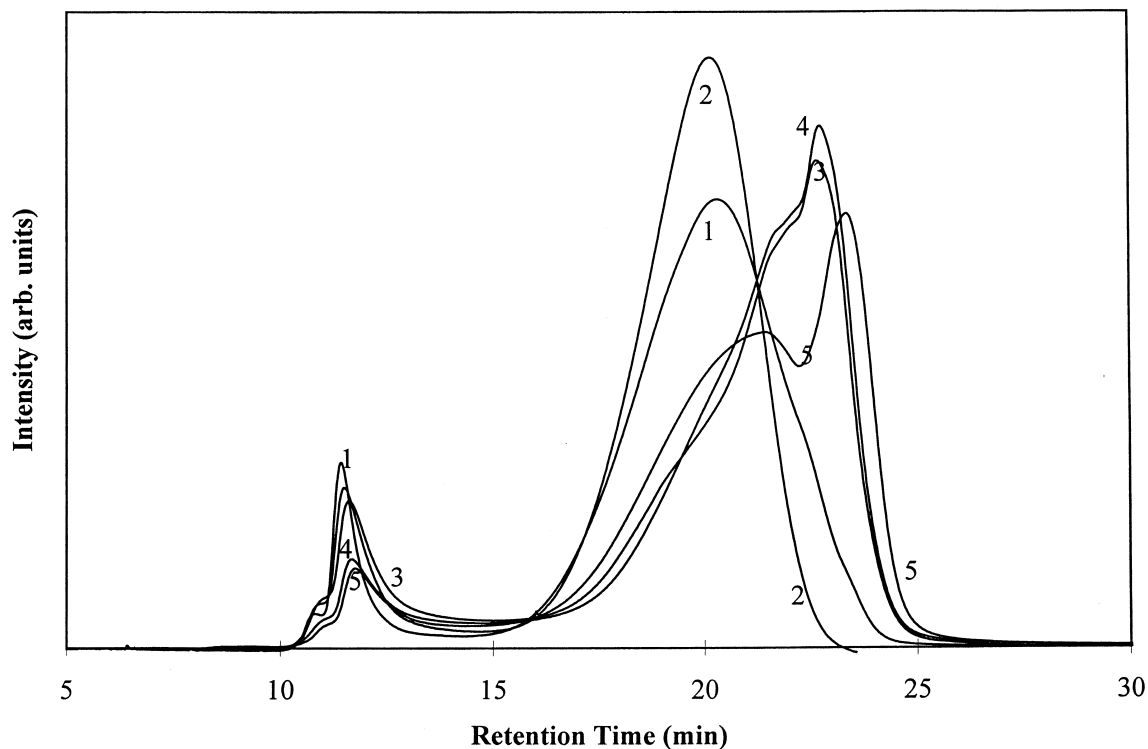
Fig. 4. Size-exclusion profiles in NMP solution for the five samples as received (curves as 1, residue Sample 1; 2, residue Sample 2; 3, pitch 1; 4, pitch 2; 5, Point of Ayr digest).

SEC and UV-F profiles of the two coal tar pitch samples, only one set of pitch data will be discussed below.

3.4. UV-F spectra of the PC fractions

Fig. 5 presents synchronous height-normalised UV-F spectra of fractions, separated by PC, using two separate solvent sequences: pyridine–acetonitrile and THF–toluene. In these diagrams, 'A' denotes the fraction immobile in both solvents, 'B' the fraction mobile in the strongly polar-immobile in the less polar solvent and 'C' the fraction mobile in both solvents.

UV-F spectra of fractions from both solvent sequences separated from the coal-derived samples (Fig. 5a and b extract; Fig. 5c and d pitch), were observed to show the following common characteristics also cf. [6,16].

(i) Decreasing mobility (mobility in just one solvent or immobility in both solvents) resulted in significantly reduced fluorescence intensities, although this is not readily apparent from these 'height-normalised' diagrams.

(ii) With increasing sample mobility on the chromatographic plates, UV-F spectra were observed to shift to shorter wavelengths.

(iii) The spectra of all four A-fractions (immobile in both solvents; Fig. 5a–d) were observed to extend to near or above 700 nm. The contrast with the original ('whole') samples (Fig. 3), where the spectra did not extend above 620–640 nm, clearly reflects the swamping of lower intensity signal at longer wavelengths (probably due to larger polynuclear aromatic ring systems) by higher intensity fluorescence due to smaller molecules (and probably due to correspondingly small ring systems). In the presence of the more mobile material (i.e., in the original samples), longer wavelength signal from partly mobile and immobile fractions was effectively invisible in UV-F spectroscopy.

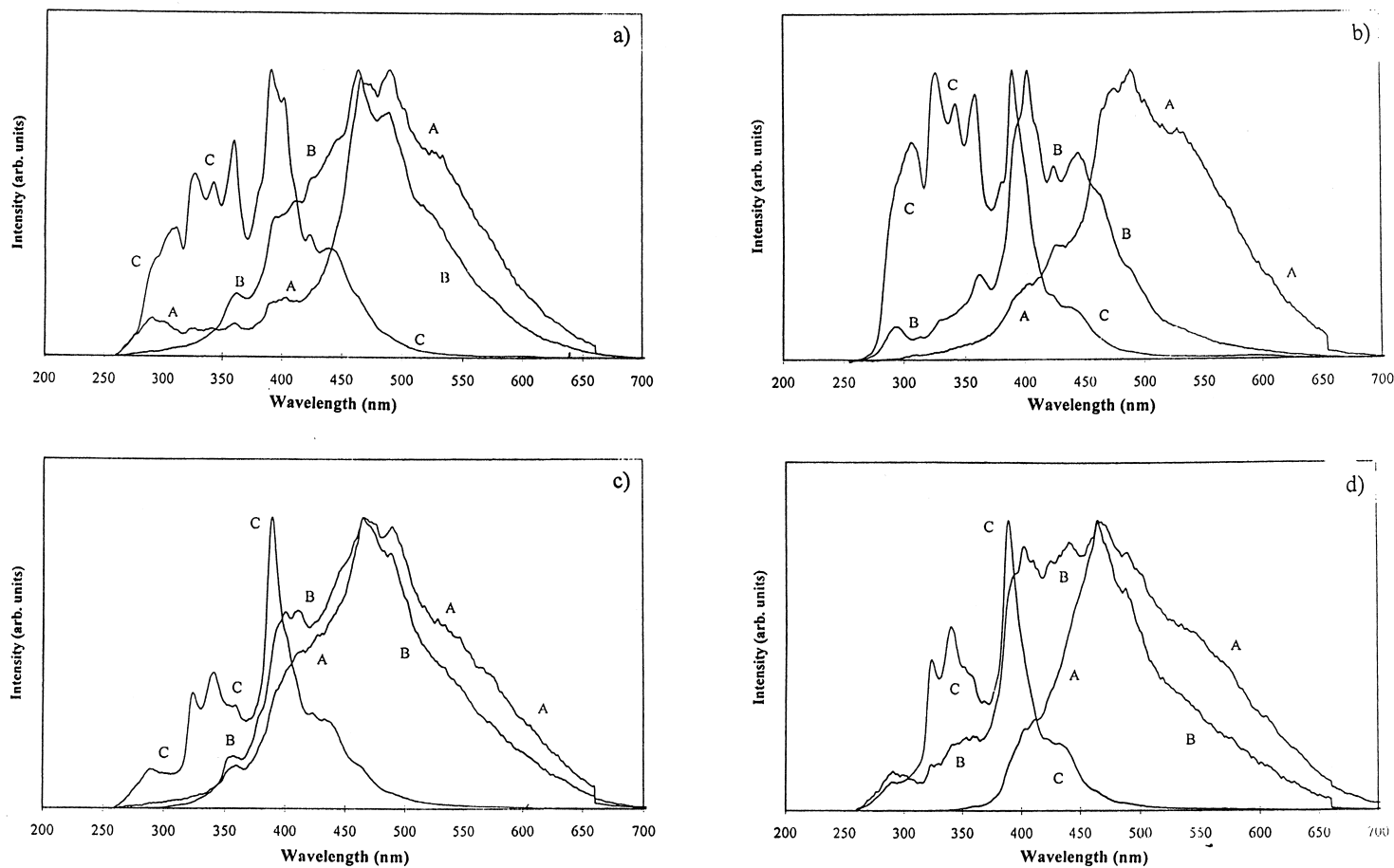As in the case of the coal-derived samples, all the

Fig. 5. Synchronous UV-fluorescence spectra of PC fractions from development in two solvents recovered in NMP solution as immobile, mobile in the first solvent or mobile in both solvents: (a) Point of Ayr fractions in THF and toluene; (b) Point of Ayr fractions in pyridine and acetonitrile; (c) pitch fractions in THF and toluene; (d) pitch fractions in pyridine and acetonitrile; (e) Sample 1 in THF and toluene; (f) Sample 1 in pyridine and acetonitrile; (g) Sample 2 in THF and toluene; (h) Sample 2 in pyridine and acetonitrile. Curves are A, immobile; B, mobile in first solvent; C, mobile in both solvents.
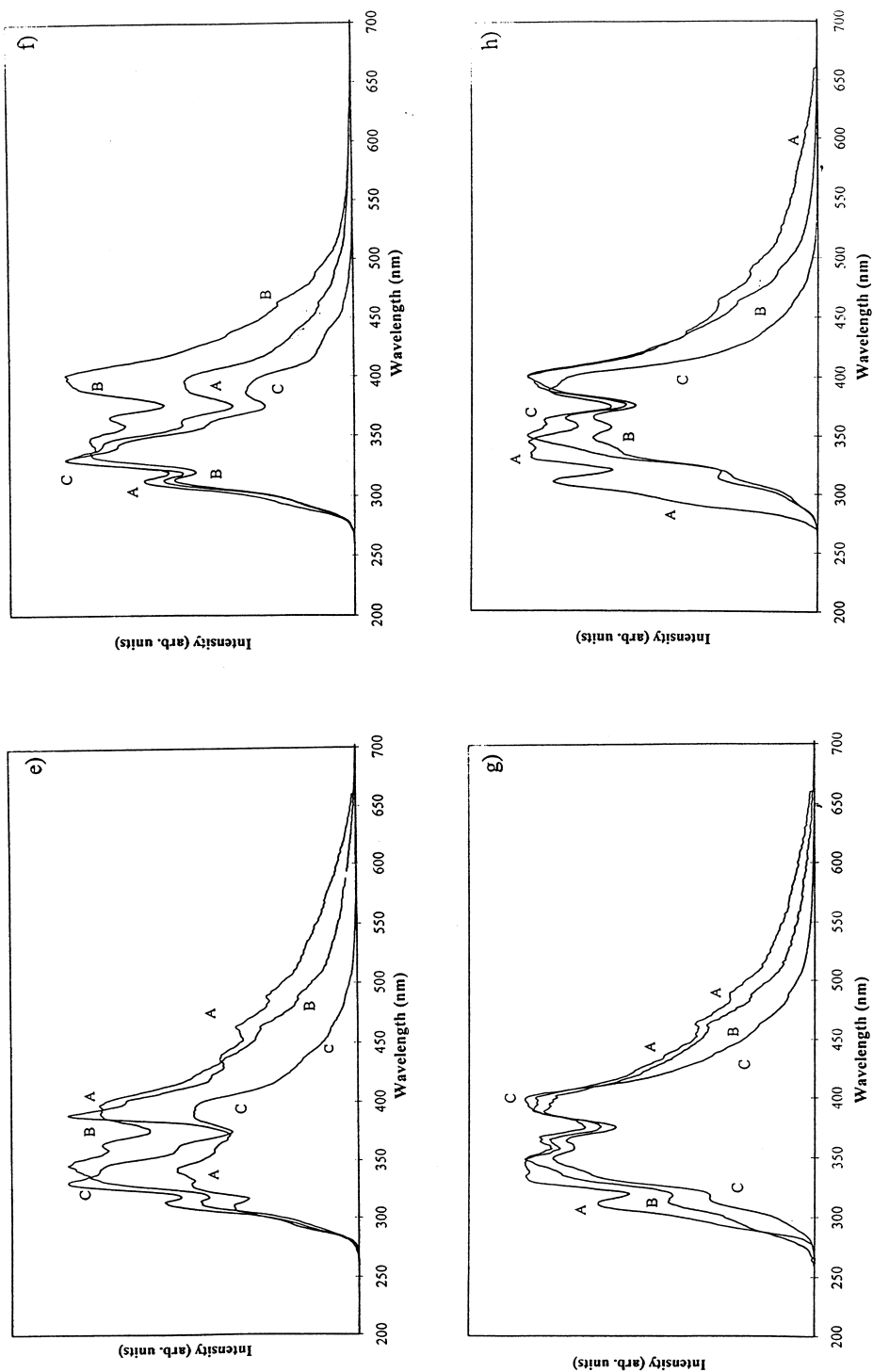
Fig. 5. (continued)

'C' fractions of the petroleum-derived vacuum residues, i.e., fractions mobile in both solvents (in either solvent sequence) showed less fluorescence intensity above 380–400 nm, compared to the less mobile fractions. The 'C' fractions showed characteristics similar to those of the original ('whole') samples, confirming earlier observations that the greater fluorescence intensities of smaller polynuclear aromatic ring systems tend to swamp signal from larger polynuclear aromatic ring systems. However, a number of significant differences may be observed between patterns in the spectra of the vacuum residue fractions and those of the coal-derived samples.

The spectra of the vacuum residue-derived samples (Fig. 5e–h) showed two prominent peaks, the first between 340 and 360 nm and the second between 400 and 420 nm. With increasing fraction mobility, the peak at the shorter wavelength (340–360 nm) could be seen to increase in intensity compared to the peak at 400–420 nm. Fig. 5e–h clearly show, therefore, that changes in the spectra associated with increasing mobility of the samples on the chromatographic plates were confined to the 280–520-nm range. However, lateral shifts of spectra, and particularly of major peaks, observed in the case of the coal-derived samples were almost totally absent. No overall trend towards fluorescence at longer wavelengths could be observed with decreasing mobility as observed with coal-derived materials (also cf. Refs. [5,6,16,22]), whilst spectra of separated fractions from coal-derived samples showed no common peaks.

In terms of evaluating the quality of separation achieved by PC, these findings suggest that the separation of the petroleum-derived vacuum residues led simply to the relative increase–decrease in the concentration of materials with distinct structural features as defined by aromatic cluster size shown by UV-F, observable within the same relatively narrow wavelength range. By contrast, a nearly complete separation of aromatic cluster size (by UV-F) was achieved in the case of the coal-derived samples.

Another major difference between the coal- and petroleum-derived fractions was observed in the relative intensities of the spectra: in addition to shifting to longer wavelengths, the spectra of less mobile fractions of the coal-derived samples gave relatively less intense signal—suggesting diminishing quantum yields for the less mobile fractions. The relatively immobile petroleum fractions did show less fluorescence intensity at the longer wavelengths (400–640 nm) compared with the more mobile material, but the trend was much less prominent than for the coal-derived materials.

Above 400 nm, fractions separated from Sample 2 (Fig. 5g and h) showed diminishing intensities with increasing mobility during PC, for both solvent sequences, whilst the pyridine–acetonitrile separation of Sample 1 did not conform to this trend. The relative positions of the spectra of the vacuum residue-derived fractions will be discussed below in greater detail.

3.5. SEC of the PC fractions

Fig. 6a and b presents SEC chromatograms of PC fractions of the coal liquefaction extract, separated by using the two solvent sequences, respectively. Both sets of fractions showed diminishing proportions of signal under the 'excluded' peak (8–13 min) with increasing mobility of the fraction suggesting diminishing MM distributions and possibly diminishing polarity—with increasing PC mobility. In both cases, the position of the retained peak (15–25 min) similarly shifted to longer elution times, with increasing mobility of the fraction. SEC chromatograms of the pitch fractions (Fig. 6c,d) showed analogous trends (also cf. Refs. [6,16]). Taken together, these results suggest that MM distributions of the PC fractions decrease with increasing mobility. This behaviour of the coal-derived samples (expected from previous experiments) differs markedly from that of the petroleum-derived vacuum residue fractions, discussed below.

Fig. 6e–h presents analogous SEC chromatograms of the vacuum residue fractions separated by and recovered from PC. In terms of elution time, the separations between the excluded and retained peaks was greater in the coal-derived samples compared to those for the petroleum-derived vacuum residue fractions, suggesting that the materials in coal-derived samples are of smaller size than those in the petroleum residues.

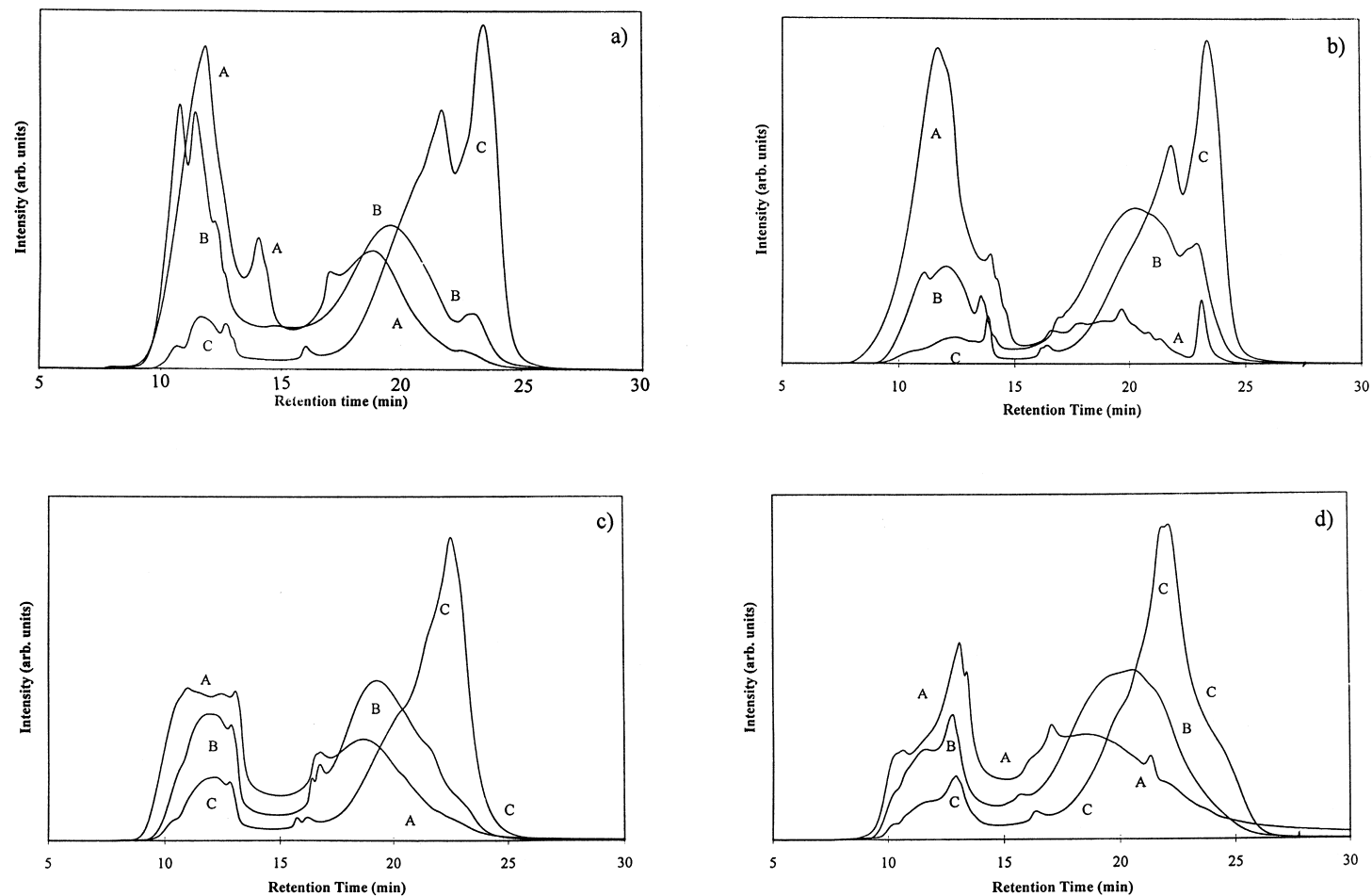As in the case of the coal-derived sample fractions, all the chromatograms of petroleum-derived

Fig. 6. Size-exclusion chromatograms of fractions from PC in NMP solvent at 350 nm UV absorbance detection: (a) Point of Ayr fractions in THF and toluene; (b) Point of Ayr fractions in pyridine and acetonitrile; (c) pitch fractions in THF and toluene; (d) pitch fractions in pyridine and acetonitrile; (e) Sample 1 in THF and toluene; (f) Sample 1 in pyridine and acetonitrile; (g) Sample 2 in THF and toluene; (h) Sample 2 in pyridine and acetonitrile. Curves are A, immobile; B, mobile in first solvent; C, mobile in both solvents.
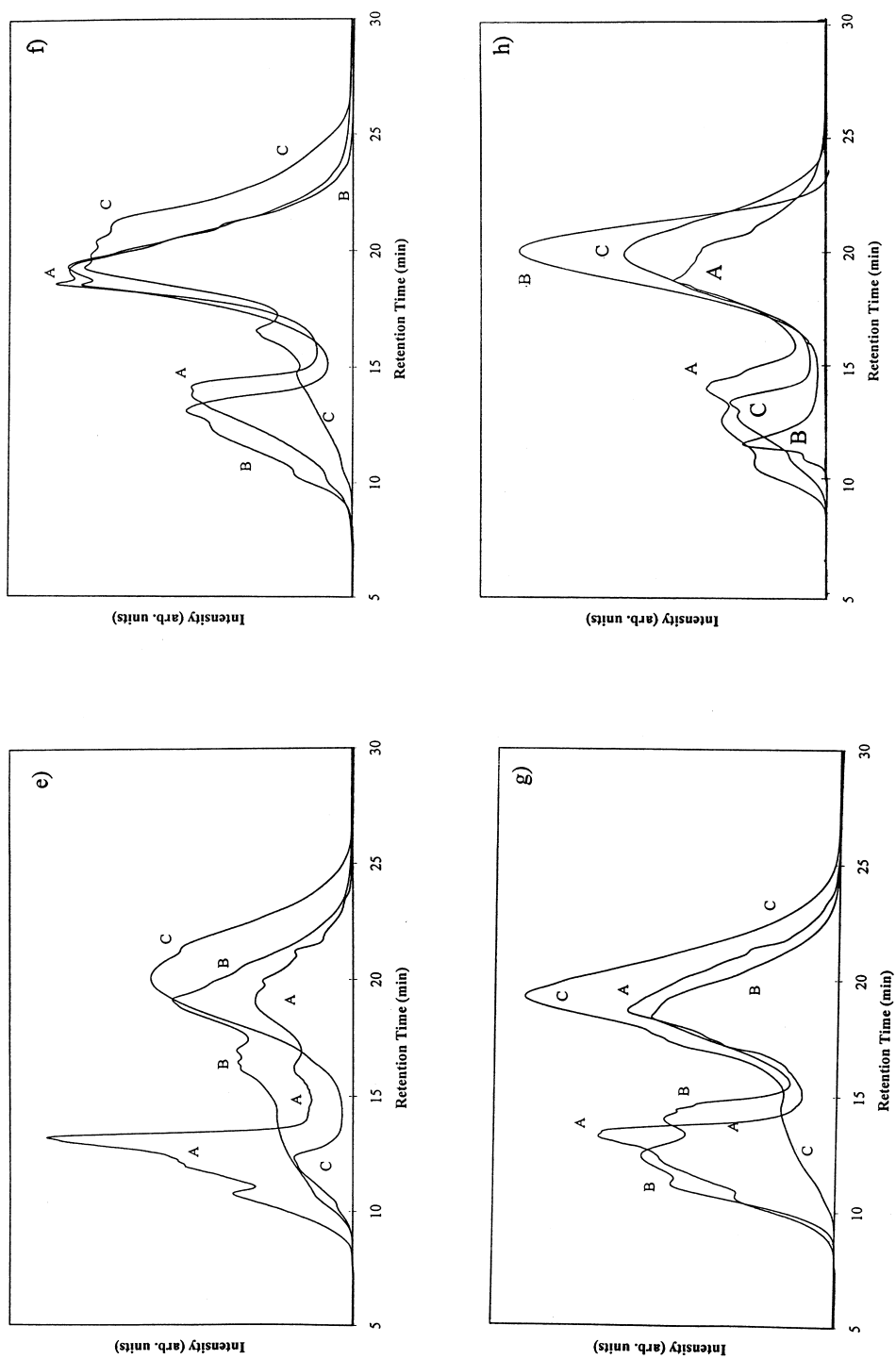
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Fig. 6. *(continued)*

vacuum residue samples first showed signal at the exclusion limit of the column (between 8 and 9 min elution time). Taken together, the peak corresponding to material excluded from column porosity (between 10 and 15 min: suggesting the presence of very large MM material) and the presence of material within the operating range of the column (peak at about 20 min), indicate a very wide range of molecular sizes.

Where two peaks are observed in size exclusion, the valley between does not reach baseline, implying a continuum of molecular shapes from small to large, with the porosity of the column limiting the resolution of the large, excluded material.

The relative proportions of the excluded and retained material were observed to change with the polarity of solvents used in PC. Less 'excluded' material was observed in both 'C' fractions (mobile in both solvents) compared to the corresponding 'B' fractions (mobile only in THF or pyridine). As in the case of the UV-F spectra, however, the apparent MM distributions of fractions 'A' and 'B' did not fit into a pattern similar to those of the fractions from coal-derived samples. The 'A' fractions (immobile in pyridine) of both Samples 1 and 2 showed smaller 'excluded' peaks than the corresponding 'B' fractions. In the case of UV-F, the discrepancy (with respect to the ordering expected, based on the coal-derived samples) had only appeared for fractions 'A' and 'B' of Sample 1 (mobile–immobile in pyridine).

UV-F spectra were taken to suggest that the range of aromatic systems in the vacuum residue fractions were similar. Assuming mobility on the PC plates to be a composite function of MM and polarity, the SEC chromatograms suggest, however, that the most polar components of the petroleum-derived vacuum residues (immobile in pyridine) may not necessarily be components with the largest MM distributions or largest polynuclear aromatic ring systems. Clearly these immobile fractions are well beyond the range of analysis by GC; at present, alternative structural characterisation methods are being investigated.

It may be useful to recall that the materials detected by both SEC and UV-F must all contain aromatic ring systems. As discussed above, waxes (aliphatic) in the residues can not be detected by the methods used here and would require isolation from the aromatics for their unequivocal observation.

However, structures such as porphyrins would be expected to absorb UV light.

In summary, the SEC profiles of the fractions show that for the coal-derived materials, decreasing mobility in PC correlated with increasing molecular size; for the vacuum residue fractions, however, the SEC profiles did not fit the same trend.

3.6. MALDI-mass spectra of the vacuum residues

We have already reported laser ablation mass spectra of the 'whole' coal tar pitch, showing a peak of intensity between 1000 and 3000 u. Laser ablation mass spectra of the pyridine insoluble fraction of the pitch were found to match MALDI-spectra, showing peaks of intensities over similar ranges of MM. The spectra were stable and relatively insensitive to the matrix preparation method [3,4]. It is thought that generating signal during laser ablation depends, at least to some extent, on the presence of relatively small molecules in the sample which would absorb the laser radiation and mimic the role of the matrix.

The MALDI-spectra generated for the 'whole' petroleum-derived vacuum residues using laser ablation (i.e., in the absence of matrix) were not intense and did not extend to high masses (spectra not shown). In the case of the two vacuum residue samples, the vacuum distillation stage appears to have removed most of the small MM material which might have played this role. The absence of material in these samples eluting at long elution times (22–25 min) in SEC would appear to support this view.

Fig. 7 presents MALDI-mass spectra of Sample 1 with 'α-cyano' and 'HABA' as matrix, and Sample 2 with 'HABA', showing peaks of intensity between 1000 and 2000 u tailing off towards 20 000 u; for comparison, a spectrum of pitch without matrix is included in Fig. 7d. By contrast, stable, wide-mass range spectra could not be generated with either sample when 9-A, DHB or sinapinic acid were used as matrix nor with Sample 2 using α-cyano as matrix. Peak intensities observed for these attempts did not exceed 500–600 u, with signal tailing off between 2000 and 3000 u.

SEC data presented above suggest that the petroleum-derived samples contain material of considerably higher MM than those observed for the coal-derived samples. Comparing the MALDI-spectra of
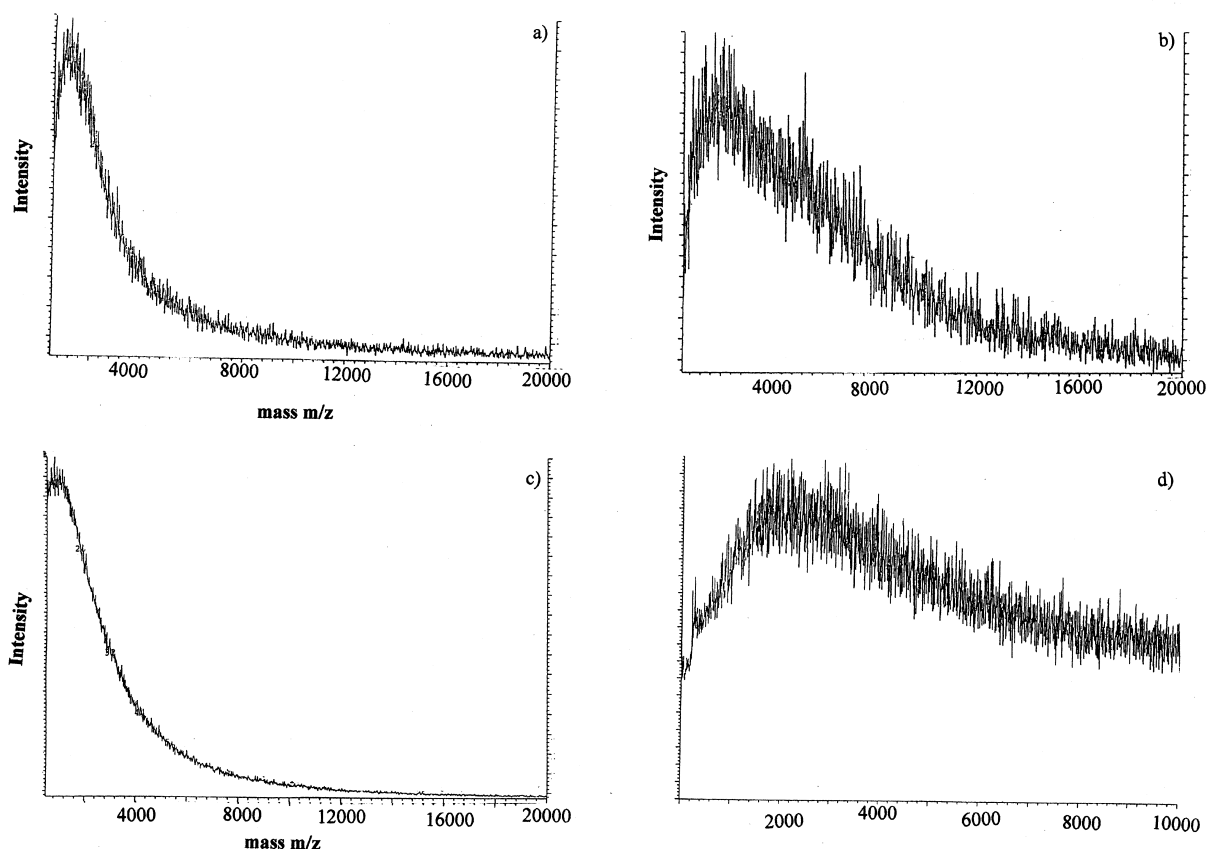
Fig. 7. MALDI-mass spectra of petroleum residues as: (a) Sample 1 with α-cyano matrix; (b) Sample 1 with HABA matrix; (c) Sample 2 with HABA matrix; (d) Pitch without matrix.

Sample 1 obtained with the two different matrices clearly shows, however, the sensitivity of the results to the type of matrix used. Clearly, it is, as yet, difficult to obtain quantitatively reliable spectra of complex mixtures by MALDI-MS. No method is available to *predict* either the effectiveness of particular matrix materials or the relative proportions of sample and matrix required to obtain an adequate spectrum.

The implication of this work is that different matrices are required for petroleum residues than those found to be successful for coal-derived liquids, probably reflecting the different chemical types and structures of these complex liquid mixtures. However, alternative target-sample preparation methods and different matrices will allow generation of better quality spectra from petroleum-derived samples. Due to the difficulties encountered in obtaining adequate

spectra from petroleum-derived samples—presumably due to their predominantly aliphatic structures—characterisation of the fractions from the planar chromatographic separations by MALDI-MS were not attempted in this study.

The polydispersity (ratio of weight average to number average MM) for such complex samples is likely to be much greater than 1.1. This is normally considered as the upper limit for the reliable characterisation of a mixture by MALDI-MS [40]. Accordingly, the mass spectra shown in this paper are certain to greatly underestimate the proportion of high mass material in the samples.

4. Conclusions

Several coal- and petroleum-derived complex liq-

uid mixtures have been separated by PC and characterised by UV-F and SEC.

In the UV-F spectra of fractions from coal-derived samples, increasing sample mobility on the chromatographic plates was accompanied by increases in fluorescence intensities; the spectra (and spectral peaks) shifted to shorter wavelengths. However, a number of significant differences were observed in the examination of the petroleum-derived vacuum residue fractions. Lateral shifts of the spectra, and particularly of the major peaks, observed in the case of the coal-derived samples were almost totally absent.

The SEC of the coal-derived fractions showed increasing MM distributions with decreasing mobility on the chromatographic plates.

In SEC, as in UV-F, the apparent MM distributions of the less mobile fractions of the vacuum residues did not fit the trend established by the coal-derived samples. The fractions immobile in pyridine showed smaller peaks of large MM material than the corresponding fractions mobile in pyridine.

Assuming mobility on the PC plates to be a composite function of MM and polarity, the SEC chromatograms suggest that the most polar components of the petroleum-derived vacuum residues (immobile in pyridine) may not necessarily be components with the largest MM distributions or largest polynuclear aromatic ring systems.

These findings suggest that the separation of the petroleum-derived vacuum residues led simply to the relative increase–decrease in the concentration of materials with distinct structural features as defined by aromatic cluster size, shown by UV-F. By contrast, a much more complete separation of aromatic cluster sizes (in UV-F) was achieved in the case of the coal-derived samples.

In agreement with results from SEC, MALDI-mass spectra of the original petroleum- and coal-derived ('whole') samples, showed broadly similar ranges of MM distributions. However, not all matrices observed to work well with coal-derived samples helped in obtaining adequate spectra of the vacuum residues. Considerable work appears necessary to formulate appropriate matrices and procedures for the MALDI-MS characterisation of petroleum residues.

The work has shown PC to be a robust, low cost, simple separation tool for complex liquid mixtures. Fractions derived by this method have been shown as suitable for further examination by other, more focused analytical methods.

Acknowledgements

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