

# Thin-layer chromatography of pitch and a petroleum vacuum residue Relation between mobility and molecular size shown by size-exclusion chromatography

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## Abstract

A coal tar pitch and a petroleum vacuum residue have been separated by TLC using pyridine, acetonitrile, toluene and pentane to develop the chromatograms. The bands of material detected were recovered in 1-methyl-2-pyrrolidinone (NMP) solvent and examined by size-exclusion chromatography (SEC) in NMP eluent. The relation between elution time in SEC and mobility on the TLC plate indicated that molecular size increased steadily with increasing immobility on the plate. This relation was reinforced by UV fluorescence spectroscopy in that the fluorescence moved to longer wavelengths with increasing immobility. The molecular size of the material excluded from the porosity of the SEC column remains undefined; some excluded material was found in all of the fractions from both samples. The valley of zero intensity separating the retained material from the excluded material may suggest a change of structure from near-planar in the retained region to three-dimensional in the excluded region.

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## 1. Introduction

Previous work [1] has explored the relation between TLC mobility and elution time in SEC, but using tetrahydrofuran (THF) as eluent. In that work, the molecular mass of material in bands recovered from TLC increased when measured by solids probe mass spectrometry; in SEC using THF as eluent, however, the elution of the different bands covered virtually the same range of elution times, with the main difference being that the lift-off of signal from baseline at the earliest elution time varied slightly. More recent work with the same coal tar pitch [2] has shown that the range of molecular mass of the sample is greatly in excess of that accessible by probe mass spectrometry (about  $m/z$  600), with material detected by matrix-assisted laser desorption ionization (MALDI) MS

up to 100 000 u [3] and indications of masses up to the order of millions of mass units by static light scattering [4] and by SEC in 1-methyl-2-pyrrolidinone (NMP) solution calibrated using polystyrenes [5] and other polymers [6].

Where fractionation of the pitch, vacuum residues and other coal-derived samples has been achieved by thin-layer chromatography or by a column chromatography method using solvent such as acetonitrile, pyridine and NMP or toluene and tetrahydrofuran, the SEC profiles using NMP as eluent have shown shifts to earlier elution (larger molecules) in the solvent solubility order toluene, acetonitrile, THF, pyridine, NMP or immobile in pyridine on the TLC plate. The evidence from UV fluorescence indicated that the fluorescence intensity decreased in the same order of solvent solubility, showing that the larger molecules did not emit the absorbed light as fluorescence, but distributed the energy into other pathways.

The present work has repeated the experiment in TLC, using the coal tar pitch and a petroleum distillate residue,

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with the solvent sequence pentane, toluene, acetonitrile and pyridine to develop the plates, but using NMP as the eluent for SEC. These two very different samples were chosen because (a) previous work [7,8] has shown that the mass range of the petroleum residue was up to about 3000 U and (b) the aromatic ring structures of the pitch were of much greater diversity than those of the petroleum residue [9]. The different bands of material migrating with the solvents were collected and extracted into NMP and examined by SEC using NMP as the eluent. The results show that the pentane-mobile fractions of both samples contained the smallest molecules and that increasing molecular mass (as measured by SEC using NMP as eluent), correlated broadly with decreasing mobility on the TLC plate, for both samples. This was not the case using SEC with THF as eluent [1].

## 2. Experimental

### 2.1. Samples

The coal tar pitch has been examined previously [1,3,5,6,10,11]. The sample is from the volatile product of high temperature coking of coal, followed by destructive distillation of the tar to yield pitch as the residue. The elemental composition of the pitch (% w/w) was C 91.4, H 4.1, N 1.3, S 0.76 and O 2.4 (by difference). It was approximately 85% soluble in pyridine and appeared to be entirely soluble in NMP.

The petroleum residue was from the Petrox refinery near Concepcion, Chile; it has been described previously [7,9]. The residue came from the bottom of an atmospheric pressure distillation column after steam stripping of volatiles remaining from the distillation. The elemental composition (% w/w) was C 86.8, H 12.9, N 0.42.

### 2.2. TLC

Whatman TLC plates were used of size 20 cm × 20 cm with a 1000 μm thickness of silica. Before use, plates were washed using the most polar solvent, pyridine, to within a short distance of the top of the plate. Sample was applied as a band at the origin as a slurry in pyridine, approximately 1 cm from the lower edge of the plate. Development was achieved using pyridine, acetonitrile, toluene and pentane, with each development extending about 40 mm beyond the origin or the previous solvent front. Before each new solvent development, the plates were dried in air and the tank was allowed to stand for at least half an hour to equilibrate the vapour phase with respect to the solvent before insertion of the plate. Because the work was carried out in hot weather, the pentane solvent front was unable to progress up the plate to the desired level because of excessive evaporation; the problem was overcome by placing the tank into a freezer at −18 °C before and during the development.  $R_f$  values were measured for the solvent fronts and bands and are shown in Table 1; the origin ( $R_f = 0$ ) was the sample deposition zone while the pentane solvent front was taken as  $R_f = 1$ .

After development and drying, the plates were examined under daylight and UV light to establish the position of bands of material for further examination. The bands were recovered by scraping off the silica into a bottle followed by extraction with ultrasonic agitation in NMP. Silica was removed by filtration at 0.6 μm and the solution examined further by SEC and UV fluorescence.

### 2.3. Size-exclusion chromatography

Procedures for size-exclusion chromatography (SEC) have been described previously [12–17]. SEC using NMP

Table 1  
Elution distances and  $R_f$  values in TLC

Coal tar pitch			Petrox distillation residue		
Solvent or band (colour)	mm	$R_f$	Solvent or band (colour)	mm	$R_f$
Pyridine	46	0.31	Pyridine	44	0.28
Acetonitrile	90	0.61	Acetonitrile	84	0.53
Toluene	128	0.87	Toluene	120	0.76
Pentane	147	1.00	Pentane	158	1.00
Band 1 (white)	147–135	1.00–0.92	Band 1 (white)	155–149	0.98–0.94
Band 2 (brown)	134–130	0.91–0.88	Band 2 (light blue)	140–130	0.89–0.82
Band 3 (dark brown)	130–128	0.88–0.87	Band 3 (light yellow)	125–120	0.79–0.76
Band 4 (light brown)	126–124	0.86–0.84	Band 4 (yellow)	120–100	0.76–0.63
Band 5 (light brown)	115–110	0.78–0.75	Band 5 (light yellow)	85–81	0.54–0.51
Band 6 (light blue)	100–98	0.68–0.67	Band 6 (dark yellow)	44–36	0.28–0.23
Band 7 (brown)	90–84	0.61–0.57	Band 7 (orange)	36–23	0.23–0.15
Band 8 (light blue)	84–80	0.57–0.54	Band 8 (brown)	0 ± 1	0 ± 0.006
Band 9 (light blue)	79–76	0.54–0.52			
Band 10 (pink)	72–66	0.49–0.45			
Band 11 (dark brown)	46–44	0.31–0.30			
Band 12 (black)	0 ± 1	0 ± 0.007			

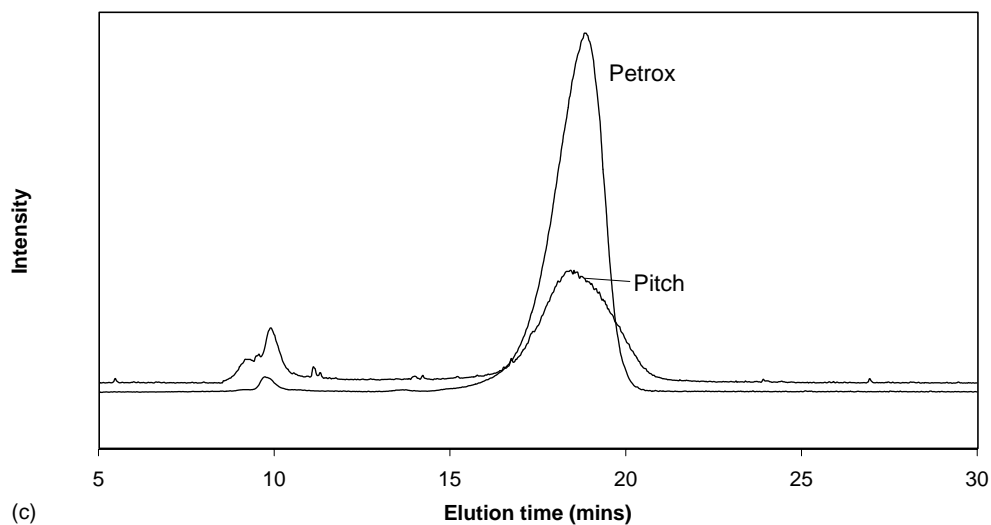
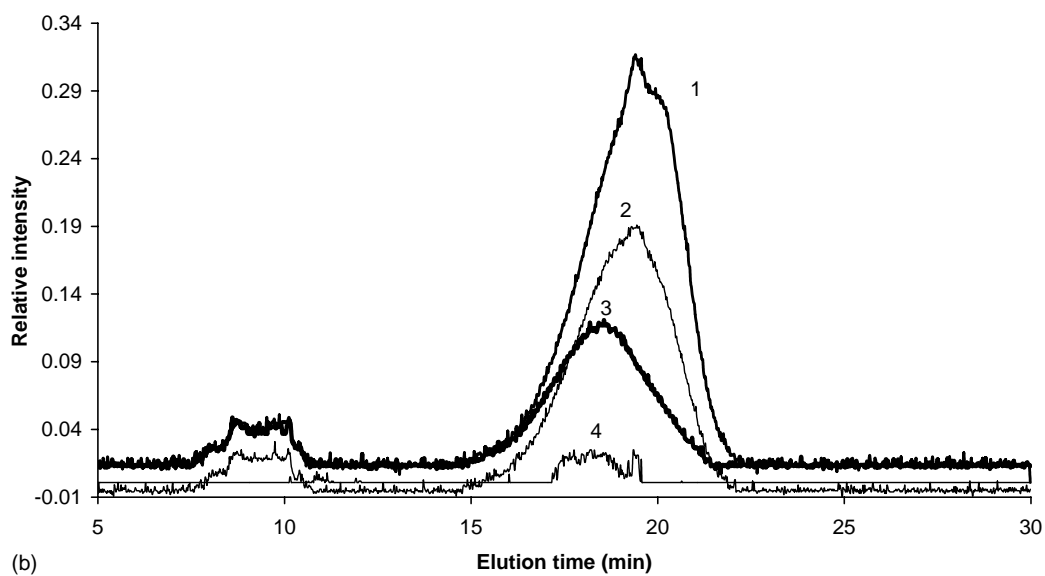
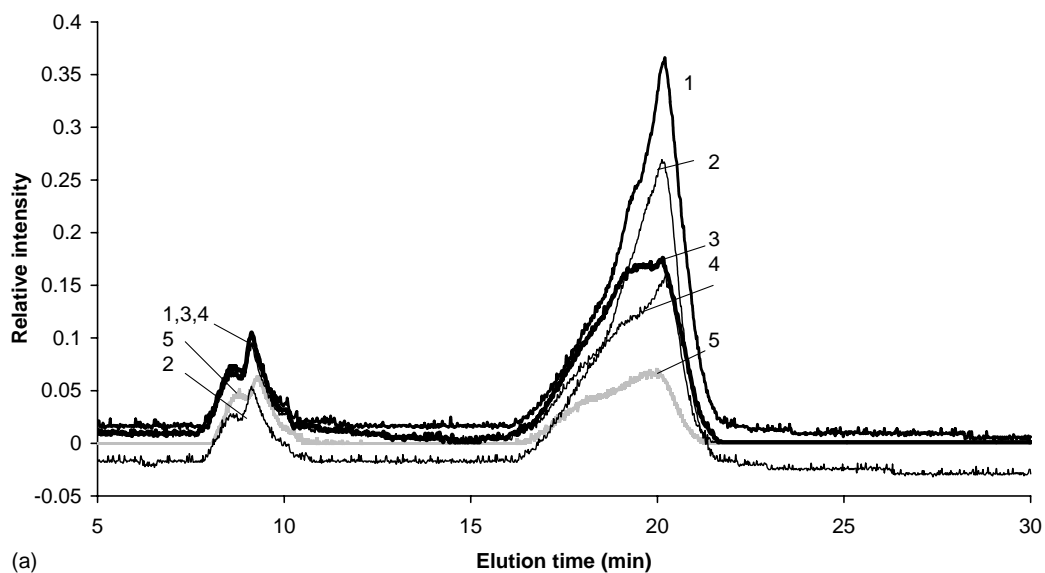


Fig. 1. The unfractionated samples: SEC profiles of (a) pitch by UV absorbance at five wavelengths, (b) Petrox distillation residue by UV absorbance, (c) both samples by ELSD, (d) synchronous UV fluorescence spectra of both samples.

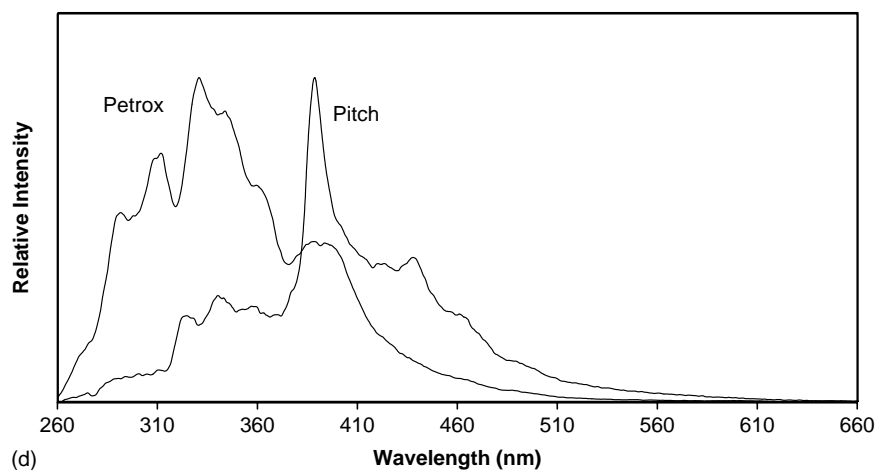


Fig. 1. (Continued).

as solvent, was carried out using a 5  $\mu\text{m}$  particle size polystyrene/polydivinylbenzene column (Mixed-D; Polymer Labs., Shropshire, UK). The porosity range of this column is such that polystyrene molecular mass standards from 100 to 300 000 U are retained by the column and elute with a linear relation between  $\log_{10}$  molecular mass and elution volume or time. Larger molecular mass polystyrene standards up to  $2 \times 10^6$  U elute at shorter times with a different relation between molecular mass and time and are classed as excluded from the column porosity; a calibration graph has been shown elsewhere [5,18,19]. The samples and the fractions have been examined by SEC with UV absorbance detection at 280, 300, 350, 370 and 450 nm at a temperature of 80 °C and a flow rate of 0.5 ml min<sup>-1</sup>. The UV detectors were an Applied Biosciences diode array detector (supplied by Perkin-Elmer, Beaconsfield, UK) with a Perkin-Elmer LC290 variable-wavelength detector in series linked to a computer-based data acquisition system. An evaporative light scattering detection (ELSD) system from Polymer Labs. was also used. Evidence presented elsewhere [5,6,17,18] has shown that the polystyrene calibration of the column is a good indicator of molecular mass ranges of coal derived materials, at least for the material retained by the column.

#### 2.4. UV fluorescence spectroscopy

The procedure has been described in detail elsewhere [20]. The Perkin-Elmer LS50 luminescence spectrometer was set to scan at 240 nm min<sup>-1</sup> with a slit width of 5 nm; synchronous spectra were acquired at a constant wavelength difference of 20 nm. A quartz cell with 1 cm path length was used. 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; only the latter have been shown. The spectra have been presented in peak-normalised mode. Solutions were generally diluted with NMP to avoid

self-absorption effects: dilution was increased until the fluorescence signal intensity began to decrease. However, the fluorescence of the larger molecules was relatively low because of the loss of energy to other energetic pathways and for the less mobile fractions, it was necessary to increase the concentration to raise the weak fluorescence intensity above the baseline noise.

### 3. Results and discussion

The SEC profiles of the unfractionated pitch and petroleum residue are shown in Fig. 1a and b, respectively, by UV absorbance, while Fig. 1c compares their chromatograms by ELSD. The pitch sample elutes slightly later than the petroleum residue sample and both samples show some excluded material between 7 and 11 min. The petroleum residue shows little UV absorbance after 350 nm while the pitch shows absorbance at all wavelengths; this reflects the variety of aromatic chromophores in the two samples. The ELSD profiles confirm the slightly earlier elution of the petroleum residue. Fig. 1d shows the synchronous UV fluorescence of the two samples, confirming the much greater range of aromatic chromophores in the pitch than in the residue.

Following fractionation on the TLC plate, the different bands visible under UV light (254 and 366 nm) were marked, the migration distances measured for solvent fronts and fluorescent bands and the  $R_f$  values calculated. Table 1 list these measurements and shows that the colour of bands of both samples became darker with decreasing mobility.

#### 3.1. Pitch fractions

Fig. 2 shows SEC profiles of the pitch fractions using UV absorbance detection. The main features of the chromatograms are (1) that the elution time of the peak eluting between 15 and 23 min shifts to earlier times with increas-

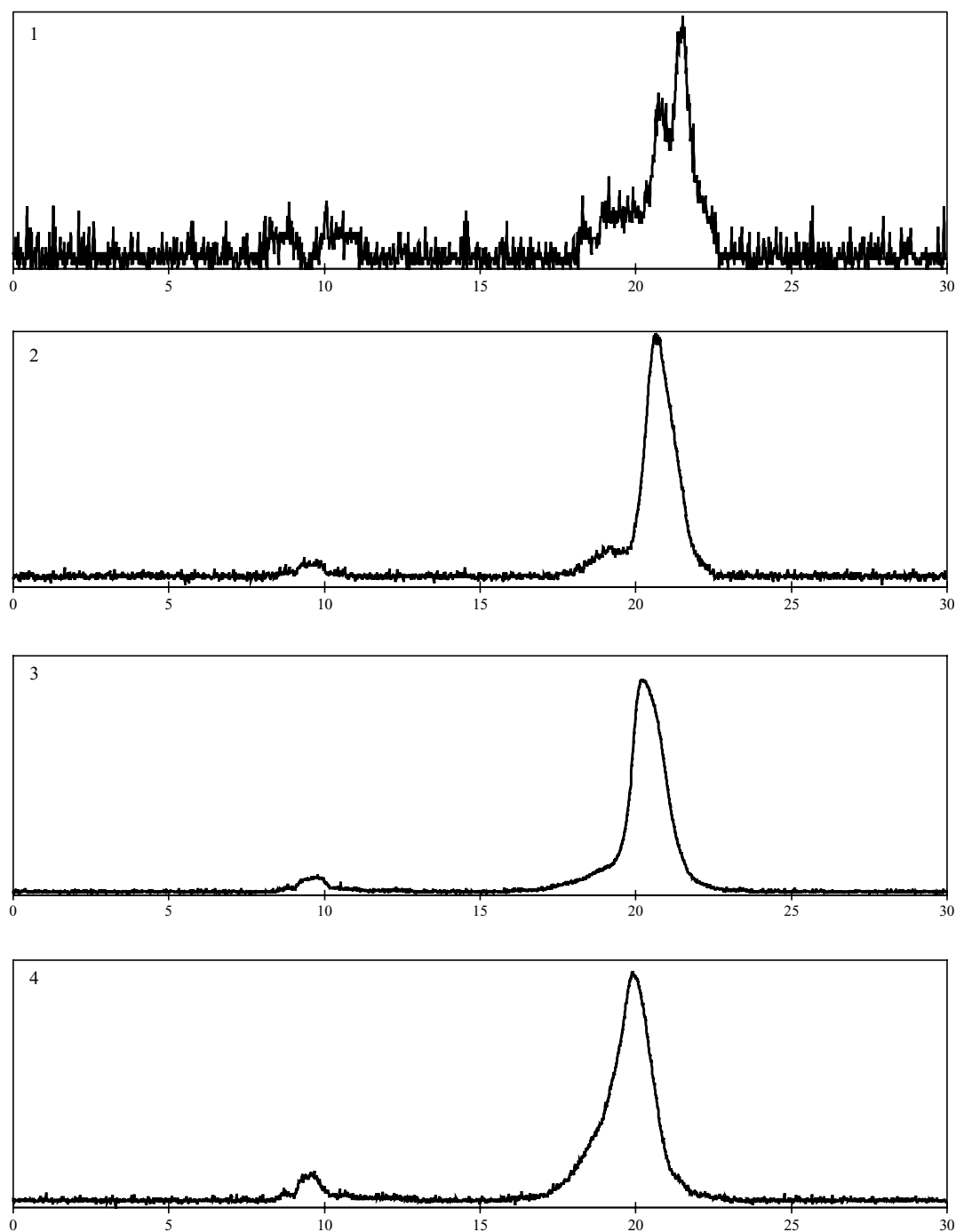


Fig. 2. SEC profiles of the 12 pitch fractions by UV absorbance detection; fraction numbers in upper left-hand corner; intensity vs. elution time (min).

ing fraction number or decreasing  $R_f$  value; (2) the wavelengths of maximum absorbance change from 280 nm for fraction 1 to 450 nm for fraction 12; (3) as the fraction number increases, the relative proportion of the excluded peak eluting between about 8 and 11 min increases. The profiles for some of the fractions were relatively weak because the sample quantity was small; this shows in the figure as excessive noise. The profiles with little noise indicate where the bulk of the sample was found. Fig. 3 shows the equivalent data using ELSD. This method operates by evaporat-

ing the solvent NMP and detecting the solid particles left in the resulting gas and vapour stream; low boiling molecules of volatility similar to and greater than the solvent (boiling point 202 °C) will be lost in the detector. Thus in Fig. 3, the profile for fraction 1, the smallest molecule fraction, shows a significant excluded peak and only a small retained peak. Also, the retained peak does not extend beyond 20 min elution time, whereas in Fig. 2, the retained peak was almost entirely after 20 min; this is the result of evaporation in the detector and the signal represents only a small portion of the

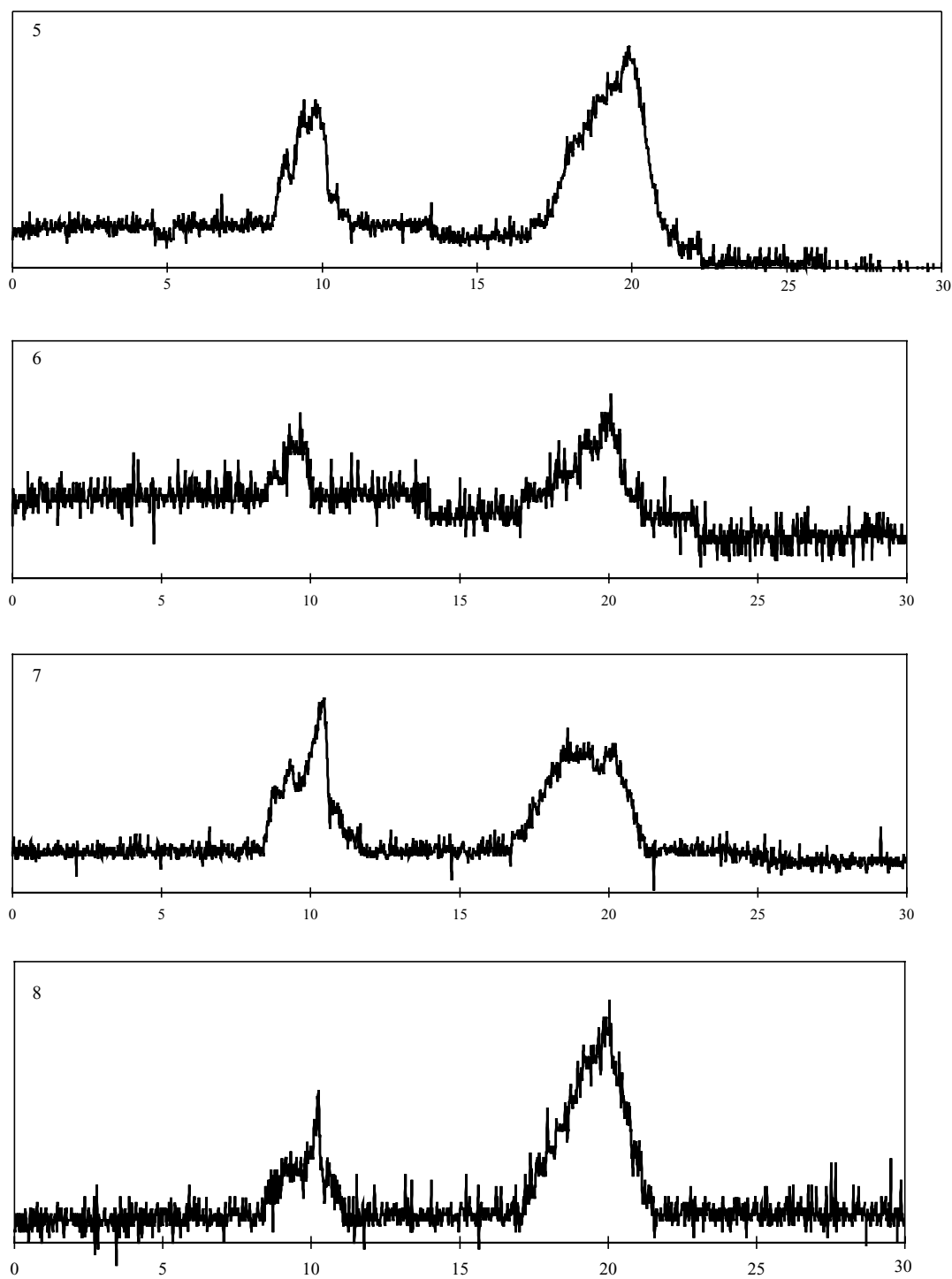


Fig. 2. (Continued)

fraction. Subsequent fractions in Fig. 3 show no signal after 20 min but the proportions of retained to excluded peaks changed in favour of the retained peaks. The first three fractions were mobile in pentane and the retained peak increased in intensity and shifted to shorter times, indicating an increase of molecular mass with decreasing mobility. For the later fractions, the retained peak becomes much less intense

relative to the excluded peak and in addition, the major intensity of the excluded peak shifts to earlier elution times, indicating larger molecular sizes for the immobile material. Fractions 4–6 were mobile in toluene and the retained peak continued to shift to shorter elution times although the intensity of fraction 6 was very low. Fractions 7–10 were mobile in acetonitrile and although the retained peak did not

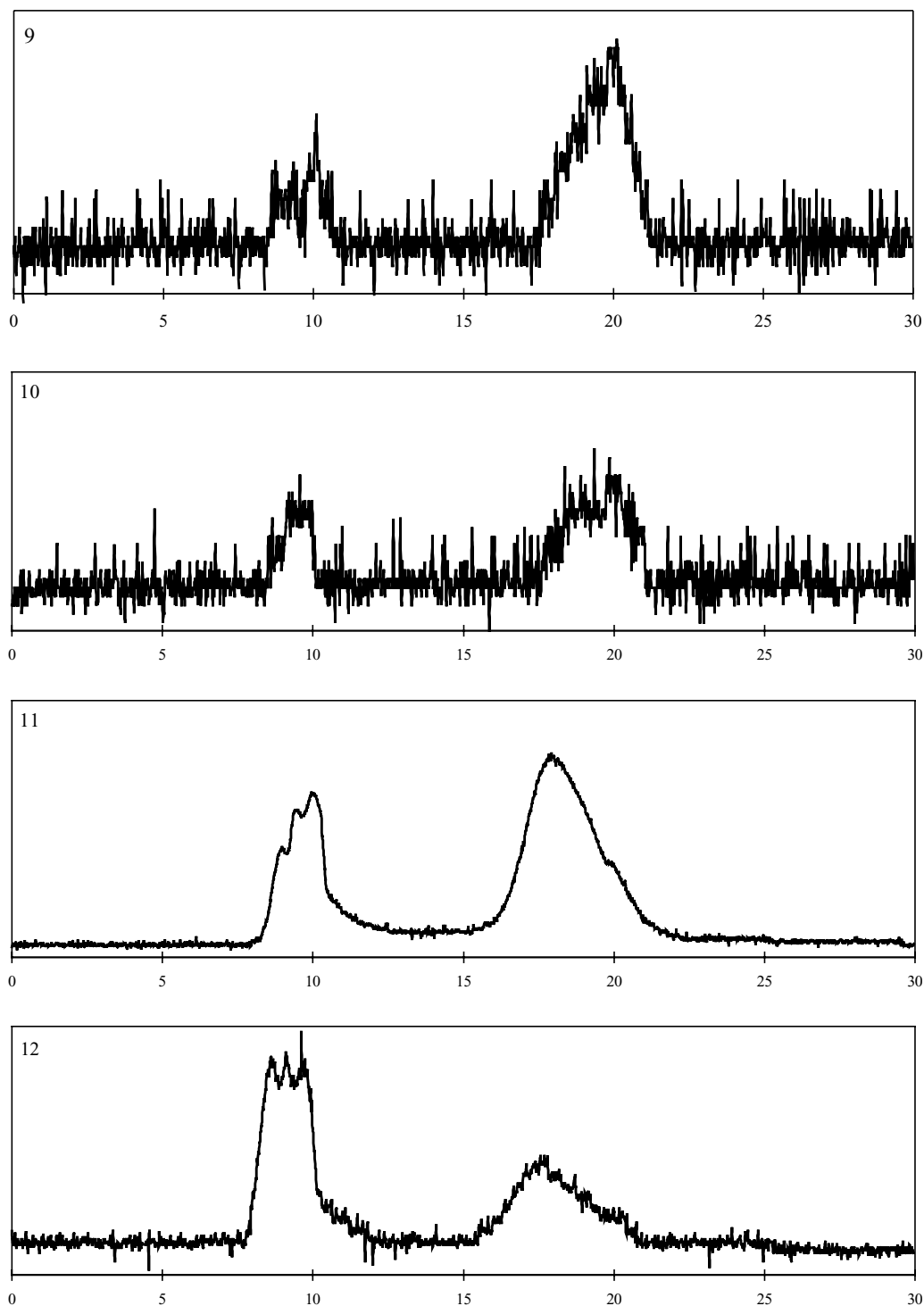


Fig. 2. (Continued).

shift to shorter times, the relative intensity of the excluded peak increased, indicating a shift to larger molecules with decreasing mobility. Fraction 11 was mobile in pyridine and the retained peak was of similar intensity to the excluded peak; it is presumed an effect of polarity has prevented the mobility of these small molecules in the less polar solvents. The immobile material of fraction 12 showed mainly ex-

cluded molecules with little signal in the retained region. The prominence of the excluded peak in all these fractions by ELSD indicates that these molecules are of relatively large mass and essentially involatile in the ELSD system compared with NMP. Their structures remain unknown.

Taken together, the SEC profiles of the pitch TLC fractions show a steady increase in molecular size in the re-

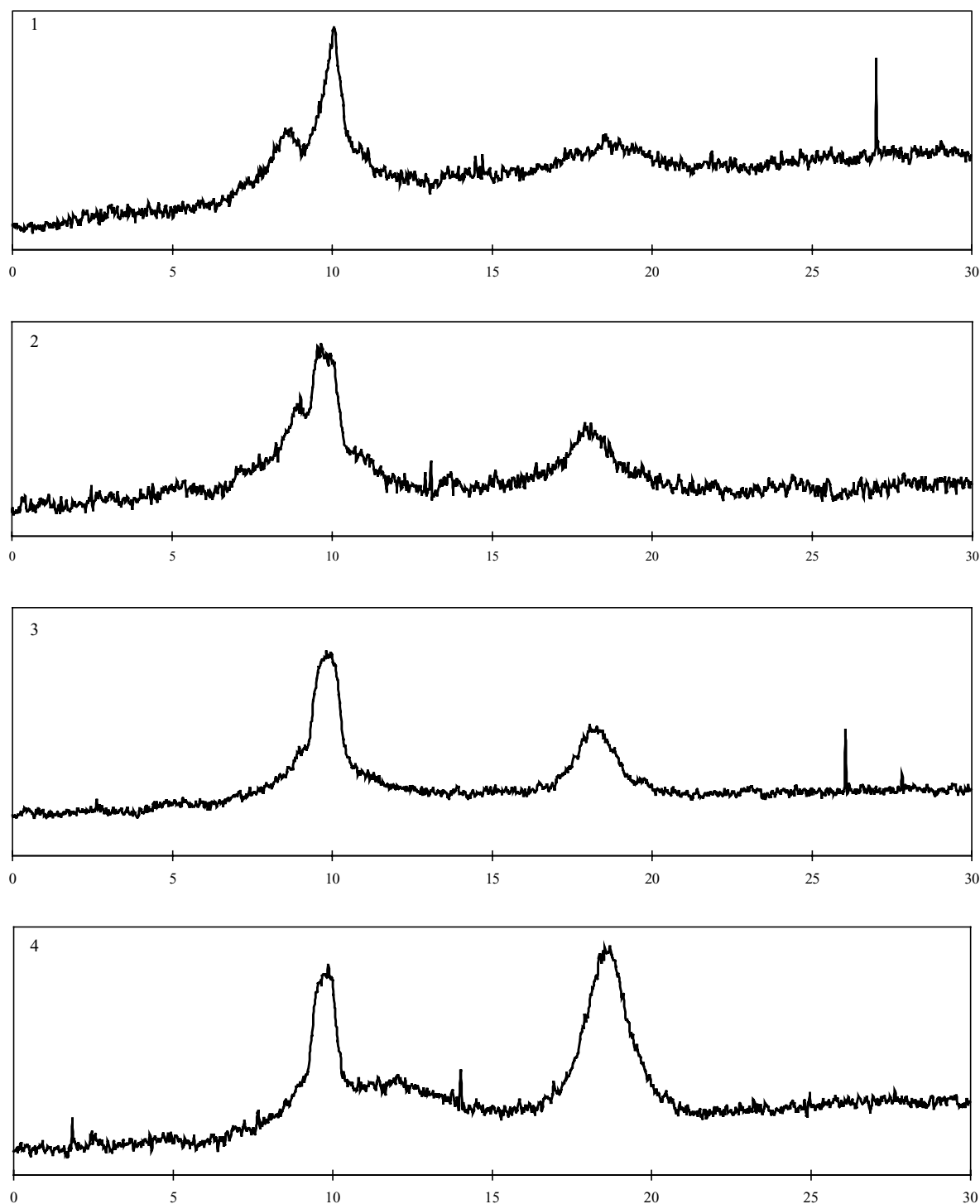


Fig. 3. SEC profiles of the 12 pitch fractions by ELSD; fraction numbers in upper left-hand corner; intensity vs. elution time (min).

tained region and an increase of the relative intensity of the excluded peak with decreasing mobility on the plate. The main effect is one of increasing molecular size with some evidence of increasing polarity of the small molecules preventing mobility in the less polar solvents.

The synchronous UV fluorescence spectra of the pitch fractions are shown in Fig. 4. The maximum intensity peak

shifts from about 300 nm for fraction 1 to about 500 nm for fraction 12, together with an increased width of the fluorescence band, indicative of increasing numbers of fluorescent chromophores, and a decrease of fluorescence intensity. This shift in the maximum intensity indicates that the aromatic chromophores in the fractions increase in size and complexity as the fraction number increases.



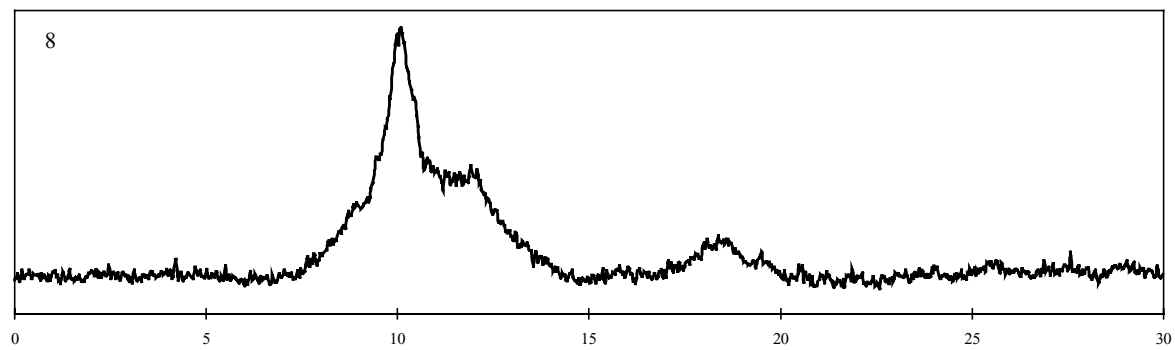
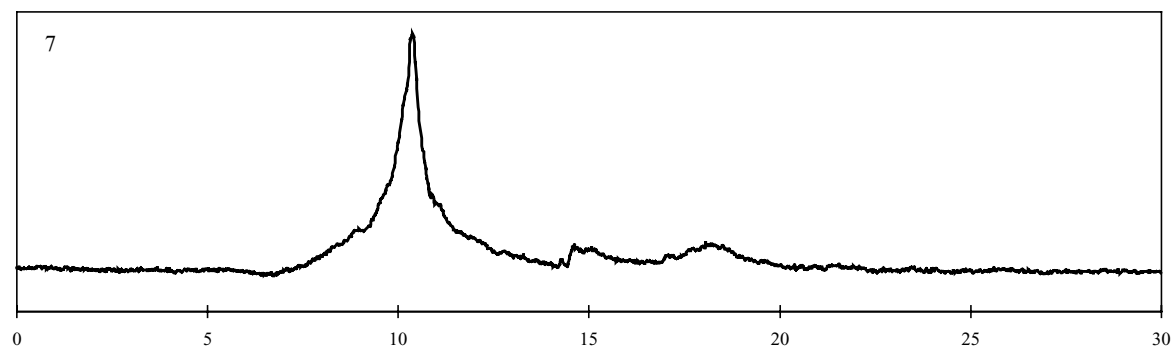
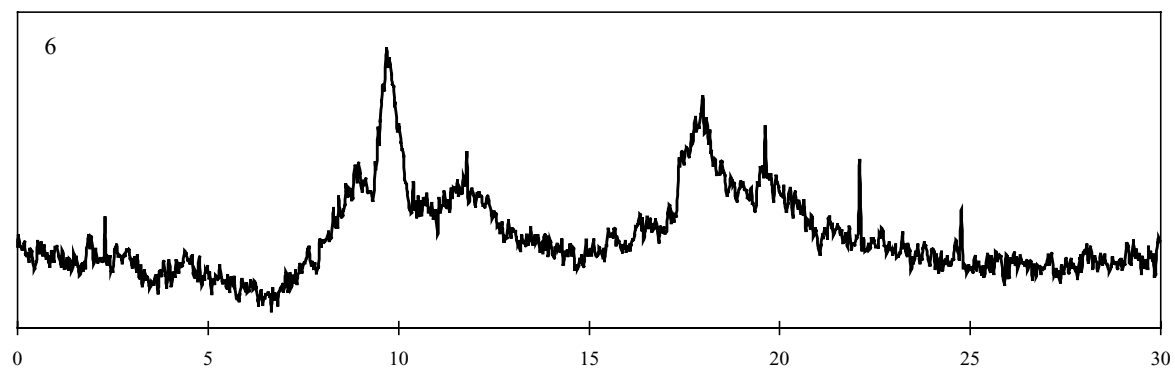
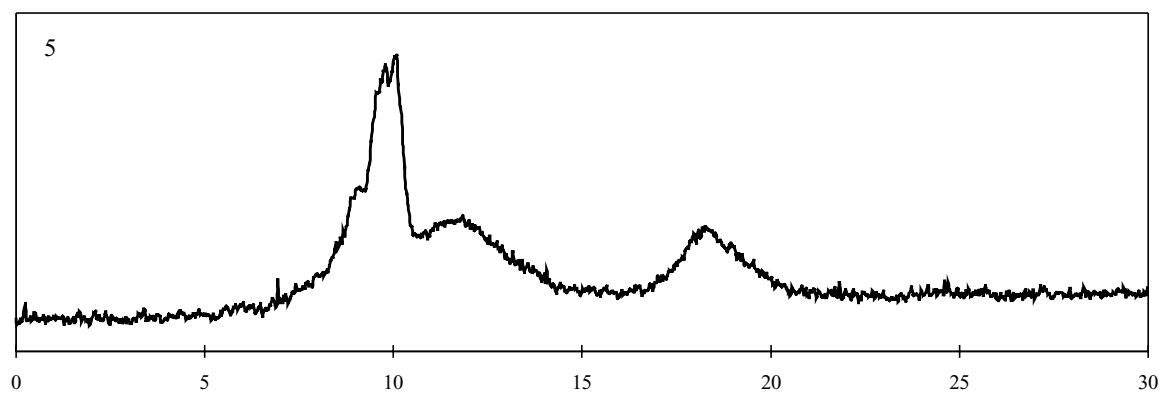


Fig. 3. (Continued)

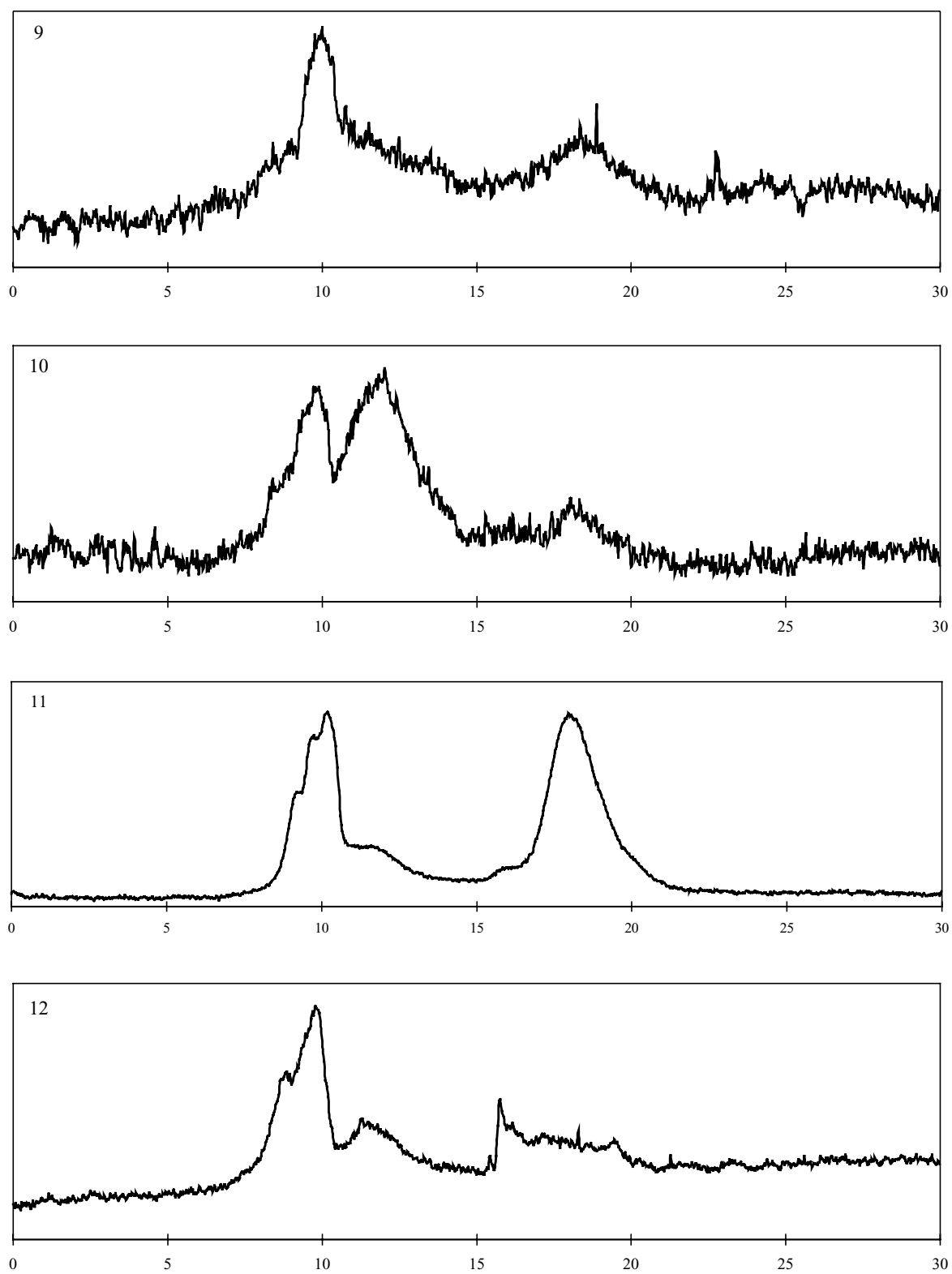


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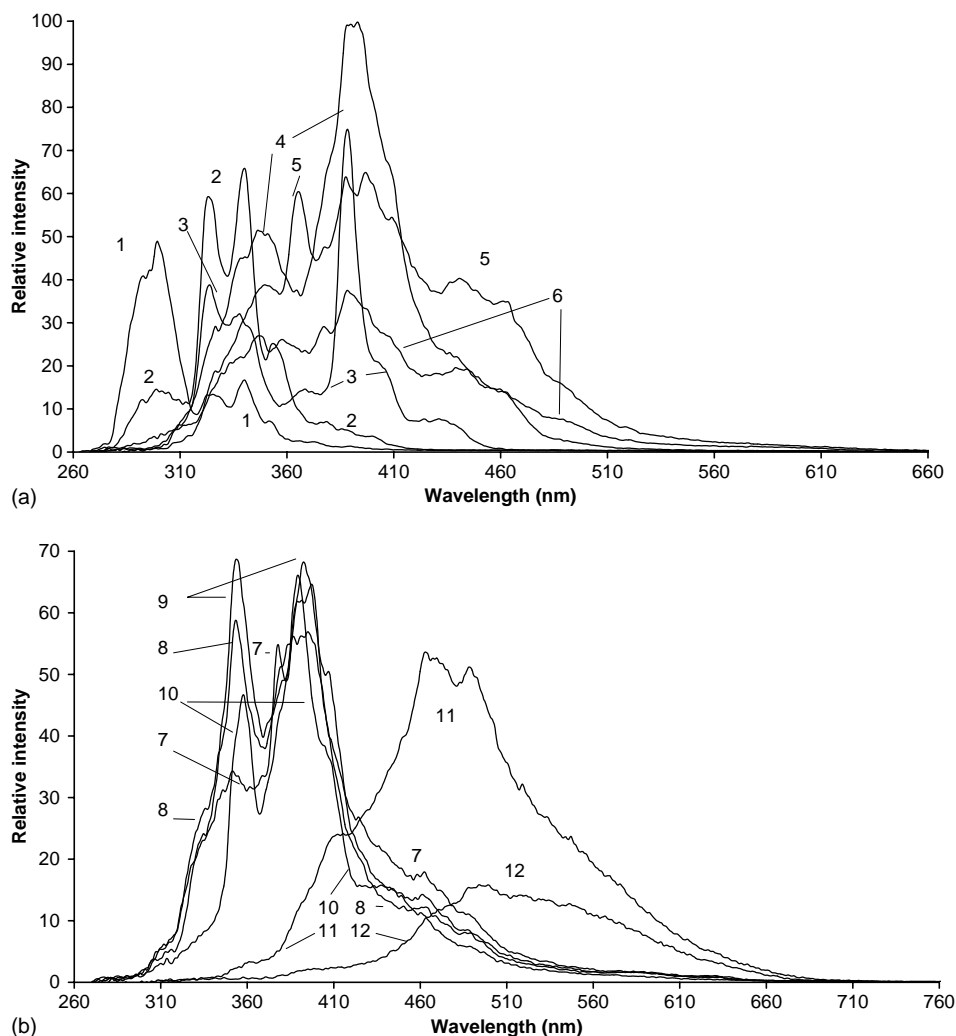


Fig. 4. Synchronous UV fluorescence spectra of (a) pitch fractions 1–6 and (b) fractions 7–12.

The data from SEC and UV fluorescence of the TLC fractions indicate that the TLC separation was governed by increasing immobility, brought about by a combination of increasing molecular size and increasing polarity. Previous work with TLC fractions [1] and examination by probe-mass spectrometry showed that the most mobile material was polycyclic aromatics, followed by nitrogen containing species; in the present work, more powerful solvents have been used in TLC but the most mobile material is expected to be similar to that of the previous work, in the pentane and toluene development regions.

#### 4. Petroleum residue

Fig. 5 shows the SEC profiles of the fractions by UV absorbance. Band 1 gave no signal by UV-A and it is probable that the reason was because the material in this band was alkyl benzenes or small aromatic rings with no absorbance outside the region of opacity of the NMP. Signal was de-

tected using the ELSD, below. Fractions 1–3 were mobile in pentane while fraction 4 was mobile in toluene; the retained peaks showed a steady shift to shorter elution times with decreasing mobility on the plate. The major intensity of the UV absorbance profiles was in the retained region of the column with elution between 15 and 23 min and no observable signal was observed in the excluded region before fraction 4. Fraction 5 showed a shift to longer elution time with an absence of excluded material, presumably reflecting a change in type of the material in the fraction compared with the previous fractions; this was material mobile in acetonitrile but immobile in toluene and the change may be inclusion of nitrogen in the molecule as pyridines and pyrroles, as observed in the previous work [1] by probe-MS. The subsequent fractions 6 and 7, mobile in pyridine, gave less intense signals with more material in the excluded region than in the retained region. Fraction 8 was the immobile material at the origin with very little signal detected.

Fig. 6 shows the SEC profiles by ELSD. Fraction 1 shows signal at about 19–20 min whereas no signal was

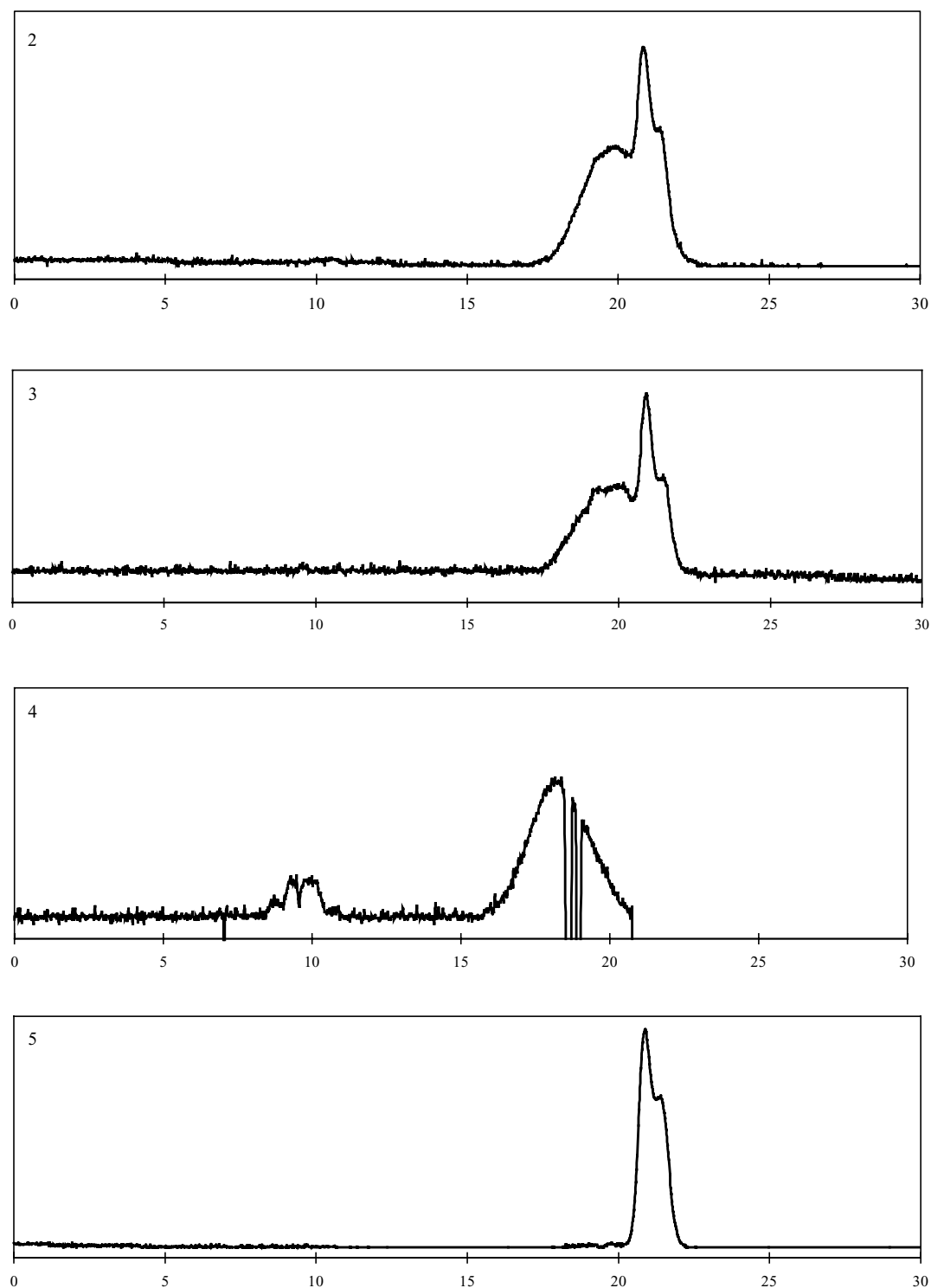


Fig. 5. SEC profiles of the Petrox distillation residue fractions by UV absorbance; fraction numbers in upper left-hand corner; intensity vs. elution time (min).

evident in the UV absorbance profile of Fig. 5. In addition, a small excluded peak was detected. Fractions 1–4 were mobile ahead of the acetonitrile solvent front and the retained peaks shifted to shorter elution times in that order, indicating increasing molecular mass with decreasing mo-

bility. These fractions also had an excluded peak. Fraction 5 which was at the acetonitrile front, showed a shift to later elution, reflecting a change of composition, which may be incorporation of nitrogen into the structures; there was a small excluded peak. Fractions 6 and 7 showed increasing

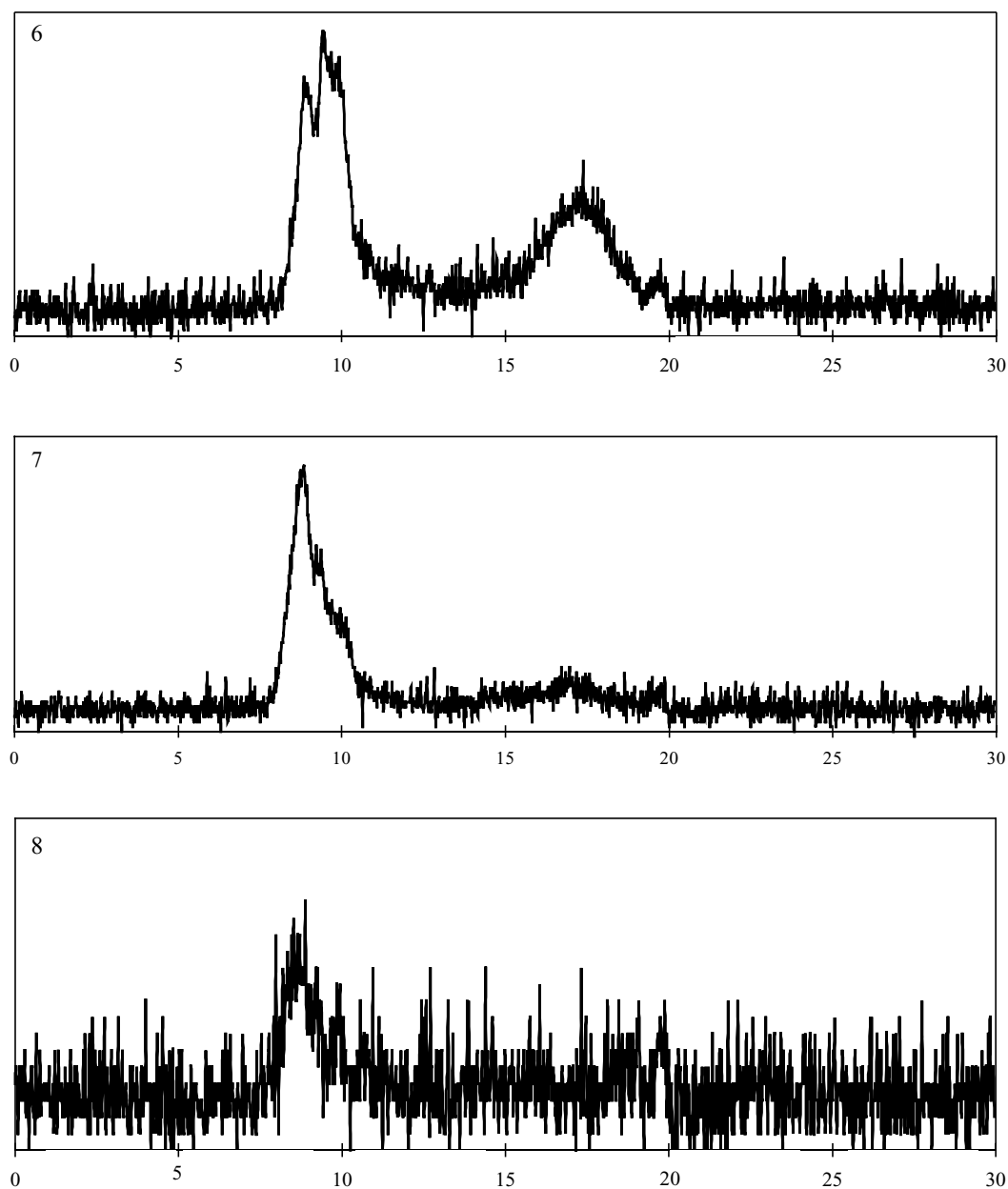


Fig. 5. (Continued).

proportions of excluded material, while very little signal was seen for fraction 8, the material remaining at the origin. It is probable that the excluded material in Fig. 6 is enhanced in relation to the retained material because of the action of the ELSD system in removing solvent and any relatively small volatile molecules of the early fractions. Previous work with petroleum vacuum residues [21] showed very little difference in elution times between UV absorbance and ELSD profiles at the longest times, but differences caused by loss of part of one fraction, would not have been obvious without fractionation. This contrasts markedly with the significant loss of low-molecular-mass signal from the pitch fractions above. We have shown that the molecular mass ranges of coal derived materials

tend to be lower than those of petroleum vacuum residues [9,22].

Fig. 7 shows synchronous UV fluorescence spectra of the petroleum fractions. Fraction 1 showed only weak fluorescence and this is probably because the main region of absorbance and fluorescence for these most mobile components of the sample was obscured by the opacity of the NMP solvent. Fractions 2–4 show relatively intense synchronous spectra with shifts to longer wavelengths characteristic of increasing aromatic cluster sizes. Fraction 5 showed a slight shift to shorter wavelengths with a reduction of fluorescence intensity, which may be attributed to the probable inclusion of nitrogen heterocyclic compounds in this material mobile in acetonitrile but immobile in toluene.

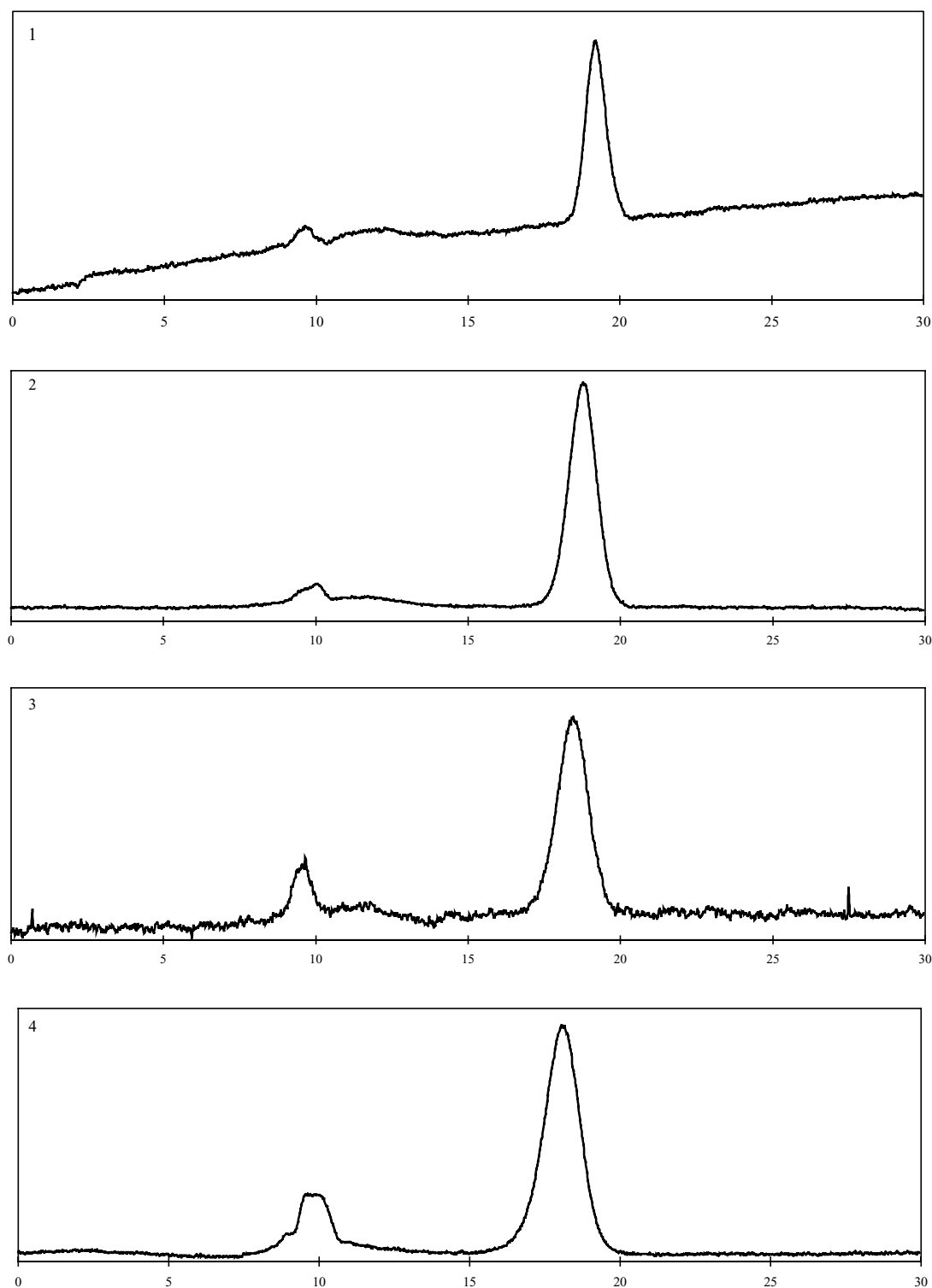


Fig. 6. SEC profiles of the Petrox distillation residues by ELSD; fraction numbers in upper left-hand corner; intensity vs. elution time (min).

Fractions 6 and 7 showed broader band synchronous fluorescence spectra, with fewer prominent peaks of intensity than for fractions 2–4. This indicates an increasing complexity of the fluorescent chromophores, which together with reduced intensity of fluorescence, indicates an increasing complexity of these molecules that were only mobile in

pyridine. The fraction 8, which was immobile in pyridine, gave only a low intensity, very broad fluorescent profile that probably indicates that the molecular complexity was greater than in fraction 7. The shifts in maximum values were less pronounced than those observed for the pitch fractions.

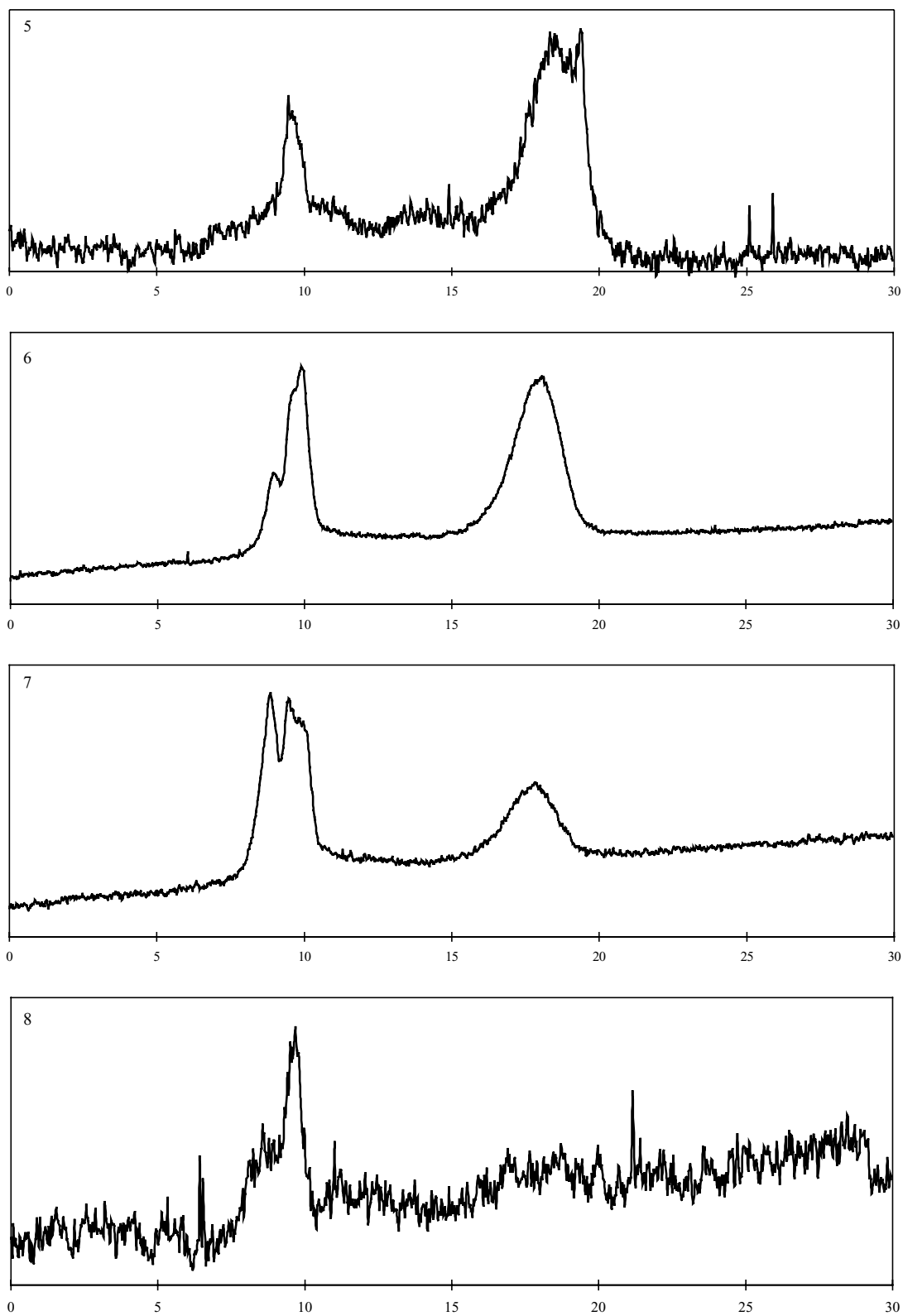


Fig. 6. (Continued).

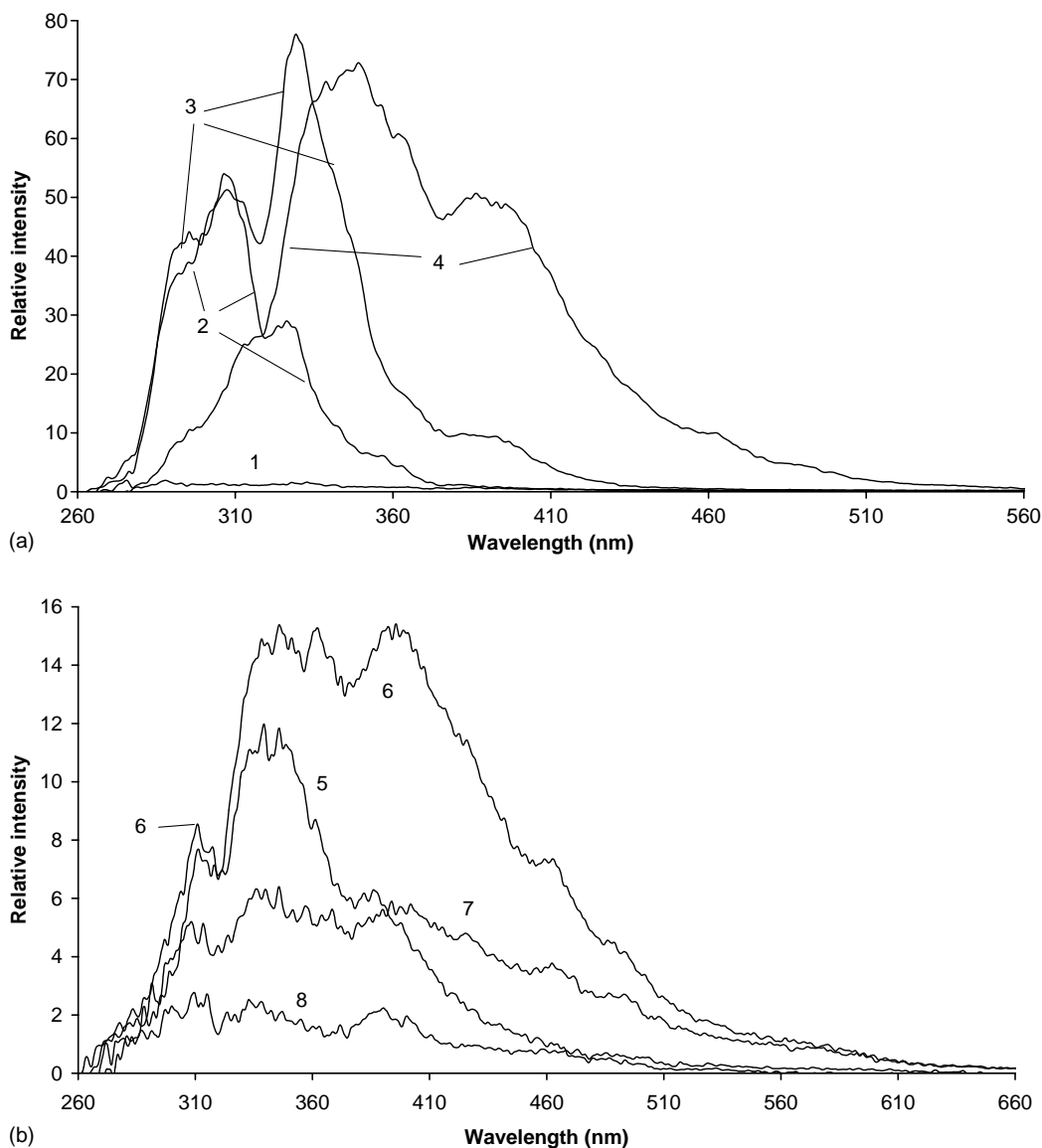


Fig. 7. Synchronous UV fluorescence spectra of the Petrox fractions (a) fractions 1–4 and (b) fractions 5–8.

## 5. General comments

### 5.1. Comparisons with unfractionated samples

The pitch and residue fractions recovered from the TLC plate compare with the unfractionated samples in showing material in the retained region, 15–22 min, which remained within the envelopes of the whole samples. For the pitch, the peak intensity of the retained material of the fractions shifted to earlier elution times with increasing immobility on the TLC plate, indicating increased mass or polarity. For the petroleum residue however, the fractions showed a distinct shift to later elution times for material at the acetonitrile solvent front, fraction 5. The profiles of the material of the pitch fractions eluting in the excluded region also showed similar profiles to that of the whole sample, within the elution time range 8–12 min approximately. The profiles of

the excluded material of the residue fractions showed different behaviour. In UV absorbance, many petroleum fractions showed no excluded peak and excluded material only became prominent after fraction 5. By ELSD, however, all of the petroleum fractions showed some excluded material, indicating the presence of some involatile material possibly of high mass and probably of low intensity in terms of abundance in the whole sample.

### 5.2. Comparisons between pitch and petroleum residue

Although the material of the petroleum residue in the retained region is of larger molecular mass than that of the pitch in the same region, the pitch contains a greater proportion of excluded material. We have shown that the polystyrene calibration of the column provides a good estimate of molecular mass of pitch fractions of narrow



polydispersity [4,6] and of the petroleum residue [21], by comparison with masses measured using MALDI-MS. The molecular structures of the excluded material of both samples appear to be different from those of the retained molecules. The valley between the peaks representing excluded and retained materials approached zero intensity for the whole samples and for all the fractions, indicating a possible change of structure. Fullerene of mass 720 U and a three-dimensional molecule, eluted from this column in the excluded region. MALDI-mass spectra of fractions of wide polydispersity of pitch [3] and of the heptane insolubles of the petroleum residue [21], both showed a continuous mass distribution with no valley of zero intensity. We have shown [8] that spherical particles with diameters between 1 and 40 nm elute from this column between 11 and 6 min. In the absence of better evidence, the change of structures from retained to excluded across the valley of approximately zero intensity must remain as speculation.

The relation between migration distance on the plates and molecular mass can be seen as one of increasing molecular mass with decreasing mobility in any one solvent. It is expected [1] that with a change to a more polar solvent, more polar molecules are likely to be mobilised. However, we note that polarity may be defined through behaviour in chromatography. In fractions of both samples, the peak of intensity of UV fluorescence shifted to longer wavelengths with decreasing mobility. This shows that the size of the aromatic chromophore increased with increasing size of the molecule.

These data show that the fractions examined in the previous work [1] by SEC using THF solvent, were not separated by a size mechanism but by a surface interaction. Since no excluded material was observed, we presume it either did not dissolve in THF or remained stuck to the column packing. In either case, THF is seen as an unsuitable solvent for SEC of aromatic materials.

## 6. Conclusions

A coal tar pitch and a petroleum distillation residue have been fractionated by planar chromatography using pentane, toluene, acetonitrile and pyridine. The examination of the fractions recovered from the plates, by SEC and UV fluorescence, showed an increase of molecular mass within the retained region of SEC and an increase of aromatic cluster size by UV fluorescence, as mobility on the plate decreased. SEC using THF as eluent did not show this trend with TLC or UV fluorescence. The pitch contained more small molecules than the residue. All fractions from both samples contained some material excluded from the column porosity and detected by ELSD but not always by the UV absorbance detector. The proportions of excluded to retained material are probably smallest in the residue fractions and rather more in the pitch fractions, but in both samples, the proportion of excluded material increased with decreasing mobility on

the plate. The separation of retained and excluded materials in SEC by a valley of zero intensity has been interpreted to show a change in molecular structure from nearly planar to three dimensional in the excluded region. The evidence for this comes from the elution behaviour of spherical particles of known diameter that elute in the excluded region.

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