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Large Molecular Mass Materials in Coal-Derived Liquids by ^{252}Cf -Plasma and Matrix-Assisted Laser Desorption Mass Spectrometry

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The paper compares responses of ^{252}Cf -plasma desorption MS (PD-MS) and matrix-assisted laser desorption (MALDI) MS to identical samples. The two pairs of samples selected for the comparison were known from previous work to differ significantly in their high mass contents. MALDI-MS showed large differences in MM distributions within both pairs of samples. The PD-MS data showed a degree of similarity between one pair of samples (pyridine soluble/insoluble fractions of a coal tar pitch); for the second pair (a coal extract and its hydrocracked product), trends from the two MS techniques agreed closely. The MM range observed by PD-MS was somewhat narrower, extending to between 3000 and 5000 u. Significant differences within pairs of samples were observed by SEC and by UV-fluorescence spectroscopy, providing somewhat closer agreement with the MALDI spectra. The two MS instruments differ in two important respects: the ionization system (i.e., plasma vs laser desorption) and the maximum available ion extraction voltage: 30 kV for the MALDI-MS instrument and 15 kV for the PD-MS. The comparison of plasma vs laser desorption mass spectroscopy could not therefore take place at high ion extraction voltages. Work at up to 30 kV in the MALDI instrument indicated better sensitivity to high-mass materials at higher ion extraction voltages. The qualitative similarity of results from the two MS techniques is nevertheless apparent; the range of MMs observed in PD-MS as well as in MALDI-MS were, furthermore, far larger than those reported by any MS technique, to date.

Introduction

Reliable estimates of molecular mass distributions of coal-derived materials (e.g., tars, extracts, pitch) are required in a number of research areas: these include combustion modeling, design of hydrocracking catalysts, and the geochemistry of coal. Coal-derived liquids are complex mixtures, containing a multiplicity of structural features and, to date, no single technique has been shown to provide *quantitative* information on their molecular mass distributions. Extensive use has been made of several mass spectroscopic techniques in work aiming to determine molecular mass (MM) distributions of coal derived liquids, as well as allied techniques such as size exclusion chromatography (SEC). Despite intense efforts, however, answers provided by many of these techniques differ widely.

An early and detailed comparison of field desorption (FD), field ionization (FIMS), and fast atom bombardment (FAB) showed FAB-MS with an LC attachment to provide the (then) widest range of molar masses observed in coal-derived liquids¹ up to about 2200 u.

Several MS-based methods, including use of a home-made laser desorption device,² have given MM distributions not much above 1100 u. Subsequent work with laser desorption mass spectrometry (LD-MS) showed peaks of main intensity between 1000 and 5000 u in pyrolysis tars and liquefaction extracts;³ in the case of solid coals, trace signal was observed at up to the detection limit of the instrument (270 000 u).⁴ More recent laser desorption based MS work undertaken in parallel with SEC experiments (using NMP, 1-methyl-2-pyrrolidinone, as eluent) has been summarized elsewhere.^{5,6} On the other hand, a number of experimental parameters have been observed to cause changes in MALDI (matrix-assisted laser desorption) spectra of

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coal-derived liquids; these parameters are sample deposition density, laser power, matrix composition, and ion extraction voltage. In the absence of criteria to define the spectra best reflecting MM distributions of the original samples themselves, the latter observations underline the semiquantitative nature of the data and the necessity for corroboration by independent analytical techniques.

In a sequence of independently conceived experiments involving combinations of ^{252}Cf -plasma desorption mass spectrometry⁷⁻⁹ and SEC (pyridine as eluent),¹⁰ the presence of MMs up to several thousand mass units has been reported. Plasma desorption mass spectrometry (PD-MS) normally operates with a thin layer of sample deposited on the target which approximates to a monolayer. The technique has been used to examine peptides¹¹ and lipids¹² as well as small molecules such as nitrogen-containing pharmaceuticals¹² and alkylaminotriazines.¹³ Volatilization and ionization are achieved by collision of a very energetic ^{252}Cf fission product with the sample. The technique produces primarily singly charged ions and is more effective with polar than with nonpolar materials. Its advantages and problems for fuel analysis have been discussed.^{8,9}

The particular sources of evident difficulties associated with determining MM distributions of coal-derived materials by MS-based techniques are not easy to identify: MMs up to 300 000 u have been observed by MALDI-MS¹⁴ in biopolymers, which are thermally far more labile entities compared to most coal-derived species. One (but probably not the only) problem inherent in the nature of coal derived samples (as complex mixtures) has recently been discussed in terms of sample polydispersity: smaller-MM components appear to suppress signal from larger-MM components^{7,15} probably due to their preferential desorption and ionization.¹⁶ Data supporting this hypothesis has recently been presented by two different groups using mixtures of commercially available polystyrene molecular mass standards;^{17,18} in the later work,¹⁷ a range of polystyrene MM standards up to 22 000 u and poly(methyl methacrylate)s up to 50 000 have been studied in some detail: MALDI spectra of single samples of low polydispersity (e.g. 1.04) were found to give peak masses (Mp) one or two monomer masses lower than the Mp observed by SEC. As the polydispersity of the polymer mixture was progressively increased, high-mass oligomers could be observed to suffer mass discrimination

in favor of the low-mass oligomers. These observations suggest that intensities at the high-mass limit of complex samples, such as coal-derived materials, may be significantly underestimated or remain altogether unobserved. In the case of a coal tar pitch, enhancement of high-mass signal could be achieved by fractionation.^{19,20}

One distinguishing feature between MS techniques used in attempts to characterize coal-derived mixtures pertains to the particular sequence of evaporation/ionization events. MS-based experience, to date, suggests that techniques where ionization occurs *after* thermal evaporation of sample molecules, e.g., GC-MS, heated probe MS, LC-MS, and FIMS, usually show lower mass ranges compared to techniques where ionization is thought in the main to precede *and* to assist desorption: FAB, FD, LD-MS, and PD-MS. Of these, the two types of instrument which have given the highest MM distributions among MS-based techniques have been PD-MS and LD-MS. The present study has compared responses of PD-MS and LD-MS to identical samples, in order check the validity of findings from the two methods against one another. The two pairs of samples selected for the comparison were (i) a coal extract and its hydrocracked product^{20,21} and (ii) the pyridine-soluble and -insoluble fractions of a coal tar pitch.^{5,6,22,23} Within each pair, previous work by size exclusion chromatography and by MALDI-MS had indicated significant differences between the high-mass contents of the two samples.

Experimental Section

Samples. The sample of coal tar pitch (C 91.4%; H 4.1%; N 1.3%; S 0.76%; and O 2.4% by difference) has been characterized in some detail.^{4,19,24-26} To prepare a pyridine-insoluble fraction, the sample was mixed with excess pyridine and the resulting slurry filtered; the cake was washed with pyridine and dried in a vacuum oven; for further examination, this sample was dissolved in NMP. The pyridine-insoluble fraction corresponded to approximately 15% (by mass) of the pitch. The pyridine-soluble fraction of the pitch was collected in solution.

The Point of Ayr (PoA) coal was extracted for 10 min with tetralin in a minibomb at 450 °C; the pentane-insoluble fraction of the extract—mostly free of tetralin-derived material—has been used in the work outlined below. Hydrocracked product was prepared in a microbomb reactor at 460 °C (60 min, 190 bar H_2 pressure), in the presence of a supported NiMo/ Al_2O_3 catalyst with tetralin as donor solvent. Both samples have been described in detail elsewhere.²⁰⁻²³

Mass Spectrometry. A Bio Ion 20 ^{252}Cf -plasma desorption, time-of-flight mass spectrometer was used to obtain molecular

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mass distributions of the samples. Samples solutions in NMP, at concentrations of approximately 10 mg mL^{-1} , were applied to aluminized Mylar disks (Applied Biosystems Inc.). The disks were vacuum-dried at room temperature. H^+ and Na^+ were used as calibration standards. Spectra were recorded at positive 10 and 15 kV ion extraction voltage with 1 ns/channel time resolution. Each spectrum corresponded to 10^6 primary ion events. The instrument calibration was checked against porcine insulin of molecular mass 5778 u; the measured molecular mass was 5790 u, within instrumental specifications. The mass range was scanned up to about 20 000 u. Number and mass average molecular weights were calculated after subtraction of the "blank" spectrum due to the Mylar disk. Further details of the procedure are given in ref 8.

MALDI-TOF spectra were obtained by a Fisons VG TOF-SPEC mass spectrometer, (VG Organic, Manchester, UK) fitted with a nitrogen UV laser (337 nm) and a VAX 4000-based data system with OPUS software. The linear TOF mode was used with an ion extraction voltage of 28 kV in positive ion mode for the coal-derived samples, but 20 kV for the standard PAH. Experiments using the THF-insoluble fraction were carried out with no matrix, at different ion extraction voltages (10, 20, and 30 kV). Samples were applied to the target in NMP solution and dried in a vacuum oven before insertion into the mass spectrometer ion source. Spectra of the pitch fractions and the product were obtained without added matrix, but for the coal extract, 2,5-dihydroxybenzoic acid (DHB), dimethoxy-4-hydroxycinnamic (sinapinic) acid, α -cyano-3-hydroxycinnamic (α -cyano) acid, 2-(4-hydroxyphenylazo)benzoic acid (HABA), and 9-anthracenecarboxylic acid (9-A) were used as matrix. During experiments carried out in the absence of matrix, samples were applied onto target disks at much higher loadings. Sample concentrations could not be determined quantitatively; sample and matrix solutions were mixed to give more matrix than sample, by a factor of at least 100.

Size Exclusion Chromatography. A 30 cm long, 7.5 mm o.d. polystyrene-divinylbenzene polymer packed SEC column (3 μm Mixed-E; Polymer Labs, Shropshire, UK) was operated at 85 °C with a flow rate of 0.45 mL min^{-1} . A variable-wavelength Perkin-Elmer LC250 UV-absorption detector was used at 350 and 450 nm. Calibration against polystyrene standards was performed at 264 nm since the eluent, NMP, is opaque at 254 nm but partially transparent at 264 nm.

UV-Fluorescence Spectrometry. A Perkin-Elmer LS50 luminescence spectrometer 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. A quartz cell with 1 cm pass 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. As relative concentrations of solutions of pitch fractions soluble and insoluble in pyridine were not determined, the spectra have been presented in peak-normalized mode. Sample solutions were diluted with NMP to avoid self-absorption effects (cf. ref 27). Details of the procedure for acquiring UV-fluorescence spectra have been given elsewhere.²⁷⁻²⁹

Results

Comparison of Mass Spectra. Figure 1 presents MALDI-TOF mass spectra of two model compounds,

rubrene and pyranthrene, of a fullerite mixture (90% C_{60} and 10% C_{70} , approximately) and the blank spectrum obtained after addition of solvent NMP to a target disk. Under the conditions used, the two polynuclear aromatics and the fullerite mixture all gave well-resolved spectra, without any added matrix; a remarkably low level of noise could be discerned in the blank spectrum. The spectra of the two model compounds showed single molecular ions within 1 or 2 units of the expected mass, reflecting the uncertainty of mass measurement with this technique. Potassium ions can be seen at m/z 39 or 40. In the fullerite spectrum, a sequence of peaks separated by 24 u, corresponding to the sequential loss of C_2 , can be observed.³⁰ It may be noted that intensities of M^{2+} and 2M^+ ions were insignificant in all the spectra. Unlike the case where a powerful Nd:YAG laser had been used,^{4,24} neither the PAH nor the fullerite mixture displayed carbon cluster sequences. PD-MS operates without a matrix and for standard materials (porcine insulin in this work) and simple molecules can generate a molecular ion.^{11-13,31} A mass spectrum for fullerene (not shown), generated by PDMS, showed a molecular ion at 720 u and C_2 fragmentation peaks, but only low-intensity doubly charged ions.

Figure 2a,b, shows MALDI mass spectra of the pyridine-soluble (with no matrix) and pyridine-insoluble (with sinapinic acid as matrix) fractions of the coal tar pitch, respectively. The spectrum of the pyridine-soluble fraction (Figure 5a) showed a peak of main intensity between 200 and 400 u and the spectrum was observed to have reached baseline by about 5000 u. In the case of the pyridine-insoluble fraction (Figure 2b) a much wider MM distribution was observed: the spectrum of the pyridine-insoluble fraction extended to well above 5000 u and did not reach the noise level of the instrument until about 100 000 u (not shown). It is not thought that differences between the two spectra arise from the presence/absence of matrix: the best spectrum (in terms of mass range and intensities) obtained for the pyridine insoluble fraction in the absence of matrix covered the same range of mass and intensities as the best spectrum obtained using sinapinic acid as matrix.⁵ In that case, however, the sample loading in the presence of matrix was very much lower than in the absence of matrix. Above a minimum sample loading necessary to obtain a spectrum, furthermore, the effect of sample loading in the absence of matrix does not appear to be critical.⁶

MALDI-spectra of the Point of Ayr coal extract with a sequence of different matrixes (DHB, sinapinic acid, α -cyano, HABA, and 9-A, respectively) have been presented in Figure 2c-g, showing some of the variations encountered with changes in matrix composition. The peak of intensity shifts to higher mass in the order sinapinic < 9A < α -cyano < HABA < DHB. The spectrum of the extract was observed to extend to at least 10 000 u, whereas that of the hydrocracked product (Figure 2h, no added matrix) was observed to have

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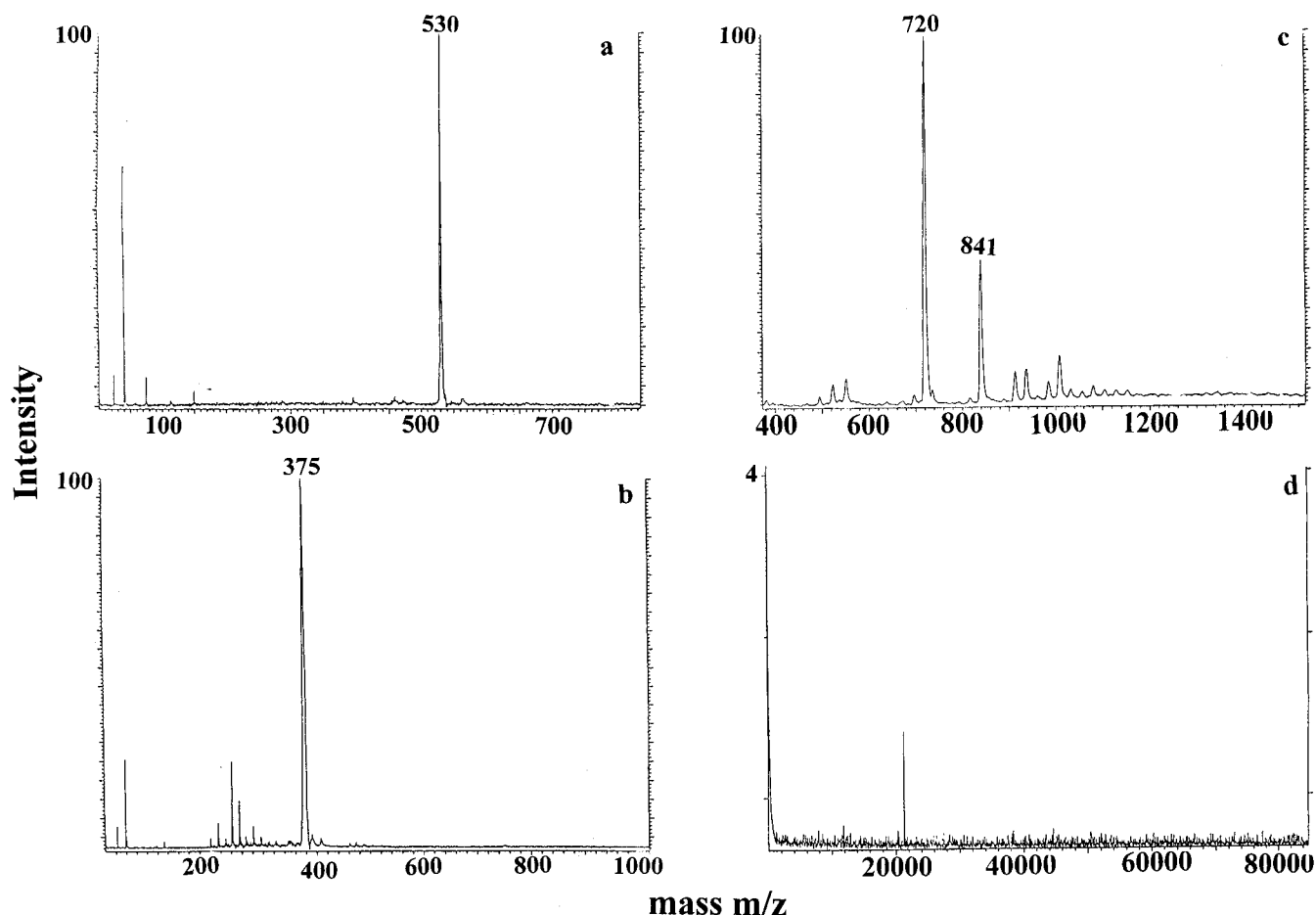


Figure 1. MALDI-TOF spectra of the model compounds and (a) rubrene, (b) pyranthrene, (c) the fullerite mixture, and (d) the NMP-solvent blank.

reached baseline by 3000 u. Considering the nature of the hydrocracking process the observed trend of changes in MM does not appear surprising. However, the SEC profiles of extract and product both show an excluded peak (described below), which corresponds to an elution volume equivalent to polystyrene of mass greater than 30 000–40 000 u; it is probable that none of these MALDI spectra detect that part of the samples corresponding to excluded in SEC.

Plasma desorption mass spectra of the pyridine-soluble and -insoluble fractions of the coal tar pitch have been presented in Figure 3, a and b, respectively; the spectra were acquired using an ion extraction voltage of 15 kV. In these PD-MS spectra, the top (more noisy) curve shows untreated data, while the lower curve represents data after background signal due to the Mylar disk had been subtracted and data smoothing carried out, using a 5-point moving average of the counts. A blank spectrum of the Mylar disk has been presented in ref 8. Spectra of the pitch pyridine-soluble and -insoluble fractions in Figure 3 show signal extending up to at least 3000 u. The proportion of low molecular mass material in the pyridine-insoluble fraction was much reduced, compared to the pyridine-soluble fraction. Number (M_n) and mass (M_w) average MMs in Table 1 suggest the pyridine-insoluble fraction of the pitch to contain only marginally more, if any, high-MM material than the pyridine-soluble fraction.

PD-MS spectra of the Point of Ayr coal extract and its hydrocracked product are shown in Figure 3 c and

d, respectively. Comparison of spectra clearly showed a sharp reduction in the proportion of material with masses above 1000 u, upon hydrocracking, with number- and weight-averaged masses reduced by approximately a factor two (Table 1). These results reflect the trend observed by MALDI more closely.

Size Exclusion Chromatography of the Samples.

Figure 4a,b presents profiles of the pyridine-soluble and -insoluble fractions of the coal tar pitch, showing significantly more intense signal at short retention times in the case of the pyridine-insoluble fraction. The insoluble fraction shows a shift of the major intensity region to larger masses compared with the pyridine solubles, as well as each sample showing evidence of excluded material, which would presumably approach the instrument baseline asymptotically in an SEC column able to accommodate the range of molecular sizes, as do the mass spectra. Differences observed between 350 and 450 nm detection indicate that the aromatic clusters of the insoluble and soluble fractions are different, with greater absorbance at 450 nm in the insoluble fraction than in the soluble fraction. As before,⁶ we have interpreted more intense signal at/near the exclusion limit of the column in terms of the presence of greater concentrations of large molecular mass material.

It may be noted that the existence and magnitude of signal at/near the exclusion limits of chromatographic columns has been interpreted in other work in terms of

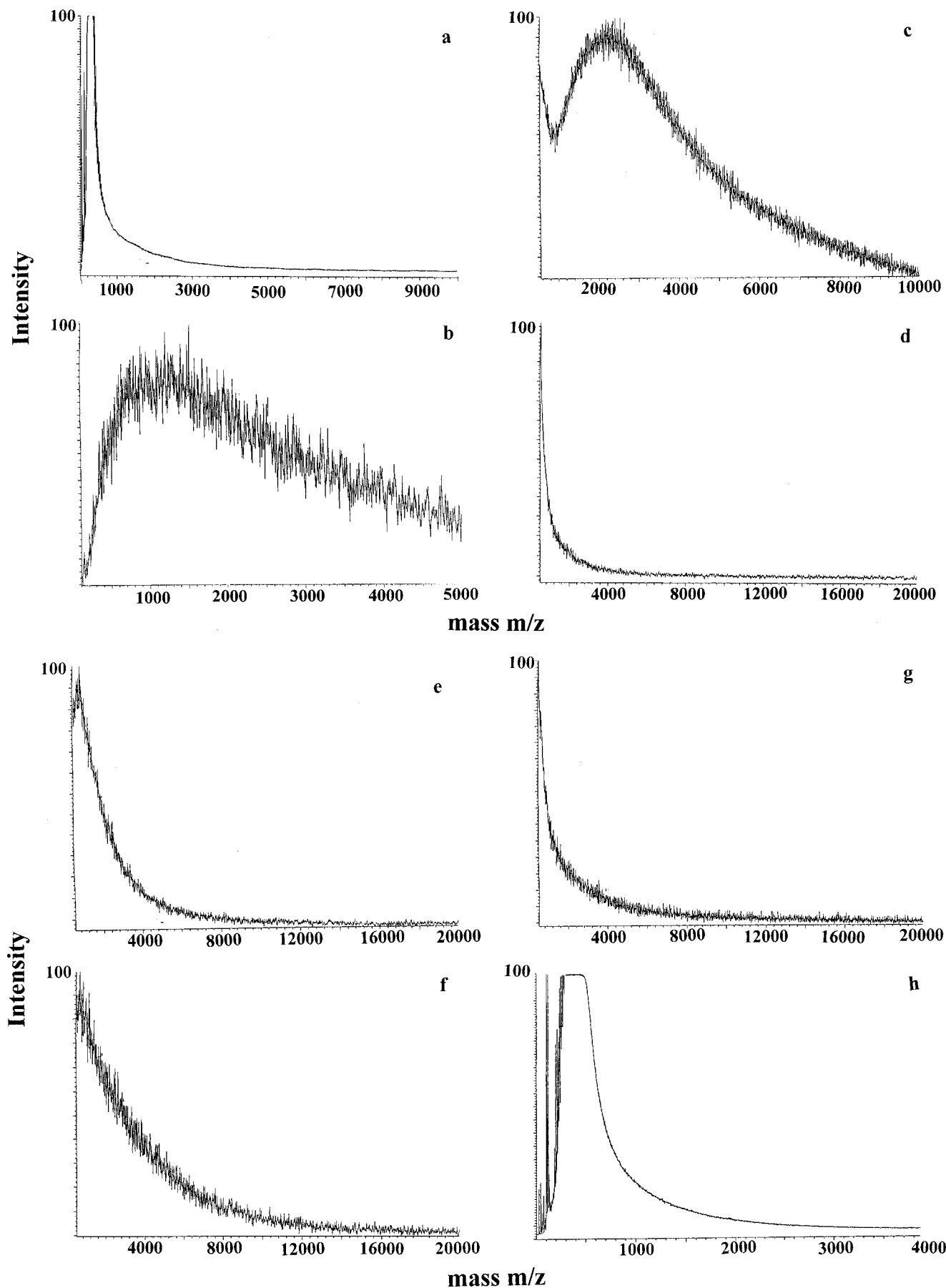


Figure 2. MALDI-TOF spectra of (a) pyridine-soluble fraction of the coal tar pitch (no matrix) and (b) pyridine-insoluble fraction of the coal tar pitch with sinapinic acid as matrix. Point of Ayr extract with different matrixes (c) 2,5 DHB, (d) sinapinic acid, (e) α -cyano, (f) HABA, and (g) 9-anthracene carboxylic acid and (h) hydrocracked product with no matrix.

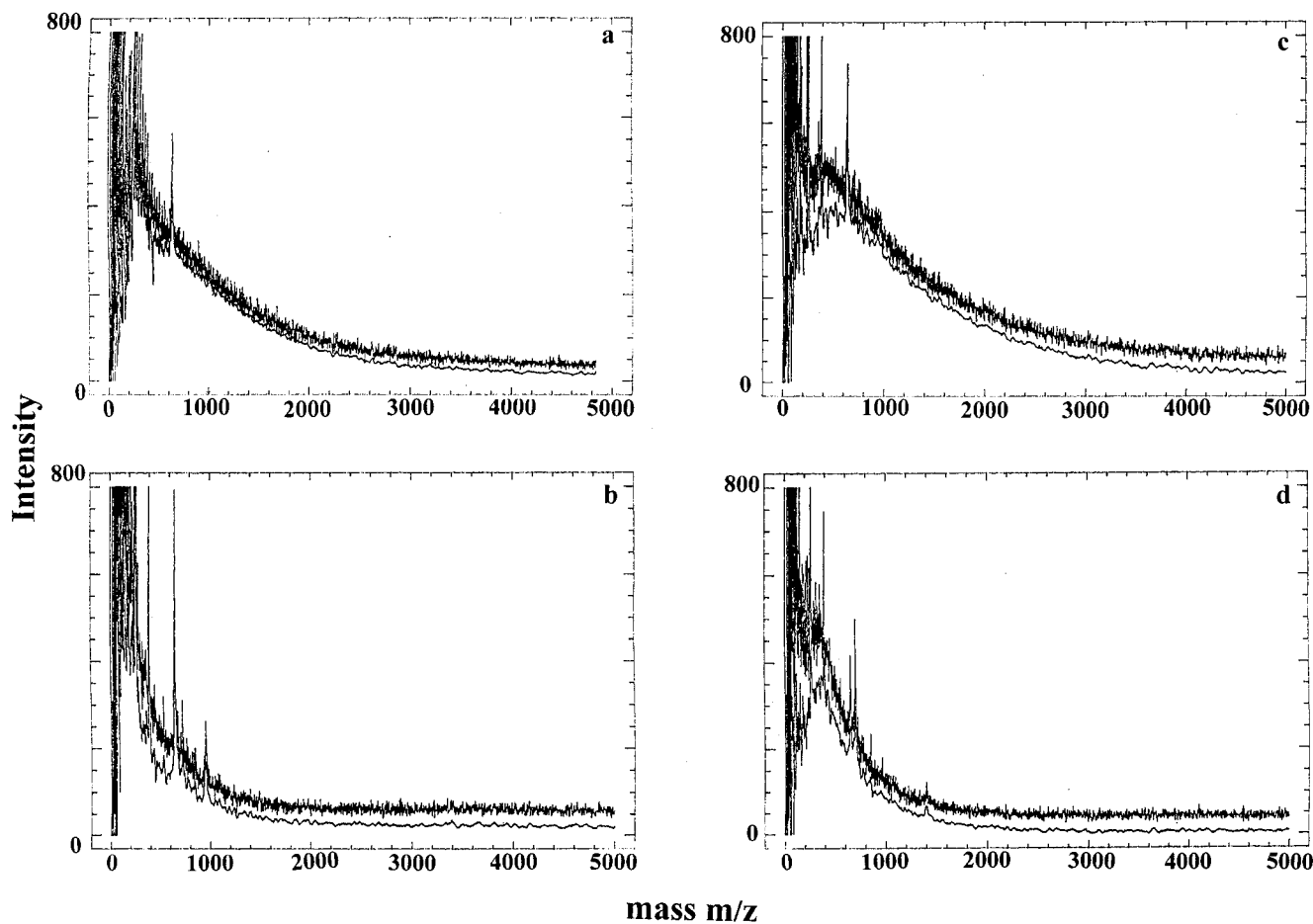


Figure 3. PDMS spectra at 15 kV ion extraction voltage of pitch fractions (a) soluble and (b) insoluble in pyridine, (c) Point of Ayr extract, and (d) hydrocracked product.

polar rather than large MM materials.^{32–35} We have shown in recent SEC work using a naphthalene mesophase pitch and a mixture of fullerenes that signal at/near the exclusion limit of the column may be clearly observed in chromatograms of entirely nonpolar samples.³⁶

Figure 4, c and d, presents SEC chromatograms of the Point of Ayr coal extract and its hydrocracking product²² with the detector set at 350 and 450 nm, respectively. Differences observed between detection at 350 and 450 nm are more pronounced for the extract than for the product, reflecting the expected much more complex range of aromatic clusters present in the extract than in the hydrocracked product. The diagrams agree with MS-based data presented above showing shifts in chromatograms to longer retention times (smaller MMs) upon hydrocracking of the extract; the effect is more pronounced at 450 nm, suggesting the reduction in size of large polynuclear aromatic ring systems—and other structural features absorbing at longer wavelengths.

UV-Fluorescence Spectroscopy of the Samples.

Figure 5a,b shows UV-fluorescence synchronous spectra

of the four samples; the spectra of the pitch fractions indicate the shift of fluorescence maximum to shorter wavelengths with increasing solubility, or reducing molecular mass as indicated by mass spectrometry and SEC. Similarly, the spectrum of the hydrocracking product shows a shift to shorter wavelengths compared with the extract, also corresponding to a shift indicated by mass spectrometry and SEC to smaller molecular size. In both cases, the fluorescence quantum yield of the larger molecular mass sample (the pyridine-insoluble pitch fraction and the coal extract) was much weaker than the fluorescence intensity of the corresponding smaller-MM sample (the pyridine soluble pitch fraction and the hydrocracked product).

Discussion

Summarizing, large differences in MM were observed by MALDI-MS within both pairs of samples. However, the PD-MS data showed similarity between the two pitch (pyridine soluble/insoluble) fractions; for the coal extract and its hydrocracked product, trends from the two MS techniques agreed. The MM range observed by PD-MS was somewhat narrower. Significant differences within pairs of samples were also observed by SEC and by UV fluorescence, providing a measure of agreement with the MALDI-spectra.

The two MS instruments differ in two important respects: the ionization system (i.e., plasma vs laser desorption) and the maximum available ion extraction

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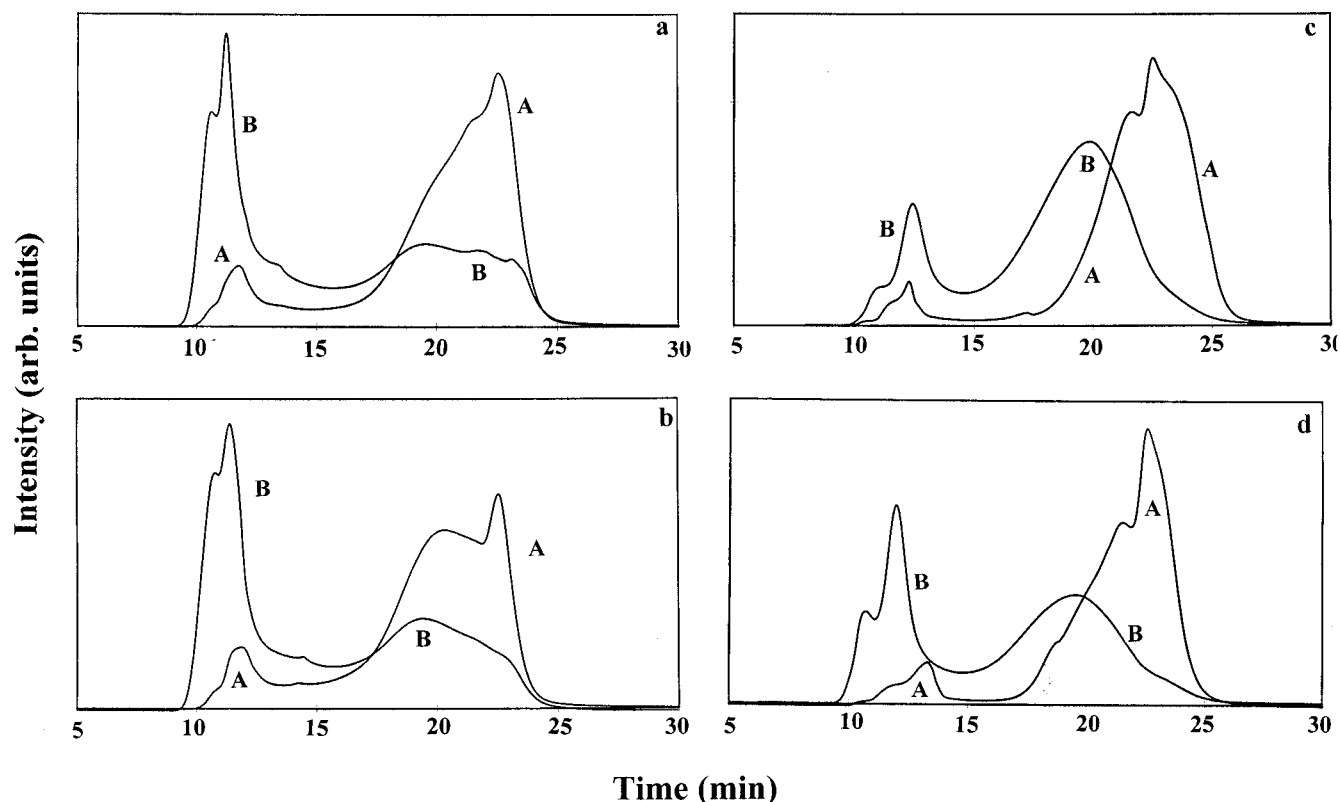


Figure 4. Size exclusion chromatograms of the pitch pyridine solubles (curve A) and insolubles (curve B) (a) at 350 and (b) at 450 nm and the Point of Ayr extract (curve B) and product (curve A); (c) at 350 and (d) at 450 nm UV absorbance.

Table 1. Average Molecular Masses Calculated from PD-MS Spectra

sample	integration range (u)	M_n (u)	M_w (u)
pyridine sols	78–3500	725	1347
pyridine insols	78–3500	622	1463
PoA coal extract	78–3500	803	1357
hydrocracking product	78–2000	438	717

voltage: 30 kV for the MALDI-MS instrument and 15 kV for the PD-MS.

Figure 6 shows the spectra of the pitch pyridine-insoluble fraction at three ion extraction voltages; the change in the sample profile is most marked at the highest voltage and it is apparent that operation of the instrument at lower voltages will tend to discriminate against the higher mass components of the sample. Similar effects have been observed for the pyridine-insoluble fraction and the whole pitch sample with variable voltage,^{5,6} but not for the pyridine-soluble fraction where the proportion of high-mass material indicated by SEC was low. These observations are in agreement with results for polymer standards in mixtures where a similar discrimination against high-mass oligomers became apparent as the polydispersity of the mixture increased.^{7,37}

Plasma desorption mass spectrometry is most effective with polar molecules, so it is surprising that it works as well as it does with these largely hydrocarbon samples. In the PD-MS instrument, increasing the ion extraction voltage from 10 to 15 kV (the maximum

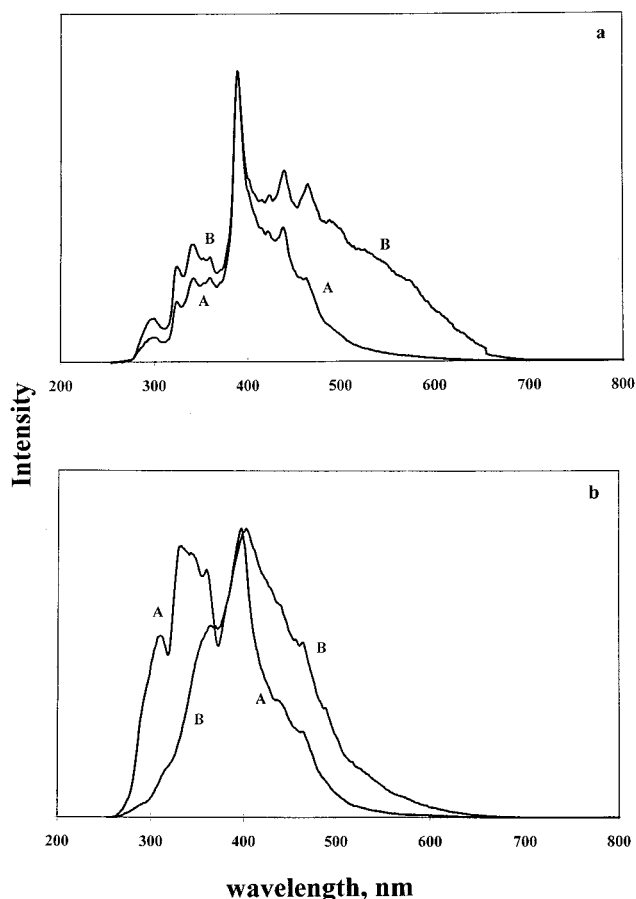


Figure 5. UV-F synchronous spectra of (a) the pitch pyridine solubles (curve A) and insolubles (curve B) and (b) the Point of Ayr extract (curve B) and product (curve A).

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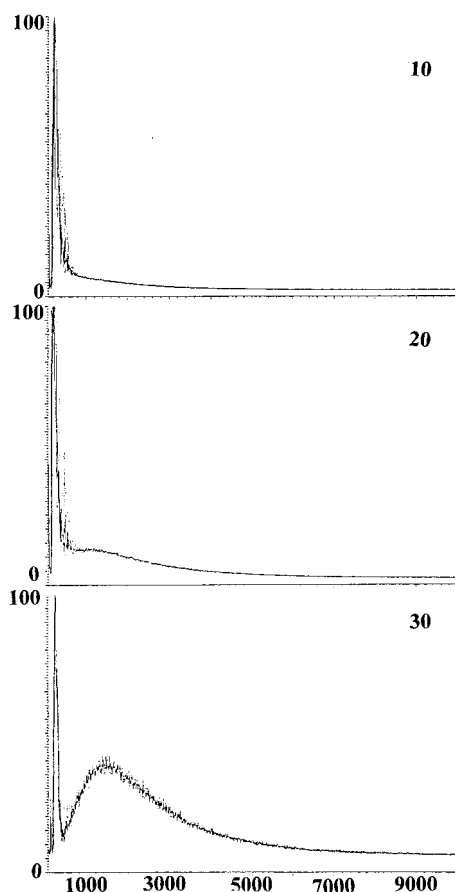


Figure 6. MALDI-TOF mass spectra of the pitch pyridine-insoluble fraction at 10, 20, and 30 kV ion extraction voltage.

available) did not uniformly change the results, but for the Point of Ayr coal extract, ion intensities above m/z 1000 were found to increase significantly. It may be noted that MALDI spectra of the same fractions indicated a greater reduction in mass on going from pyridine insolubles to pyridine solubles, or from coal extract to hydrocracked product, probably because they were obtained at higher ion extraction voltages than the plasma spectra and therefore detected more of the high mass material.

A straightforward comparison in this work of plasma vs laser desorption mass spectra is not possible at high ion extraction voltages, although the higher voltages appear to help in the observation of the highest MM materials. The qualitative similarity of results from the two MS techniques is nevertheless apparent. It is also worth noting that the range of MMs observed in PD-MS as well as in MALDI-MS are far larger than those from any other MS technique reported to date.

Summary and Conclusions

Molecular mass (MM) distributions of coal derived liquids determined by different mass spectroscopic

techniques and by size exclusion chromatography often differ widely. At best, the MS-based data is semiquantitative in nature and corroboration by independent analytical techniques is necessary. The present study has compared responses of PD-MS and LD-MS to identical samples, to check the validity of findings from the two methods against one another. The two pairs of samples selected for the comparison were known from previous work to differ significantly in their high-mass contents.

1. MALDI-MS showed large differences in MM-distributions within both pairs of samples. The PD-MS data showed a degree of similarity between the two pitch (pyridine soluble/insoluble) fractions; for the coal extract and its hydrocracked product, trends from the two MS techniques agreed. The MM range observed by PD-MS was somewhat narrower. Significant differences within pairs of samples were also observed by SEC and by UV fluorescence, providing closer agreement with the MALDI spectra.

2. The two MS-instruments differ in two important respects: the ionization system (i.e., plasma vs laser desorption) and the maximum available ion extraction voltage, 30 kV for the MALDI-MS instrument and 15 kV for the PD-MS. The comparison of plasma vs laser desorption mass spectroscopy did not therefore take place at high ion extraction voltages. Work at up to 30 kV in the MALDI instrument indicated better sensitivity to high-mass materials at higher ion extraction voltages.

3. The qualitative similarity of results from the two MS techniques is nevertheless apparent. It is also worth noting that the range of MMs observed in PD-MS as well as in MALDI-MS are far larger than those from any other MS technique reported to date.

4. However, shortcomings of mass spectrometry in the examination of samples of wide polydispersity probably mean that the high-mass materials corresponding to that part of the fraction excluded in SEC have not yet been observed.

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