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N-Methyl-2-pyrrolidinone as a mobile phase in the size-exclusion chromatography of coal derivatives

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Abstract

This paper reviews the current state of molecular mass determination for fossil fuel materials by chromatographic methods and describes improvements which can be made to both the chromatographic separation and the detection of eluting material. Most significantly, N-methyl-2-pyrrolidinone (NMP) offers a number of advantages as a mobile phase in the size-exclusion chromatography (SEC) of coal derivatives. Much more coal-derived material dissolves in NMP and solute–column packing interactions common with SEC solvents such as tetrahydrofuran are much reduced. NMP is compatible with UV absorption and UV fluorescence detection

Keywords: Mobile phase composition; Coal; Detection, LC; Methylpyrrolidinone; Polystyrene

1. Introduction

The demands for more efficient and effective coal beneficiation have continually increased due to increasingly strict environmental legislation and to continually present financial pressures. This has led to the development of new coal conversion processes as well as the improvement of more familiar methods. Alongside these developments, the need to know more about the original coal and the products derived from it has inevitably also grown. It is vital to know what a process has produced but perhaps more important to know what the starting material was. The complexity and heterogeneity of coal make these last two questions extremely complicated issues and there are a number of different ways in which they can be answered.

The molecular mass or molecular size of the species present in coal and its derivatives is an important consideration in the design of processes for coal conversion, particularly the selection and preparation of porous catalysts and in assessing the effectiveness of such processes, and as a way to determine the mechanisms of such conversions. This paper is one of a number in which we describe our work which is aimed at improving the determination of molecular mass information.

There are a number of techniques for determining molecular masses (MM), although when applied to such complex mixtures as fossil fuels, most are only capable of giving an average value. However two techniques, size-exclusion chromatography (SEC) and mass spectrometry (MS) are capable of producing a molecular mass distribution for such mixtures which can be far more informative. In this paper we discuss the application of SEC to coal-derived

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materials and review significant recent developments in MS of similar materials, with the implication of such work outlined in the final discussion. The SEC technique is, in principle, simpler to employ than MS with sample preparation involving only dissolution in the chromatographic solvent and with the appropriate apparatus being considerably less expensive. SEC is also more likely to be utilized in a process development or plant monitoring environment because of the greater robustness of the apparatus. The emphasis of the work is the investigation of a new mobile phase in which to perform the chromatographic separation in order to define reliable procedures for the determination of molecular mass distributions of coal products relevant to liquefaction, gasification, pyrolysis and combustion.

SEC separates solute molecules of differing size through their different degrees of permeation into a porous stationary phase. This technique, when applied to fossil fuel materials has three main drawbacks. First, whole coals are well known to have limited solubility in typical chromatographic solvents and this extends to the derived products. This reduces the usefulness of information obtained from a chromatographic method as it applies only to the soluble portion. Second, there is typically considerable physical interaction between the solute and the column packing material creating a second separation mechanism. Finally there is the question of calibration of SEC columns for these kind of samples. SEC is fundamentally a comparison method. As a polystyrene molecule is unlikely to have the same shape and structure in solution as a coal molecule, considerable caution must be exercised when comparing the retention of the sample to these common calibrants.

The most routinely used columns for SEC are based upon polymeric gels [1] based on divinylbenzene. The separation of coal derivatives produced by these materials have been extensively investigated and this work can be divided into three, not unrelated, groups. One approach has been to study the elution characteristics of a series of model compounds. The effect of molecular size, stereochemistry and functionality on the retention time of species present in coal then becomes visible. This approach is typified by the work of Lafleur and co-workers [2–4] who have reported the complexity of the problems encountered with even simple polycyclic aromatic compounds (PACs) of similar composition but different structure. These are exemplified by the observations of many groups that the elution of cata annelated PACs can vary directly or inversely with molecular size [2] (and references therein) depending on the mobile and stationary phase combinations used. Indeed, a poly(divinylbenzene) column with dichloromethane solvent has been used [2] to separate unsubstituted polyaromatic hydrocarbons into, not only, cata and peri structural types (peri annelated molecules contain a naphthalene group where the 1 and 8 positions are non-neighboring components of another aromatic ring unlike cata structures.), but even further into non-planar and planar cata species, and even to the extent of determining the degree of peri-condensation itself. This system can also be used to indicate the degree of thermal processing through the determination of the ratio of substituted to unsubstituted PACs [5,6]. Of direct relevance to the present work is the paper by Lafleur and Nakagawa [3] in which N-methyl-2-pyrrolidinone (NMP) was used as mobile phase; polycyclic aromatic hydrocarbons (PAHs) and many PACs were separated predominantly on the basis of size, with non-size effects evident for polar compounds. Lafleur and Plummer [4] investigated the modification of the stationary phase, but no significant reduction in non-size effects was produced by sulphonation of the poly(divinylbenzene) packing. The main disadvantage of these studies continues to be the restricted molecular mass range accessible with organic compounds which can be bought off the shelf. Very few of these model compounds with a mass greater than 500 are available, whereas molecular masses in excess of 1500 have been reported for coal derivatives by heated probe and field ionization MS [7] and in excess of 3000 by laser desorption MS [8,9].

The second approach has been to investigate the separation of coal-derived samples on the basis of differing functionality. Philip and Anthony [10,11] reported the separation of coal-derived liquids into aromatic, phenolic and asphaltenic fractions by SEC on a Styragel column with both tetrahydrofuran (THF) and toluene as the mobile phase. Unfortunately their assignment of functionality to elution regions was made on the basis of the gas chromatographic analyses of the fractions and only part of each sample would be accessible to this technique.

Richards et al. [12] used elemental and functional group analyses, NMR and voltammetry to examine the structure of coal extracts and their dependence on molecular mass. They reported that for supercritical gas extracts and hydrogen donor solvent extracts there are trends depending on hydroxyl content or aliphatic substituent size. Evans et al. [13] have observed that phenols and amines in coal tars have anomalously low retention volumes in THF and that chloroform can separate the same sample into polynuclear aromatics, phenols and aliphatics. This would seem to be in broad agreement with Lafleur's [2] chromatographic work on model compounds. Mulligan et al. [14] have used SEC with dimethylformamide as solvent and calibration with both model compounds and previously characterized coal-derived fractions, to provide information on both size and chemical type of samples.

The final approach has been the larger scale fractionation of a coal or petroleum derived sample into narrow retention-volume defined elements and the determination of the average molecular mass of each of these by another technique, often vapour pressure osmometry (VPO). Schanne and Heanel [15] separated a technical coal extract into 6 fractions, on Sephadex LH-60–pyridine gel at 60°C with pyridine as eluent. They found a linear relationship between the logarithm of the VPO-measured average molecular mass of the fractions and their elution volume. Despite these fractions being not particularly narrowly defined, in terms of retention time, and probably having a large polydispersity, the largest had an average MM of 3580. The same group [16] also later used the same procedures to calibrate an analytical system up to 2500 with a high temperature coal tar pitch. Bartle et al. [17] have investigated a number of procedures for the calibration of SEC for coal derivatives. They have chromatographically separated asphaltenes, methylated asphaltenes, benzene insolubles and methylated benzene insolubles of both supercritical gas and hydrogen donor solvent extracts of British coals, and a coal tar pitch. The preparative scale separation was performed on PL-Gel columns and with THF as solvent, with fractions characterized by VPO. Again a fairly good linear relationship between log[MM] and V_R, the retention volume, was obtained, although the highest values were obtained for asphaltene samples where the association [18–21] of molecular species may contribute to an increased apparent average molecular mass. The authors pointed out that for best results the calibration of SEC columns should be made with characterized preparative SEC subfractions of materials similar, or ideally identical, to the sample of interest. Buchanan et al. [22] separated the pyridine soxhlet extract of Illinois No. 5 coal on 200–400 mesh SX-1 and SX-2 Bio-Beads. The fractions so produced were again characterized by VPO with a maximum number average molecular mass of 2280 being recorded, before being used to calibrate an SEC system based on polystyrene–divinylbenzene packed Ultragel columns. Molwer et al. [23] have used SEC fractions from a pyrolysis tar to calibrate an analytical column up to ~ 920. Zander [24] has also investigated the variation in nitrogen content of SEC subfractions produced for the calibration of an Ultra-Styragel columns.

Each of these approaches has its own merits and applications. The results from the model compound elution studies and the solvent dependent functional group separations could be taken together to imply that size or mass determination is impossible for fuel derived materials using SEC. However, the successes of the third method suggest that this technique does have a role to play in such characterizations, provided strong mobile phase solvents are employed and a reliable mass determination technique has been applied to SEC fractionated portions of the sample material to provide calibration. In addition, with number average molecular masses of the order of 2500, regularly measured by VPO, clearly these samples must contain molecular species with masses in excess of this, up to at least 5000. The choice of mobile phase is clearly vital in work of this nature. Of equal importance is the detection method employed. Ideally this should be sensitive to the entire chemical diversity of the solute analyzed and have an equal, or determinable, variation of response with molecular mass. In practice these two requirements are never both fulfilled by a single technique, although multiple detectors can be utilized. We therefore report on detector capabilities for one typical and one new mobile phase.

2. Experimental

Two chromatographic systems were employed in

this study. In the conventional SEC system THF was delivered from a Merck Hitachi L6000A solvent pump at 1 ml min^{-1}. Sample injection was performed via a Rheodyne 7125 valve fitted with a 20-μl sample loop. The column set consisted of two Jordi Gel columns (500+100Å pore size, 5 μm poly(divinylbenzene) packing, 250×10 mm) with 5 μm guard column operated at room temperature. Detection was by an Applied Chromatography Systems UV absorption monitor (ACS-750/11) with exchangeable UV filters and a detector cell volume of 10 μl. In series with this was placed a Varex evaporative light scattering detector (model IIa) which was operated at optimized conditions (drift tube temperature: 90°C, nitrogen carrier gas flowrate: 50 ml/min). The detector outputs were fed to an in-house constructed data acquisition system and sampled every 1 s.

The second SEC system consisted of another Merck Hitachi L6000A pump delivering 0.5 ml min^{-1} of NMP. Detection was through a Jasco 875 variable wavelength UV-absorption detector (190–600 nm) with a 4-μl volume high pressure cell. The eluent then passes through a Shimadzu fluorescence HPLC monitor (model RF-530, 240–650 nm) with a 12-μl square quartz flow cell. Data capture facilities were also available. Injection was again via a Rheodyne 7125 valve with 20-μl sample loop. Separations were achieved using a Polymer Labs PL-Gel Mixed E Column with guard (3 μm styrene–divinylbenzene copolymer packing, 300×7.5 mm). The column was housed in a gas chromatography oven and operated at 80°C. A preheating coil was placed between the pump and injector, but inside the oven, to ensure thermal equilibration of the solvent.

2.1. Reagents and samples

HiPerSol HPLC grade, unstabilized THF was supplied by BDH. 99+% HPLC grade NMP was supplied by Sigma-Aldrich. Because of the hygroscopic nature of both solvents they were maintained under an inert atmosphere and purged with dry nitrogen during use. Polystyrene standards were obtained from Polymer Labs.

The number of samples examined in this study was kept small and these were chosen to be representative of a wide range of coal-derived materials. The first of these was a coal tar pitch, a highly thermally degraded material. The second was a Point of Ayr coal hydrogen donor solvent extract from the British Coal Point of Ayr Liquefaction pilot plant, collected after the digestion stage but before hydrotreating, and so only lightly thermally treated. Liquefaction products from Point of Ayr coal, Crumlin lignite and their blends, when coprocessed with hydrogenated anthracene oil (1:2 mixture, 415°C, 30 atm, 60 min; 1 atm=101325 Pa), were also examined.

2.2. Procedure

Samples for injection were dissolved in the appropriate solvent at concentrations of 1–10 mg ml^{-1}. The coal solutions were sonicated at room temperature for 10 min and then syringe-filtered prior to use to remove insoluble material. The columns were conditioned for 30 min at the required operating temperature prior to each set of analyses. Retention times and chromatograms are reported as obtained from the data capture files. Each apparatus was calibrated with polystyrene standards before use.

3. Results

Fig. 1 shows the UV absorption detected chromatogram, detected at 254 nm, of the coal tar pitch as separated on the conventional THF based SEC

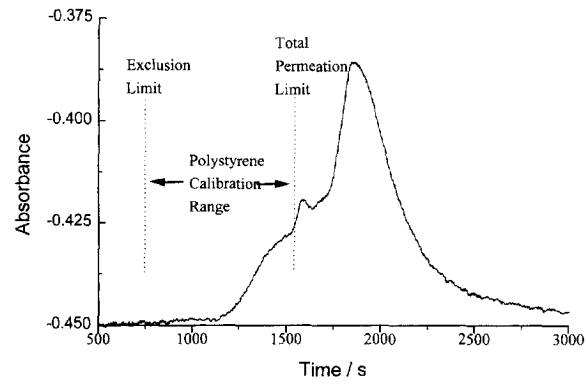

Fig. 1. Chromatogram of soft coal tar pitch in THF detected by UV absorption at 254 nm including the limits of the polystyrene calibration.

apparatus. This is in good agreement with similar investigations reported elsewhere [25]. Also indicated here is the range of the calibration of the columns with polystyrene standards; the complete calibration is shown in Fig. 2. The first figure illustrates the problems caused by the interaction of solute molecules with the column stationary phase. The reversible adsorption of species on to the packing retards the passage of solutes through the column. This leads to the elution of material after the total permeation limit of the column set; in this case defined as the retention time of toluene. Clearly, the original sample does not contain single ring aromatic species. Nor is it expected to contain much non-aromatic, but conjugated material. The delayed elution must be due to column interaction and so the separation is now due to, at least, two mechanisms: size dependent exclusion from the porous gel and essentially normal phase adsorption chromatography as used in HPLC. It is impossible, or at least unwise, to assign a molecular mass or distribution to any part of the chromatogram on the basis of the polystyrene calibration. The extent of non-size retention is clearly dependent upon the chemical functionality and structure of individual species and not constant for all the solute molecules in the sample.

As part of an examination of available detectors suitable for the chromatography of fossil fuels, the chromatograms of the same pitch sample detected by UV absorption at 280 nm and by evaporative light scattering detection (ELSD) are presented in Fig. 3. Comparison reveals that the two UV traces are

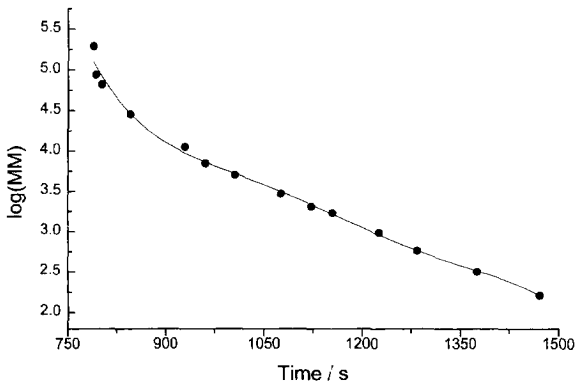

Fig. 2. Calibration of the Jordi-Gel columns with polystyrene standards. The line of least squares best fit, a 5th order polynomial, is also shown.

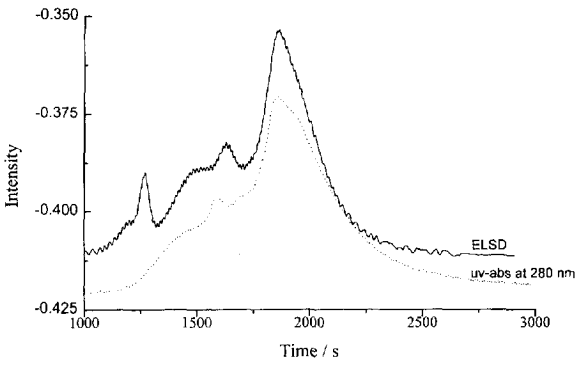

Fig. 3. Comparison of UV absorption and evaporative light scattering detectors for the examination of coal derived materials.

qualitatively very similar, with that at 254 nm being slightly more intense. This suggests that wavelengths other than the most typically employed 254 nm can be used in this type of work. The ELSD trace appears very similar at longer retention times to the UV traces, and is in fact more intense, revealing a greater sensitivity. There is however an important difference in the chromatograms at short retention times. The ELSD trace shows an extra peak and shoulder between times 1100 and 1250 s. If the earliest eluting material is indeed the largest molecular structure in the sample, this detector is far more sensitive to their presence than the UV detectors. This is in agreement with previous studies [26–28] in which the ELSD has been compared to UV and DRI detectors.

Fig. 4a shows the UV chromatograms from the products of the series of blended coal liquefaction experiments. It is difficult to distinguish between the traces and consequently impossible to assess any changes brought about by operating at conditions designed to improve yields by maximizing any interaction between the two coals. Fig. 4b illustrates the early eluting part of the ELSD detected chromatograms. The difference between the two whole coals is evident in the extra maximum at 1275 s in the 100% Crumlin trace. The co-processed samples contain this peak with intensities proportional to the amount of Crumlin present in the original sample for liquefaction. The processing can now be better evaluated through analysis using ELSD.

The nature of coal-derived materials and of the original coals themselves is such that they are not

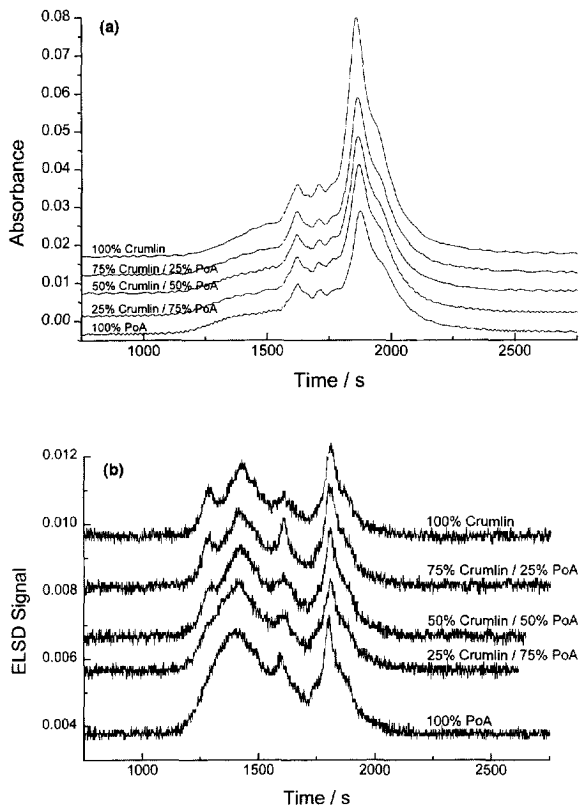

Fig. 4. Application of different detection techniques to the SEC of blended coal liquefaction products. (a) UV absorption at 254 nm, (b) ELSD. Note the difference in the early eluting, high mass, part of the chromatograms.

wholly soluble in typical chromatographic solvents so polar solvents are necessary and the amount of sample which can be analyzed is solvent dependent. There are a growing number of reports in the literature [29–32] where enhanced extraction yields from whole coals have been reported. Often these have employed mixed solvent systems [30,33–36] and additional additives [37]. One such system, NMP and carbon disulphide (1:1) gave yields of up to 60% [33]. The use of mixed solvents, though commonplace in HPLC, is rare in SEC. Of principal concern is how the different solvent molecules would equilibrate within the gel pores, and how this alters the local solubility of the solute. In the case of CS_2, when used with NMP, its high volatility may lead to changes in the mobile phase composition and cause changes in solubility and solvation, ultimately affecting the solute retention volume. NMP has itself been investigated as the mobile phase for thin layer chromatography (TLC) on silica gel plates [25,38] and was consistently found to give the highest R_F values of a number of solvents for coal extracts and a number of larger polyaromatic compounds.

However, NMP also has a number of drawbacks as a chromatographic solvent. Its high viscosity makes it difficult to pump, and creates a high backpressure when passed through modern high efficiency SEC columns which are packed with very small particles ($\leq$10 μm). Utilization of such columns is possible but low flow rates and operation at elevated temperatures are necessary. Detection methods are also restricted with NMP. Its high boiling point (212°C) precludes use of ELSD. Its UV absorption spectra stretches up to just below 400 nm with a total cut-off at 260 nm. Fortunately the partial transparency means operation at 280 nm is possible, albeit with reduced sensitivity. The high viscosity of NMP reduces the effectiveness of the low sensitivity viscometric detector, and the housing of the columns in an oven and the subsequent cooling of mobile phase on passing into a viscometric or refractive index detector can cause baseline problems. These considerations have led to routine operation with the UV absorption and fluorescence detectors at wavelengths of 280 nm and greater, sometimes supplemented by a refractive index detector. These detection restrictions are outweighed by the ability to examine more of the coal-derived material than has been previously possible.

Prior to coal investigations the NMP-SEC apparatus was calibrated with polystyrene standards, despite the previously discussed unsuitability for coal samples, to ensure that a size dependent separation of a simple sample occurs with this system. The dependence of elution time on molecular mass of the polystyrene standards is shown in Fig. 5. Typically such data is often presumed to fit the relationship [39,40]:

$$\log(\mathrm{MM}) = a - bV_R$$

where a and b are experimentally determined constants. Although our mid-range data does show this linear relationship a more widely appropriate work-

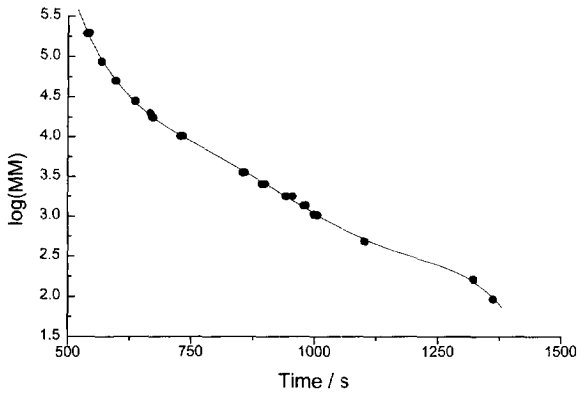

Fig. 5. Evaluation and calibration of the Mixed-E column with NMP as the mobile phase.

ing approximation is the 5th order polynomial shown.

The top line of Fig. 6 shows the UV absorption chromatogram detected at 280 nm of the soft pitch produced using the NMP-SEC apparatus. The most important feature here is that all the sample has eluted by ~1350 s. The elution time of toluene, and therefore the total permeation limit is 1365 s. It follows that all the coal sample elutes before, or up to, the permeation limit. This suggests that none of the solute is being significantly delayed on its passage through the packing material. There is no adsorption of solute on to the column packing. This represents a considerable improvement over the use of THF. Between about 750 and 1365 s, in Fig. 6, there is a peak corresponding to material being separated by the column. There is a second peak at ~550 s which has some structure. The polystyrene calibration suggests this earliest peak corresponds to large molecular species which are being excluded from the packing material pores.

This figure shows the chromatograms for the pitch with detection at a number of different absorption wavelengths. The sample absorbs at wavelengths from 280 to 500 nm and beyond. The traces are not identical because although a species absorbing at 500 nm will probably also do so at 280 nm, the reverse is not necessarily true. The ratio of the intensities of the resolved peak to that of the excluded peak also changes with monitoring wavelength. At longer wavelengths the excluded peak becomes more significant and the above ratio increases. This indicates, for PAHs at least, that the excluded material is indeed larger than that being retained and separated by the column. It is impossible to attribute a molecular mass to these excluded species, because as the calibration in Fig. 5 indicates, very small changes in retention near this limit correspond to very large increases in mass, and species above a critical size will all co-elute at this limit.

Fig. 7 shows the chromatograms of the THF and NMP soluble portions of the soft pitch with NMP eluent and UV absorption detection and allows fairer comparison. The majority of the THF soluble material elutes within the resolving region of the column. There is almost baseline separation between the resolved and the much smaller excluded material peak. This is in contrast to the NMP case where there is a continuous range of material detected. This

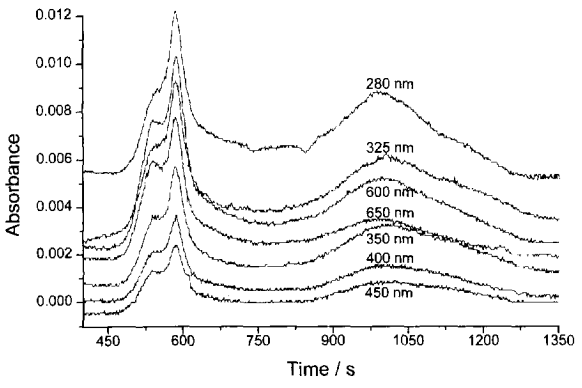

Fig. 6. SEC chromatograms of the coal tar pitch with NMP as the eluent and UV absorption detection at a number of wavelengths (chromatograms are offset).

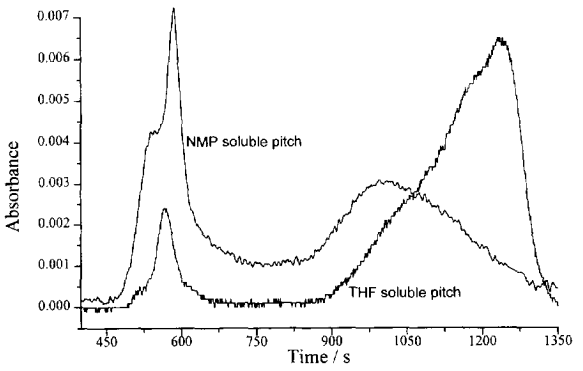

Fig. 7. Chromatograms illustrating the effect of SEC solvent on the amount of the original sample which can be analysed.

illustrates the greater solvent strength of NMP. It is interesting to note that when the THF insoluble but NMP soluble portion of the pitch is examined there is considerable overlap with the THF soluble fraction. This indicates that the solubility of the sample is not just a function of molecular size but also chemical functionality.

The improvements brought about by operating the column at an elevated temperature are illustrated in Fig. 8. On comparing the two UV fluorescence detected chromatograms of a Point of Ayr coal liquefaction extract at 20°C and 80°C, there are two points to emphasize (it should be noted that in these particular experiments the eluent flow rate was 0.2 ml min^{-1}, hence the much larger retention times). First, the passage through the column of the sample as a whole is faster at the higher temperature. This can be attributed to the lower viscosity of the solvent allowing faster mass transport of solute molecules. Secondly the sample peak is narrower at 80°C, with no long tail to later times. This can be explained by a combination of the increased rate of mass transfer and, perhaps more importantly, a reduction in chemical interaction between the solute and the column packing. Any attractive interactions will be less effective at higher temperatures when molecules have more kinetic energy. As a consequence of the solute eluting over a shorter timescale, the peak fluorescence detected is ~10% larger; the system has a higher effective sensitivity at higher temperatures. The reduced analysis times at raised temperatures are also always to be welcomed.

The final observation which can be made from this figure stems from a comparison of the UV absorption and UV fluorescence traces detected at 20°C, which were obtained simultaneously. The absorption peak is much broader, beginning at shorter elution times, but finishing at the same time as the fluorescence trace. This indicates that while the fluorescence detection is excellent for the smaller molecular species, larger molecules are invisible to this technique. This is attributed to the decreased fluorescence quantum yield of larger molecules which have many more channels through which to dissipate energy. It is also clear that species eluting at the exclusion limit exhibit no fluorescence at these wavelengths, but a small fluorescence has been detected for other samples [41] at and above 400 nm.

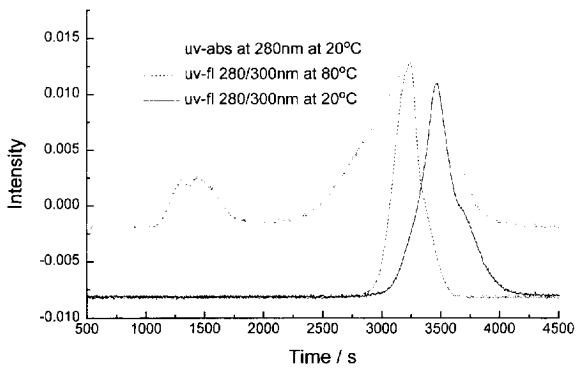

Fig. 8. Effect of column temperature, and detection method, on chromatograms.

4. Discussion

At this point there are also a number of publications on the MS of these and similar materials which should be brought in to the discussion of molecular mass determination. As mentioned in the introduction (Section 1), traditional MS techniques have a restricted mass range. However, the more recently developed laser ablation methods such as laser desorption MS and matrix-assisted laser desorption ionization MS (MALDI-MS) have extended the mass range over which coal materials have been detected to 12 000 [42] and 270 000 [43], respectively. In a series of studies by two of us (AAH and RK) the technique of MALDI-MS has been developed for, and applied to, a range of fossil fuel samples. An examination of the Argonne Premium coal samples by MALDI-MS [44] with sinapinic acid as the matrix revealed large amounts of material up to 5000 and an upper mass limit to the continuum of material to the order of 100 000. In this work this mass limit was found to show a relationship to the carbon content or rank of the coal. Examination of the liquefaction extracts and pyrolysis tars [45] of the same set of coals also showed material at masses significantly in excess of those detectable by the older MS methods, with higher upper limits for the flowing solvent extracts than the volatalized tars, as expected. Analogous results have also been obtained for kerogens [46] and their extracts. Hence, these extended ranges of molecular mass material now

accessible are comparable to those routinely available by SEC.

We have also investigated the effect of solvent and chromatographic separation of samples on their MALDI-MS spectra. Examination of the pitch used in this paper after fractionation by planar chromatography [47] showed that the average molecular mass increased with decreasing mobility in the eluting solvents. This was observed for a number of different solvent systems with, in all cases, the upper mass limit of the different mobility samples being similar. We have also reported initial work comparing the MMDs from SEC and MALDI-MS [48] and this work is continuing. A number of important points have been raised by this and associated work. Firstly it is more difficult to obtain good MALDI-MS spectra of the heaviest material in coal samples. Far more significantly it is also possible to get inaccurate MMDs from samples containing a wide range of molecular masses, with recent papers suggesting fractionation of samples and separate measurements on each fraction [49,50]. Finally the use, and subsequent effects, of a matrix material can be avoided because the range of significant absorption of coal samples includes the wavelength of the ablating laser. These are all points we are currently investigating and will have significant influence on the ability to provide methods for improved and routine molecular mass determination.

5. Conclusions

The experimental chromatographic work described in this paper suggests that NMP is compatible with the requirements for a solvent for fossil fuel derived materials. One of the main problems associated with the SEC of coal-derived materials, that of solute–packing interactions, has been overcome by the use of NMP as the mobile phase; the combination of stronger solvent and operation at raised temperatures being important. In addition, we have noted similar observations when a synthetic mesophase pitch was studied indicating that the problems encountered in SEC of fossil fuel derivatives are not solely attributable to the presence of heteroatoms. However, reliable molecular mass distributions still cannot be assigned to samples because of questions about the suitability of polystyrene molecules as calibrants. In addition, since some elution can now occur before the permeation limit of the column, it cannot be assumed that separation is exclusively due to a size separation mechanism. The combination of highly polar solute molecules with a polar solvent may be causing the early elution of some material [3].

Despite these uncertainties the NMP-SEC system offers encouragement in the pursuit of a chromatographic method for molecular mass determination of fossil fuel derivatives. Furthermore, the analysis of much more of the original sample is possible with NMP. This system is already able to permit better comparison of products from coal processing experiments. While UV fluorescence is not a universal detection method, it is compatible with this solvent and can provide some information for coal-derived samples. UV absorption, albeit operated at longer wavelength, continues to be the detection method of choice. However when NMP based SEC can be combined with ELSD designed to operate above the boiling point of NMP, we will have a powerful chromatographic system.

The opportunity for combining the results from our MALDI-MS and NMP based SEC studies suggests the potential for the absolute calibration of the SEC of coal-derived materials. In progressing towards this ultimate goal further investigations of MALDI-MS and the comparison of chromatographic solvents for SEC will be reported.

Acknowledgments

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