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DETERMINATION OF MOLECULAR WEIGHTS OF COAL DERIVED LIQUIDS BY GEL PERMEATION CHROMATOGRAPHY–HIGH-PERFORMANCE LIQUID CHROMATOGRAPHY

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(First received June 22nd, 1984; revised manuscript received March 15th, 1985)

SUMMARY

A rapid gel permeation chromatographic–high-performance liquid chromatographic procedure for the determination of qualitative and quantitative molecular weight data of coal derived liquids (CDLs) is described. The method analyses class fractions from a CDL and individual calibration curves for each class are derived using standards with similar structures, polarity and functionalities to those present in the particular fraction. The combination of appropriate class calibration data points allowed the derivation of calibration curves for the more complex materials such as the total CDL. This approach minimizes elution behavioural effects peculiar to particular compound classes *e.g.*, H-bonding complexation of phenols, as they are included in the class calibration curve. A comparison of the number average molecular weights determined by this method with those by vapor pressure osmometry gave excellent agreement.

INTRODUCTION

A major problem in the area of research into the direct liquefaction of coal is the determination of molecular weights (MW) of coal derived liquids (CDLs) and their fractions. Various methods have been used including cryoscopy¹, vapor pressure osmometry (VPO)^{2–7}, mass spectrometry (MS)^{8–12}, gel permeation chromatography (GPC)¹³ and GPC–high-performance liquid chromatography (HPLC)^{14–18}. Some of these methods (cryoscopy, VPO) give only a single numerical value, *viz.*; the number-average MW (\bar{M}_n), while others (MS, GPC and GPC–HPLC) also give MW profiles. The use of a single value, \bar{M}_n , is limited in this situation due to the complex heterogeneous nature of the materials. An MW profile is more informative if only in a qualitative sense, as it allows comparison with those oils produced under different reaction conditions and hence the determination of MW trends. Although a quantitative value of the MW is desirable, in order to appreciate the average structural size of the material in coal derived liquids, it is of little value without a corresponding profile to give the range of MW. Quantitatively, a profile is also more informative in that it allows not only the calculation of \bar{M}_n , but also \bar{M}_w (weight-average MW)

and MWD (the MW distribution, which is a measure of the polydispersity of the sample¹⁹) thus giving better insight to trends that can be qualitatively obvious. The calculations for \bar{M}_n , \bar{M}_w and MWD (eqns. 1–3) are the same for each case; however, quantitative data requires the use of appropriate calibration standards.

$$\bar{M}_n = \frac{\sum_{i=1}^n H_i}{\sum_{i=1}^n (H_i/M_i)} \quad (1)$$

$$\bar{M}_w = \frac{\sum_{i=1}^n H_i M_i}{\sum_{i=1}^n H_i} \quad (2)$$

$$\text{MWD} = \frac{\bar{M}_w}{\bar{M}_n} \quad (3)$$

where H_i is the peak height of component and M_i is the molecular weight corresponding to elution volume of component, as determined from calibration graph.

GPC and now more commonly GPC–HPLC provide rapid and relatively inexpensive methods for both the qualitative and quantitative MW analyses of CDLs. The mechanism of size-exclusion separation is still uncertain with some claiming the elution volume (V_e) is a function of the length of the molecule^{17,20,21} while others believe it is a function of the molecular volume^{22,23}. However, MW can still be correlated to V_e and hence quantitative values, determined by the use of a calibration curve derived from appropriate standards. These standards ideally should be structurally similar to the components in the mixture to be analyzed. Since GPC–HPLC has predominantly been used in the routine analyses of polymers the majority of commercially available standards are different MW linear-chain molecules, typically *n*-alkanes, polystyrene, polypropylene, polyethylene oxide and polyethylene glycol polymers. These standards have been used for CDL analysis¹⁵, although only to give semi-quantitative information. Considering the complex, highly functionalized and aromatic nature of CDL components, the use of polymer standards for MW calibration has disadvantages. The GPC elution behaviour of small molecules with a variety of functionalities have been studied^{20–26}. Although these examples include phenols, alcohols, esters, amines and carboxylic acids, they have generally contained long alkyl side chains. The intention was to allow the effect of the functional group on the molecule relative to the parent alkane to be assessed. These studies, although showing that functionality causes deviations from alkane behaviour, were of a theoretical rather than an applied nature. These long chain mono- and di-functionalized alkanes, if present in coal derived liquids are in negligible amounts. Appropriate calibration standards that are structurally and functionally similar to the sample continue to be major problems in the MW analysis of CDLs.

Khan¹⁸ has recently reported an approach to overcoming calibration prob-

lems. Using the hexane soluble portion of the 200°C boiling range fraction of a CDL he has separated it into discrete fractions by GPC-HPLC, then determined each of their \bar{M}_n values by VPO to produce a calibration curve based on the product itself. The other boiling point range fractions (up to 520°C) then had their \bar{M}_n , \bar{M}_w and MWD determined using this calibration curve. Overall this approach is satisfactory although there are several problems with its rationale and practice. (1) The fraction used to derive the calibration curve was material boiling below 200°C; it structurally may not represent the higher boiling CDLs. (2) It is derived from a catalyzed process (H-Coal) which produces a CDL as a refinery feedstock, hence it is analogous to crude oil. This CDL is very different structurally, physically and chemically to those produced by other processes *e.g.*, solvent refined coal (SRC) and Synthoil, which are often the initial coal dissolution products. These are typically very viscous (often being solid at ambient temperature), polar, functionalized and aromatic, containing a vast array of compounds. It is unlikely, therefore that a particular small boiling point range fraction of this type of material would provide a realistic MW calibration curve for these higher boiling fractions. (3) The quantitative MW data was derived from profiles produced by UV detection. This technique for absolute quantitation requires knowledge of molar extinction coefficients for each component as absorbance is only proportional to concentration, and hence the intensity at a particular V_e . The accuracy of the MW data is therefore open to question.

The need for appropriate class calibration standards and refractive index (RI) detection for complex material such as CDL MW analyses is evident. This paper reports a different, and we believe a more satisfactory approach whereby the rationale has been to use acid, base and neutral fractions separated from a total CDL by functionality. In these fractions, the types and classes of compounds present are known. A calibration curve for each compound class has been derived using standards that are structurally and functionally similar to those known to compose the CDL fractions. Hence, the behaviour of each class of components on GPC can be assessed. The combination of the different class calibration curves then allows the derivation of those same curves for the total CDL and total neutrals fraction. The \bar{M}_n determined by this method and reported here for the total CDL respective fractions have been compared with those from VPO with very good agreement being obtained.

EXPERIMENTAL

Apparatus

The GPC-HPLC system consisted of a UK6 injector and R401 differential refractometer detector (Waters Assoc., Milford, MA, U.S.A.), a 110A single chambered pump and a Model 153 UV detector operating at 254 nm (Altex, Berkeley, CA, U.S.A.). The UV and RI chromatograms were recorded on a Houston Instruments Omniscrite dual channel recorder. The columns (30 cm × 8 mm I.D.), connected in the following order from the pump to prevent decomposition of the smallest pore size²⁷, were 1000 Å, 500 Å, and 100 Å μ Styragel (Waters Assoc.). Tetrahydrofuran (THF) served as solvent for all the standards and CDL samples. These were filtered through a 0.5- μ m filter, using a sample clarification kit (Waters Assoc.) to remove any insoluble particles prior to analysis. The sample size injected was 50 μ l of a 1.0% (w/v) solution. The flow-rate was maintained at 1.0 ml/min.

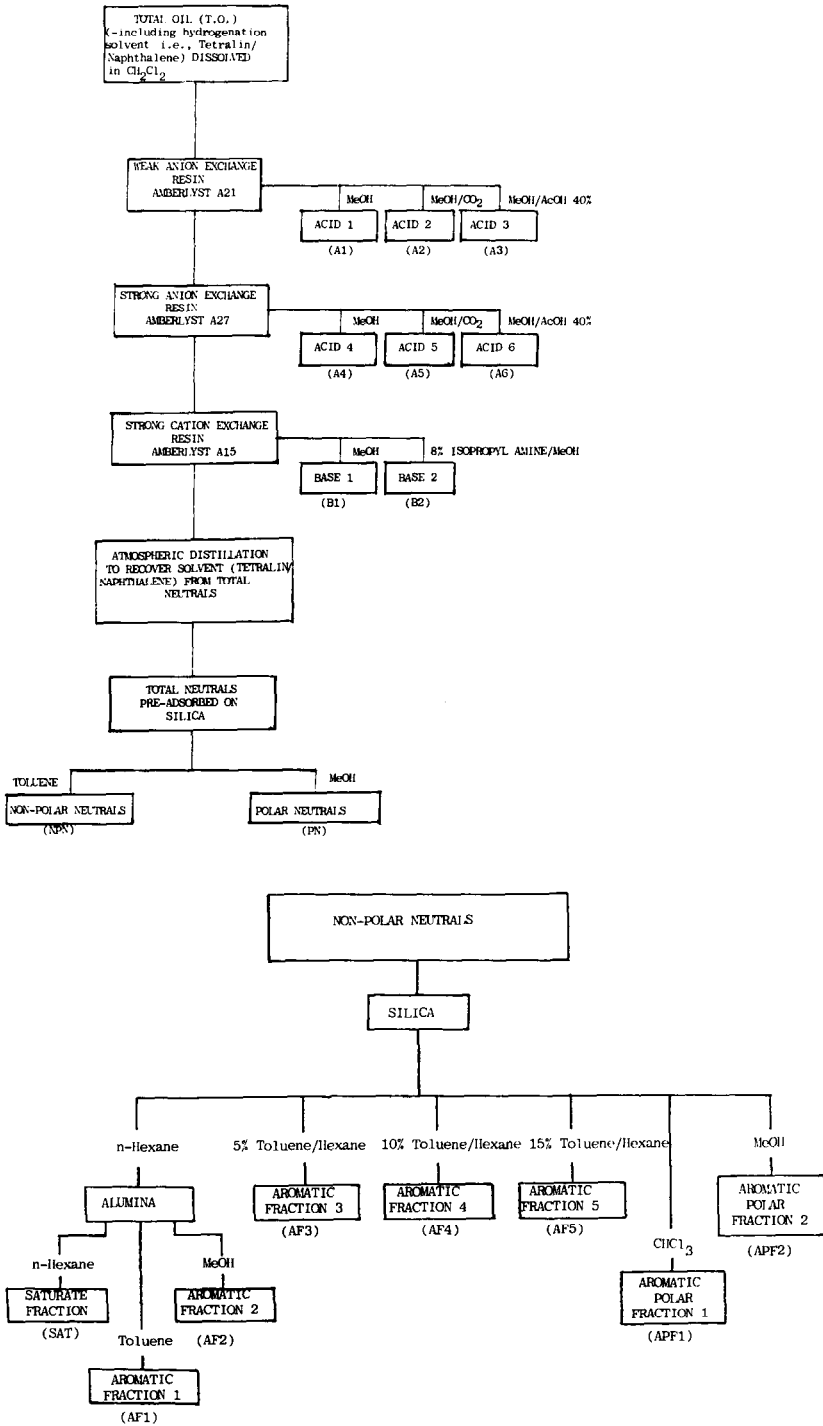


Fig. 1. Resin separation schemes.

The \bar{M}_n of the CDL samples, determined by VPO were performed on a Knauer No. 11 vapor pressure osmometer with THF as the solvent. Calibration was accomplished using benzil (MW, 210) as the standard and at least four different concentrations were used for each sample analyzed.

Reagents

The same THF was used for both GPC-HPLC and VPO and was unstabilized (UV-grade, Waters Assoc.). The standards (Table I) were procured commercially or synthesized. They were purified before use and their purity checked by both physical constants and HPLC [C_{18} column (30 cm \times 3.9 mm I.D.); methanol as solvent].

Coal derived liquid

The CDL was produced by the uncatalyzed hydrogenation in tetralin of a Victorian brown coal. The coal was from the Loy Yang field (bore 1277, 67–68 m) and was a medium-light lithotype. The liquefaction was performed using a 1-l magnetostirred-batch autoclave at the following conditions: temperature, 375°C; reaction time at temperature, 2 h; initial hydrogen pressure, 1500 p.s.i.; Coal-solvent ratio was 1:2. The CDL is a tar at ambient temperature and was separated by ion-exchange and adsorption chromatography into various acidic, basic and neutral fractions which were characterized by spectroscopic and analytical methods. The separation procedure is outlined in Fig. 1. Details of the procedure and characterization are given in ref. 28. Gas chromatography (GC)-MS analyses of representative fractions have shown that alkyl substituted mono- and di-hydric phenols and naphthols are the major components of the acid A1 fraction; alkyl substituted pyridines and quinolines for the base fraction, B2; and mono-, di-, tri- and tetra-aromatic hydrocarbons for the aromatic fraction, AF1.

RESULTS AND DISCUSSION

The intention of this study was to analyse a total CDL already separated into its compound classes, and to assess their behaviour on GPC by use of model compounds which are structurally and functionally similar. Indirectly, the elution behaviour and hence MW data of these fractions can then be obtained by use of appropriate class calibration curves. The model compounds (Table I) are separated into five distinct classes: aliphatics, aromatics, acids (phenols), bases and polar neutrals; these reflected the components of the CDL fractions.

The behaviour for low MW compounds on GPC is much more complex than equating molecular size to V_e , as is observed with polymers. Rather the major determinants of elution behaviour appear to be polarity, aromaticity and functionality^{16,24}. Because the depolymerization of the coal matrix during liquefaction produces lower MW fragments, the model compounds used in this study are typically, of lower MW and hence susceptible to non-ideal elution behaviour. This is illustrated here by the comparison of three similar MW compounds; toluene (MW, 92; V_e , 30.3 ml), aniline (MW, 93; V_e , 26.5 ml) and phenol (MW, 94; V_e , 27.7 ml). Although they each possess a mono aromatic nucleus they are functionally different. The neutral molecule (toluene) elutes much later than either its acidic (phenol) or basic (aniline) counterparts. The latter both contain active hydrogen groups which are known^{17,22,24,25} to

TABLE I

GPC ELUTION DATA FOR COMPOUNDS USED AS STANDARDS

Columns, 100 Å and 500 Å μ Styragel; solution, 1% in THF; flow-rate, 1 ml/min.

<i>Compound class</i>	<i>MW</i>	<i>Log MW</i>	<i>V_e (ml)</i>
<i>Aliphatics</i>			
Nonane	128	2.11	27.2
Dodecane	134	2.13	26.3
Hexadecane	224	2.35	24.7
Tetracosane	338	2.53	24.0
Tricontane	422	2.63	23.2
Polyethylene glycol	800	2.90	21.8
Polypropylene glycol	1200	3.08	20.4
Polypropylene glycol	2000	3.30	19.5
Polystyrene	2220	3.35	19.7
Polystyrene	3570	3.55	19.1
Polypropylene glycol	4000	3.60	17.7
Polystyrene	9168	3.96	17.6
<i>Aromatics</i>			
Toluene	92	1.89	30.3
Naphthalene	128	2.11	30.5
Tetralin	132	2.12	30.5
2-Methylnaphthalene	142	2.15	26.8
Diphenyl	154	2.19	27.4
Acenophthene	154	2.19	31.4
2,6-Dimethylnaphthalene	156	2.19	29.6
Phenanthrene	178	2.25	30.2
Anthracene	178	2.25	30.1
Dibenzyl	182	2.26	26.1
Fluoranthene	202	2.31	29.9
Pyrene	202	2.31	30.9
Benzanthracene	228	2.36	29.5
Chrysene	228	2.36	29.9
Triphenylene	228	2.36	29.7
<i>p</i> -Terphenyl	230	2.36	29.8
Retene	234	2.37	28.2
Dibenzopyrene	306	2.49	30.1
Coronene	306	2.49	31.4
Dibenzo(<i>g,p</i>)chrysene	328	2.52	27.6
Ovalene	398	2.60	29.0
Rubene	532	2.73	25.7
<i>Acids (phenols)</i>			
Phenol	94	1.97	27.7
<i>p</i> -Cresol	108	2.03	27.4
Catechol	110	2.04	26.5
Resorcinol	110	2.04	26.4
<i>p</i> -Ethylphenol	122	2.09	27.1
2,3,5-Trimethylphenol	136	2.13	27.2
2-Hydroxy-5-methylbenzaldehyde	136	2.13	29.6
Salicylic acid	138	2.14	27.3
2-Naphthol	144	2.16	25.1
Tetralinol	148	2.17	27.8
2,7-Dihydroxynaphthalene	160	2.20	25.8

TABLE I (continued)

<i>Compound class</i>	<i>MW</i>	<i>Log MW</i>	<i>V_e (ml)</i>
4-Propyl-2-methoxyphenol	166	2.22	27.1
<i>p</i> -Hydroxydiphenyl	170	2.23	26.8
1,2-Dihydroxy-3-carbomethoxynaphthalene	186	2.27	27.0
1-Hydroxyphenanthrene	194	2.29	26.1
4-Hydroxyphenanthrene	194	2.29	26.7
6-Hydroxy-2-phenylbenzofuran	210	2.32	26.5
4-Hydroxy-2-phenylbenzofuran	210	2.32	26.5
2,6-Di- <i>tert.</i> -butyl-4-methylphenol	220	2.34	26.3
7-Hydroxy-8-acetyl-4-methylcoumarin	220	2.34	27.3
1-Hydroxyanthoquinone (juglone)	224	2.35	29.0
2-Hydroxy-4-benzyloxybenzaldehyde	228	2.36	26.9
5-Hydroxy-3-carboxy-2-phenylbenzofuran	254	2.40	25.5
1-(2'-Hydroxymethylphenyl)-2-hydroxy-7-methoxynaphthalene	279	2.45	25.6
5-Hydroxy-3-carboethoxy-2-phenylbenzofuran	282	2.45	25.9
<i>Bases</i>			
Pyridine	79	1.90	29.4
Aniline	93	1.97	26.5
N-Methylaniline	107	2.03	27.3
Indole	117	2.07	28.0
N,N-Dimethylaminopyridine	122	2.09	31.7
Quinoline	129	2.11	29.2
1-Aminonaphthalene	143	2.16	26.5
2-Aminonaphthalene	143	2.16	26.5
Carbazole	167	2.22	29.2
Diphenylamine	169	2.23	27.7
1,2,3,4-Tetrahydrocarbazole	171	2.23	25.8
2-Benzylbenzimidazole	208	2.32	27.4
1,2-Dihydrobenzocarbazole	219	2.34	28.0
2'-Phenyl-2-ethylbenzimidazole	222	2.35	25.5
9-Chloro-3-nitroacridine	258	2.41	26.8
2,3-Diphenylquinoxaline	258	2.41	25.9
1,8-Bis(3-aminoacridine-9-ylamino)octane	528	2.72	26.0
<i>Polar neutrals</i>			
Benzofuran	118	2.07	30.5
1,4-Naphthoquinone	158	2.20	27.3
Dibenzofuran	168	2.23	29.8
Diphenyl ether	170	2.23	26.9
Benzophenone	170	2.23	26.7
Fluorenone	180	2.26	27.5
Diphenyl carbinol	184	2.26	26.8
Phenanthrene	196	2.29	27.7
Dibenzyl ether	198	2.30	26.0
Anthraquinone	208	2.32	27.6
9,10-Phenanthraquinone	208	2.32	26.1
Spiro[fluorene-9,9'(10'H)-phenanthren]-10'-one	344	2.54	24.1
1-Carbomethoxy-3-carboethoxy-6-methoxy-7-phenoxy-naphthalene	390	2.59	23.6

form H-bonded complexes with THF in GPC. This results in the compound having a greater apparent molecular size and hence displaying non-ideal behaviour. The application of inappropriate calibration curves may produce MW values that are several orders of magnitude too large.

As models have been selected in order that their GPC behaviour should approximate closely to that of the fractions, any such interactions are compensated for in the resultant calibration curve *i.e.*, the V_e will reflect the *actual* not the apparent MW. Solute-solute interactions, which are usually a problem in very concentrated solutions and where acid-base complexation can occur, have been minimized in this study. This was achieved by the use of low sample concentrations (2.0%, w/v) and the separation of acids and bases (except for the total CDL) prior to GPC analysis. The possibility of adsorption phenomena, generally of little concern in GPC, are also reduced by low sample concentration.

The μ Styragel columns were selected to give a mass range up to 15 000 a.m.u., with the individual columns having the following resolution: column (1) MW < 700, 100 Å; column (2) 700 < MW < 12 000, 500 Å; column (3) 12 000 < MW < 15 000, 1000 Å. This mass range was considered adequate as MW profiles of CDL determined by field desorption and ionization MS do not much extend beyond 1200 a.m.u.⁹⁻¹¹. The typically broad resolution given by these columns for a total CDL can be seen in the UV and RI traces (Fig. 2). The GPC chromatograms of the different fractions are also similarly dispersed due to their complex nature; but they are functionally and physicochemically much less heterogeneous.

A major problem with obtaining suitable calibration standards is the limited mass range available. These are typically 300-500 a.m.u. for most synthetic organic compounds. The MW range above 550 a.m.u. was calibrated using polar polymer standards such as polyethylene and polypropylene glycol. These do not reflect adequately, structurally and functionally, the components comprising the various fractions. However, at this MW range the very small proportion of CDL material above 700 a.m.u.¹² and the lack of suitable MW standards suggest that this approach is the most rational and pragmatic. The emphasis has thus been placed on the MW range below 700 a.m.u. as the five compound classes show quite different trends in this region. The individual calibration curves for these classes are shown in Figs. 3-7.

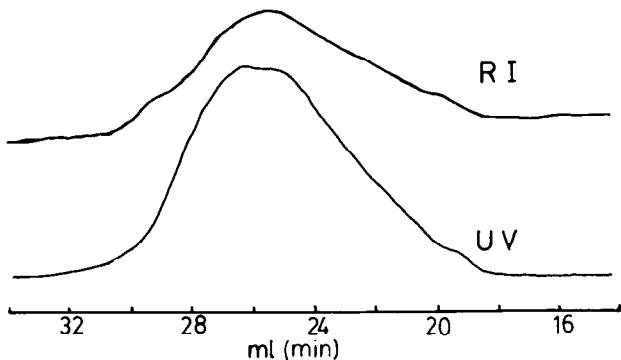


Fig. 2. UV and RI chromatograms of an unseparated CDL.

Primary calibration curves

Aliphatics. The *n*-alkanes and straight-chain polymer standards included polar polymers such as polyethylene and polypropylene glycol. Several workers have reported^{16,21,25} the effect of monofunctional substitution by groups such as hydroxyl and carboxyl on the elution behaviour of long linear-chain alkanes. They found that although alcohols and acids appeared larger, due to solvation effects, both series approached asymptotically the alkane calibration curve. Hence, the error involved in calibrating with either functionalized polymers would be minimal, especially at the higher MW region in which they were used. These aliphatic standards gave the expected, almost linear increase in V_e with decreasing MW, as shown by calibration curve A (Fig. 3). Cyclic aliphatics which are known to be present in CDL^{29,30} were not used as standards in this study as it has been reported¹⁶ that their elution behaviour is analogous to the equivalent *n*-alkanes.

Aromatics. The aromatic standards chosen were structurally diverse displaying various forms of condensation and alkyl substitution. Edstrom and Petro²⁴ determined the elution behaviour of over 100 poly-aromatic hydrocarbons (PAHs) and found it to be a complex function of size, shape and polarity. They indicated that the type and position of alkyl substituents can greatly affect a compound's elution characteristics. This is in marked contrast to Hendrickson and Moore²⁰, and Philip and Anthony¹⁷ who maintain that elution behaviour, even for PAHs is a function of effective chain length. The latter have reported compounds such as coronene and anthracene having effective chain lengths of six; thus suggesting that these molecules have the same V_e values as *n*-hexane. In this study we did not find this relationship as the values of V_e for coronene (MW, 306) and anthracene (MW, 178) were 31.4 ml and 30.1 ml, respectively. Similarly, it was found that the *n*-C₉ alkane, (MW, 128; V_e , 27.2 ml) and its equivalent chain aromatic hydrocarbons ovalene (MW, 398; V_e , 29.0 ml) and rubrene (MW, 537; V_e , 25.7) did not observe this "effective chain length" elution behaviour. Our data suggest that this hypothesis is too simplistic for aromatic systems (*cf.* Edstrom and Petro²⁴).

Alkyl substituents can alter elution behaviour considerably compared to the unsubstituted parent aromatic compound. For example, the monoalkylated naph-

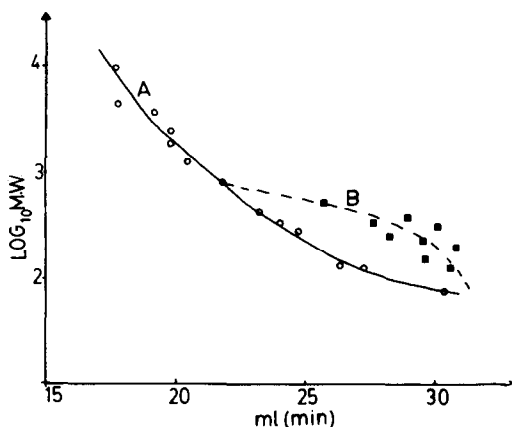


Fig. 3. Aliphatic and aromatic calibration curve derived from components listed in Table I. ○, Aliphatics; ■, aromatics.

thalenes elute before the dialkylated, which elute before the unsubstituted parent aromatic compound. Thus the dialkylated compound would appear to be of lower MW than the monoalkylated compound. Similar structural perturbation of the elution order for substituted anthracenes were observed by Edstrom and Petro²⁴.

The aromatic calibration curve B (Fig. 3) shows by its non-linearity the influences of marked structural effects. It curves upwards, away from the corresponding aliphatic curve A. Hausler *et al.*¹⁶ have similarly observed that fused ring aromatics give very different calibration plots to *n*-alkanes. This observation, they suggested, may indicate that separation occurs by mechanisms other than by size exclusion. These workers also reported elution behaviour as being dependent on the number of aromatic rings and not on their structural nature. They observed the elution behaviour of compounds such as binaphthyl and biphenyl to mimic their fused-ring analogues. Our study did not find this correlation and the data suggests such a relationship, if it exists, is more complex. The salient feature of this elution study of aromatic hydrocarbon standards is the non-predictability of elution behaviour. Because it is a complex function of many criteria, a calibration curve can only be derived experimentally and is shown in Fig. 3.

Acids (phenols). The acidic material in the total CDL is predominantly phenolic^{28,30,31}. This phenolic material includes mono-, di- and polyhydroxy species which are present on rings that may extend to large fused aromatic systems. The model compounds were chosen for their structural and functional diversity. The formation of H-bonding complexes and the resultant apparent increase in molecular size was observed for all the phenolic standards in this study. Their V_e values were all lower than the corresponding parent hydrocarbons, *e.g.* *p*-cresol (MW, 108; V_e , 27.4 ml) and toluene (MW, 92; V_e , 30.3 ml). The overall effect of H-bonding complexation tended to override subtle structural differences. Single-ring monohydric phenols eluted later than their dihydric analogues; *cf.* the comparative elution behaviours of phenol (MW, 94; V_e , 27.7 ml) and catechol (MW, 110; V_e , 26.5 ml). However, this "diol" elution effect was reversed for diaromatic phenols such as 2-hydroxynaphthalene (MW, 144; V_e , 25.1 ml) and 2,7-dihydroxynaphthalene (MW, 160; V_e , 25.8 ml). The monohydric phenol series had diaromatic eluting before the monoaromatics, with the triaromatic eluting in between; this is well illustrated by phenol, 2-naphthol and 1-phenanthrol (MW, 194; V_e , 26.1 ml). The elution of phenanthrol midway between phenol and naphthol is unexpected, and may be related to its non-linear, catacondensed structure. This may limit accessibility of the THF and hence complex formation.

Tetralinol (MW, 148; V_e , 27.8 ml), which is a hydroaromatic species, has elution behaviour very similar to alkylated monophenols such as *p*-cresol (MW, 108; V_e , 27.4 ml) and 2,3,5-trimethyl phenol (MW, 132; V_e , 27.2 ml), thus confirming its alkylated nature. The parent hydrocarbons, toluene and tetralin, have almost identical elution volumes (30.3 ml and 30.5 ml, respectively), however these are also identical to naphthalene (V_e , 30.5 ml). Unlike the case with naphthol and tetralinol there is no MW discrimination. This difference in behaviour between class analogues makes rationalization difficult.

The experimental calibration curve C (Fig. 4) shows that elution of lower MW phenolic material is structurally, functionally, as well as MW dependent.

Bases. The bases present in the total CDL have been reported³²⁻³⁵ to be of two

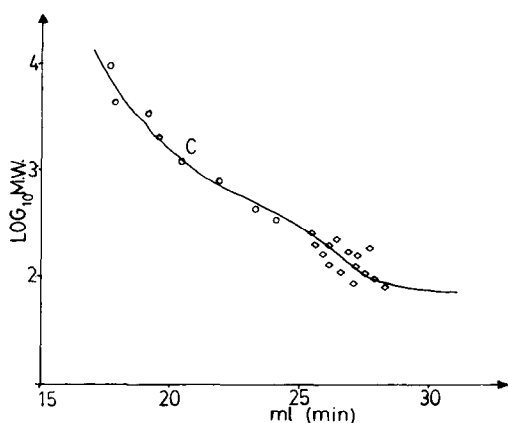


Fig. 4. Acid (phenol) calibration curve. \diamond , Acids; \circ , polyol aliphatic standards as in Figs. 3, 5 and 6.

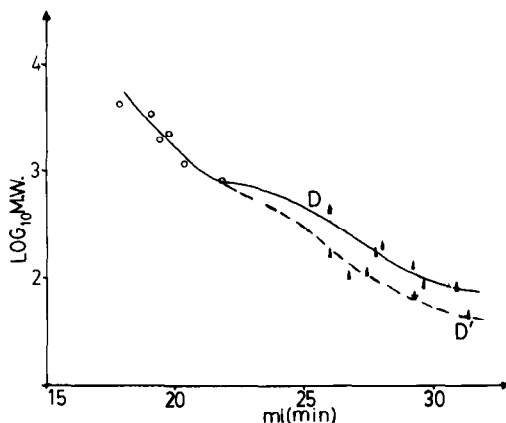


Fig. 5. Base calibration curve. —, Heterocyclic aromatics; ---, aromatic amines.

structural types; aromatic amines such as aniline and heterocyclic aromatics such as pyridine. The elution behaviours of both types were investigated and found to differ substantially. This is illustrated in Fig. 5 by the two distinctly different base calibration curves D (heterocyclic aromatics) and D' (aromatic amines); for the components of each clustered into two separate groups. A comparison of each type shows that the aromatic amines elute at lower V_e values than their heterocyclic aromatic counterparts. This is not unexpected as aromatic amines can form H-bonding complexes, thus increasing their apparent molecular size, whereas the heterocyclic aromatics apparently do not, and their elution behaviour is similar to the parent aromatic hydrocarbons. Both types of bases showed the same trends for the number of fused aromatic rings with both mono- and di-aromatic species having very similar or identical elution volumes. This non-MW dependent elution behaviour was not observed for a substituted acridine (a fused three-ring heterocyclic aromatic) which eluted as predicted, well before quinoline. This perturbation of elution behaviour for both basic types with mono- and di-aromatic systems is again difficult to rationalize.

Hausler *et al.*¹⁶ have reported that aromatic amines undergo a gel sorption phenomenon in addition to size exclusion, whereas ring-nitrogen containing systems behave in a similar manner to hydrocarbon aromatics. This gel adsorption hypothesis, although capable of explaining the differences in elution behaviour for the different types of bases, does not predict the elution order observed to be opposite to that expected, as the aromatic amines would be retained longer on the gel. This explanation may be too simplistic as it does not seriously consider the effect of solvent H-bonding complexation with aromatic amines.

The calibration curve (Fig. 5) used in the quantitative determination of the MW of the CDL bases was curve D. This was again experimentally derived and the models chosen were mainly heterocyclic aromatic in nature³¹ in order to approximate to the composition of the base fraction used in this study.

Polar neutrals. The polar neutral fraction of the CDL used in this study contained predominantly oxygenated functionalities such as ethers (both diaryl and heterocyclic *e.g.* furans), ketones (including quinoid structures), esters and alcohols,

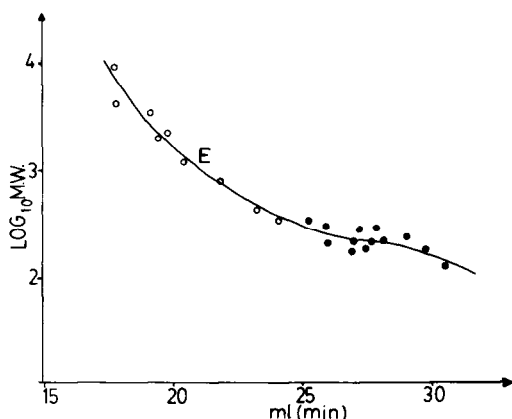


Fig. 6. Polar neutrals (●) calibration curve. ○, See Fig. 4.

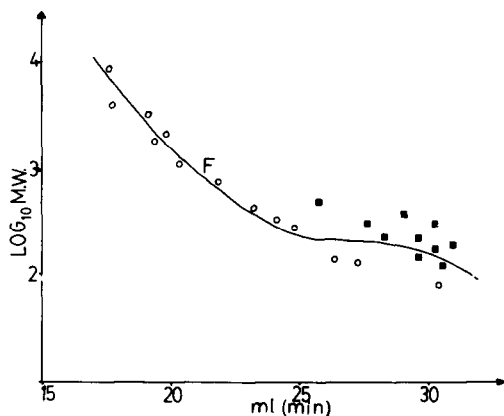


Fig. 7. Non-polar neutrals calibration curve derived from a combination of aliphatic and aromatic standards listed in Table I and plotted in Fig. 3.

all associated with aromatic systems²⁸. The standards used for this calibration curve E (Fig. 6), reflect these functionalities and aromatic structures. Again elution behaviour reflects complex relationships but the calibration curve approaches linearity in the lower MW region (350–150 a.m.u.) showing a general decrease in V_e with increasing MW.

For all the calibration curves, both primary and secondary, the line-of-best-fit was manually drawn so as to bisect the clusters of points.

Secondary calibration curves

The secondary calibration curves were derived by appropriate combinations of the primary curves. The calibration curve F (Fig. 7), was derived by combining the data points from curves A and B as this fraction consists of non-polar neutral saturate and aromatic hydrocarbons³⁶. The total neutrals are comprised of the non-polar and polar neutral fractions, thus it contains saturate and aromatic hydrocarbons, and oxygen functionalized aromatics. The calibration curve G, (Fig. 8) was thus derived by combining the data points of curves A, B and E. Similarly the calibration curve H, for the total CDL (Fig. 9) was derived by combining the data points from all the primary fractions (A–E), as it contains all these compound classes³¹.

The quantitative MW for each fraction and the total CDL was determined using eqns. 1–3 given earlier. This can be done either manually, which is time consuming, or rapidly using a computer programme which incorporates as well as the three equations all the calibration curves and allows selection of the one appropriate to a particular situation³⁷.

Comparison of MW data with that from vapor pressure osmometry

The MW data for all the fractions and CDL are shown in Table II. The approach used in this study was substantiated independently by separately determining the MW of the same fractions by an alternate method, VPO. THF was used as the solvent for these measurements as solute–solute and solute–solvent interactions also occur in VPO. It was also desirable to use the same solvent for both methods as any

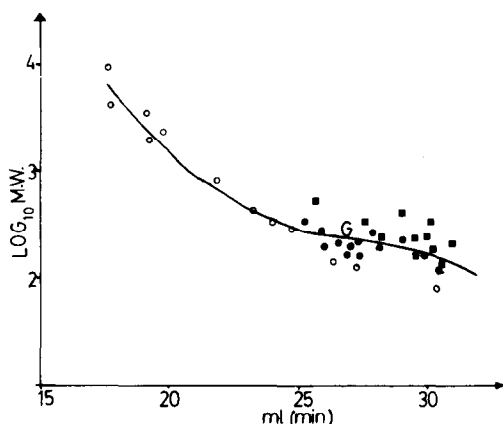


Fig. 8. Total neutrals calibration curve derived from a combination of aliphatic, aromatic and polar neutrals listed in Table I and plotted individually in Figs. 3 and 6.

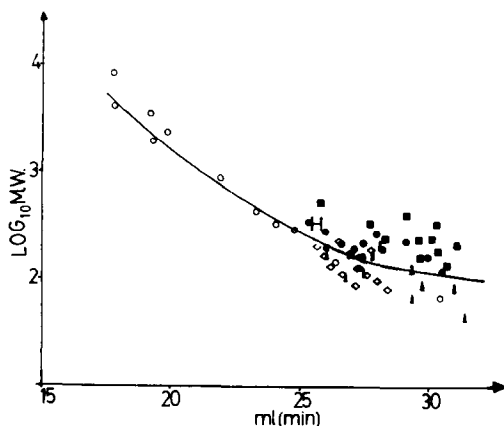


Fig. 9. Total CDL calibration curve derived from all classes listed in Table I and plotted individually in Figs. 3-6.

solvent induced effects would then cancel. The agreement between the \bar{M}_n determined by the two methods is generally excellent (*cf.* Table II). This is also shown comparatively by the ratio of the two \bar{M}_n values. There are a few exceptions, mainly acidic fractions A6 where the GPC-HPLC \bar{M}_n value is 708, and the VPO \bar{M}_n value 1040. This fraction is highly functionalized, it is also the most polar³¹ of the weak acid fractions and would be expected to have significant solute-solvent interactions in VPO; the disparity in values is then not surprising. This fraction accounts for less than 2% (w/w) of the total CDL, and an error in its MW determination should have little effect on the overall MW data of CDL. The other exceptions, B1 and B2 still show good agreement between the two methods. The lower values from GPC-HPLC

TABLE II

COMPARISON OF MW DETERMINED BY GPC-HPLC AND VPO

Fraction*	GPC-HPLC			VPO \bar{M}_n	$\frac{\bar{M}_n \text{ (GPC-HPLC)}}{\bar{M}_n \text{ (VPO)}}$
	\bar{M}_n	\bar{M}_w	MWD		
Total CDL	498	1059	2.11	487	1.02
A1	338	510	1.51	340	0.99
A3	441	853	1.93	460	0.96
A4	632	1074	1.70	570	1.11
A6	708	1373	1.94	1040	0.68
B1	442	649	1.47	500	0.88
B2	471	687	1.46	570	0.83
TN	260	299	1.15	265	0.98
NPN	225	272	1.21	248	0.91
PN	390	700	1.79	407	0.96

* Fraction nomenclature: A = acid; B = base; TN = total neutrals; NPN = non-polar neutrals; PN = polar neutrals. Description of separation method and differences in fractions of same chemical class are given in ref. 28 and illustrated in Fig. 1.

compared to VPO most probably arise from using a calibration curve based only on heterocyclic aromatic bases. The CDL base fraction also contains minor amounts of aromatic amines hence the calibration curve should ideally be a weighted combination of the curves for the two base types. The aromatic amines would also be expected to form H-bonded complexes in the VPO, thereby increasing their apparent MW. The same trend of B2 to show a slightly larger MW than B1 was observed by both methods. The excellent agreement between the \bar{M}_n values for the non-polar neutrals, total neutrals and total CDL supports the combination of the data points from the component class curves in this method of approach. Similarly, the overall excellent agreement of VPO and GPC-HPLC derived \bar{M}_n values gives strong support to the rationale of this study *viz.*, determining individual class calibration curves and then recombining them to determine MW data for more complex fractions.

The MW and MWD can also be derived from the GPC-HPLC data, thus allowing greater insight to the MW range of the fraction. The fractions all have broad, little resolved MW distributions as shown by the large values of MWD (Table II, Fig. 2), indicating their polydisperse nature. This is not surprising as the fractions although separated by class, are composed of many components of differing MW and physicochemical properties and hence elution behaviours. The large values for \bar{M}_w further support the MW diversity of these fractions. This lack of resolution for class CDL fractions was also observed by Hausler *et al.*¹⁶ in an SRC. Similarly, they accredited this to the complexity of the material, also noting that some species in the SRC were separated via a non-size exclusion mechanism, suspecting these to be predominantly fused-ring aromatics and aromatic amines. However, the fractions reported here all had lower MWD than the CDL revealing the effect of separation.

The further separation of a fraction into more detailed and specific classes generally increases the resolution on GPC separation and decreased the molecular weight range *i.e.* the MWD. This is illustrated by separating the non-polar neutrals into its various classes of saturates and aromatic hydrocarbons (Table III). The \bar{M}_n values are close to those determined by VPO¹⁸ for the hexane soluble portion of a CDL. Those solvent fractions^{1,38} would contain similar hydrocarbon neutral material to the fractions reported on here. The close agreement between the GPC-HPLC determined \bar{M}_n for the hydrocarbon fractions from this work; and the VPO deter-

TABLE III
MW OF SATURATE AND AROMATIC FRACTIONS FROM A COAL DERIVED LIQUID

Fraction*	\bar{M}_n	\bar{M}_w	MWD
SAT	160	198	1.24
AF1	158	172	1.09
AF2	223	283	1.27
AF3	247	291	1.18
AF4	219	254	1.16
AF5	237	274	1.16
APF1	308	462	1.50
APF2	440	693	1.58

* Fraction nomenclature: SAT = saturates; AF = aromatic fraction; APF = aromatic polar fraction. See refs. 28 and 36 for structural evaluations.

mined \bar{M}_n for the hydrocarbon fractions from this work; and the VPO determined \bar{M}_n for the solubility fractions from other workers further confirms the rational of this method. The increase in \bar{M}_n , \bar{M}_w and MWD for APF1 and APF2 compared to the non-polar neutral fraction is a result of their higher heteroatom contents and aromaticities³⁶. The variation in MW data of these sub-fractions again reflects the complexity of the initial fraction and often the class-dependant range of differing MW material comprising it.

CONCLUSIONS

(i) Total CDLs, are complex in their composition and hence GPC chromatograms are typically broad reflecting the molecular weight dispersity.

(ii) The calibration curves reported here from GPC-HPLC separations have to be empirically drawn up, as a consequence of the molecular complexities of both the contributing compound classes as well as the total CDL.

(iii) The total CDL calibration curve when empirically constructed from a combination of component class curves leads to an average MW having a high degree of reliability.

(iv) This MW value can be refined further to the class level at any one elution time, by reference to the calibration curves of the contributing component classes.

(v) The use of GPC-HPLC and the approach developed in this paper have advantages over other methods for determining MW of CDLs.

(vi) The procedure is rapid (a typical analysis time being 40 min); relatively inexpensive, easy to operate and manipulate. At the least the procedure will give an MW profile and if desired values for \bar{M}_n , \bar{M}_w and MWD.

ACKNOWLEDGEMENTS

M. G. Strachan acknowledges the award of a University of Melbourne Post-graduate Research Award. Ms. B. E. Shumann and Ms. C. Gardiner are especially thanked for their technical assistance in obtaining chromatograms for many of the standards and CDL material.

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