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## CHARACTERISATION OF "DEASPHALTENED" PETROLEUM RESIDUES BY GEL PERMEATION CHROMATOGRAPHY

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### SUMMARY

A gel permeation system for the determination of the molecular weight distribution of crude oil residues is described. The errors caused by the non-ideal behaviour of petroleum residues on GPC columns and attempts to eliminate them are discussed. The results for a number of residues are included and the definition of a suitable algorithm for the conversion of molecular weights to boiling points is discussed.

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### INTRODUCTION

The processing of petroleum residues requires some knowledge of their properties because in spite of their uniformly dark and viscous appearance these residues vary markedly in their properties and compositions according to their source and previous processing history. Knowledge of their properties is required for optimisation of existing processes and for the design and development of new ones, particularly the computation of phase equilibrium data. The true boiling point (TBP) curve is a vital input parameter to these computations. The TBP curve is a function of per cent weight distilled and temperature, *i.e.* a boiling point ( $T_b$ ) distribution. However, current techniques impose an upper limit on this function well below the final boiling point (FBP) of a crude (Fig. 1).

Information concerning petroleum residues is sparse. It is, of course, possible to measure bulk physical properties, *e.g.* specific gravity, viscosity; which have assisted experienced refiners to establish certain empirical routes to estimates of the TBP curve. But those routes are strewn with untested assumptions and arbitrary parameters<sup>1</sup>. Hard analytical data which would enable more realistic calculations to be made are largely lacking. Gel permeation chromatography (GPC) has been employed in several studies of petroleum residues. Oelert<sup>2</sup> applied the technique to petroleum residues for the purpose of estimating ring/non-ring compounds<sup>2</sup> and to

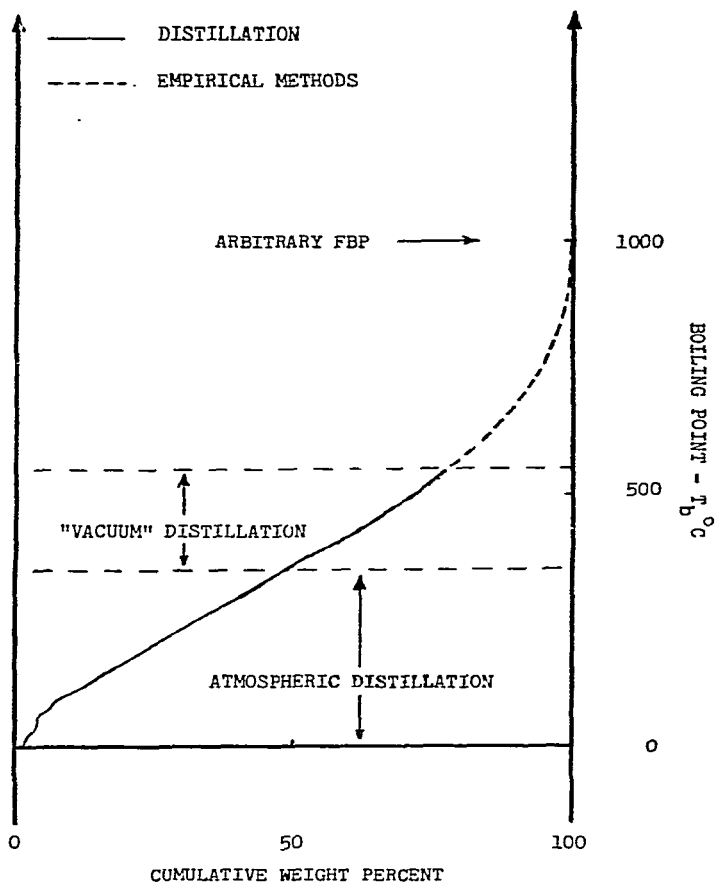


Fig. 1. Elements of a complete true boiling point curve of a crude petroleum.

the investigation of narrow cuts from vacuum distillation<sup>3</sup>. Albaugh *et al.*<sup>4</sup> have determined heteroatom distribution with respect to molecular weight. Mass spectrometry and nuclear magnetic resonance spectrometry have been effectively used to study hydrocarbon type and structure trends in GPC fractions<sup>5,6</sup> and Done and Reid<sup>7</sup> have devised a crude petroleum fingerprinting scheme.

The adoption of GPC represents a radical, if indirect, approach to the problem since it is unconstrained by vapour pressure limitations and should reach well beyond the upper limits of a crude oil. Although the technique has been applied to crude petroleum and petroleum products for other purposes, no attempt has been made to approach the completion of the TBP curve by this route.

#### *Gel permeation chromatography*

The theory and mechanisms of GPC are well-known and described in detail elsewhere (*e.g.* refs. 8–11). Comments in this sphere are confined to some aspects which impinge directly upon this application. In theory this is an attractive technique for the determination of  $M_n$  distributions (as a function of hydrodynamic volume) of

petroleum residues. However, hydrodynamic volume is only linearly related to  $M_n$  for individual members of a single chemical type, e.g. *n*-paraffins, monodisperse polystyrenes. However, in a solute mixture containing a variety of chemical types hydrodynamic volumes may not be identical for all components of equal molecular weight. Therefore, the ideal linear relationship is no longer valid. A crude oil residue contains components of widely differing polarity, e.g. non-polar paraffins and naphthenes (alicyclic compounds), moderately polar aromatics (mononuclear, cata- and peri-condensed) and polar sulphur, nitrogen and oxygen heterocyclics, to mention but a few. Each class will interact with the gel surface to a different degree. The strength of the interaction increases with increasing solute polarity and decreasing solvent polarity. It is, therefore, clear that the ideal linear relationship,  $\log M_n$  against elution volume ( $V_e$ ), cannot be expected to remain valid in this case. In addition, the lack of a significant number of standards of known  $M_n$  and of similar chemical nature to residue components ensured that no direct calibration could be attempted.

## EXPERIMENTAL

### *Apparatus and materials*

The GPC system finally adopted for this investigation is illustrated in Fig. 2.

The column array consists of three  $250 \times 9$  mm O.D. Micrel microparticulate poly(styrene-divinyl benzene) columns of  $10^4$ ,  $10^3$  and  $5 \times 10^2$  Å nominal pore size and one  $300 \times 9$  mm I.D. column of  $10^2$  Å nominal pore size. The columns were connected in series in descending order of pore size with minimum lengths of 0.25 mm I.D. stainless-steel tube. They were installed in a circulating air oven at 35°C.

Solvent was pumped by a reciprocating pump fitted into a Hewlett-Packard 1010B liquid chromatograph. Under normal circumstances the pump delivered mobile phase at  $1.0 \text{ ml min}^{-1}$  with a stability better than  $\pm 1\%$ . Samples were injected with a six-port sample injection valve fitted with a  $500\text{-}\mu\text{l}$  loop. The effluent detector

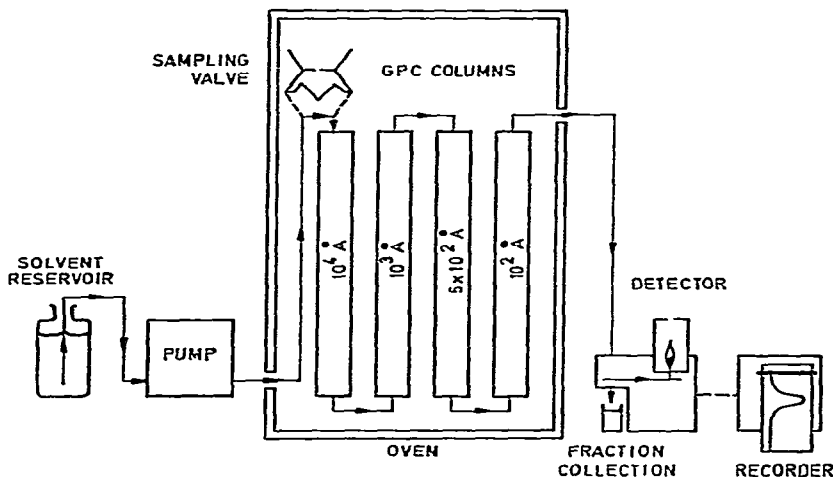


Fig. 2. Apparatus employed for the determination of molecular weight distribution of petroleum residues.

was a Pye Unicam LCM2 moving wire/flame-ionisation detector. It was chosen in preference to any other liquid chromatographic detector because of its almost uniform response to most hydrocarbon types. Fraction collection was by means of a simple manual method using a series of clean oven-fired 7-ml screw cap vials. The output signal of the LCM2 detector was recorded on a flat bed strip-chart recorder. Solvents were redistilled in glass before use and passed through a 2- $\mu\text{m}$  filter before reaching the column array.

### Procedure

Atmospheric residues (*ca.* >350 or 370°C according to availability) of Iranian Heavy, Arabian Light, Forties and a North American crude were *n*-heptane deasphalted in accordance with the Institute of Petroleum standard method (IP 143). The deasphalted residue was recovered by removing solvent first with dry nitrogen at 60°C and finally under vacuum at 60°C until constant weight was reached. The deasphalted oil was dissolved in mobile phase (*ca.* 25 mg ml<sup>-1</sup>) and approximately 1 mg ml<sup>-1</sup> 860°K polystyrene internal standard was added. The solution was transferred to the 500- $\mu\text{l}$  valve injection loop and injected onto the column array. As the crest of the internal standard peak emerged a stop-watch was started and the ensuing broad oil peak was cut into ten fractions at predetermined intervals (Fig. 3) ranging from 1 to 6 min (1.0 to 6.0 ml). The chart paper was marked automatically between each fraction. This exercise was repeated until approximately 2 mg had been collected from the least abundant fractions. The elution volumes of the internal standard peak and the residue peak were noted and the mean of the difference was calculated. The fractions were rejected from any run which deviated from the mean value by more than  $\pm 3$  sec ( $\pm 0.05$  ml). Identical fractions from all valid runs were bulked and solvent was removed on a rotary evaporator and the material was transferred to weighed vials using the minimum volume of solvent, which was finally removed under nitrogen and vacuum at 60°C until constant weight was reached. The weight of each recovered fraction was noted. The molecular weight ( $M_n$ ) of each fraction was determined by

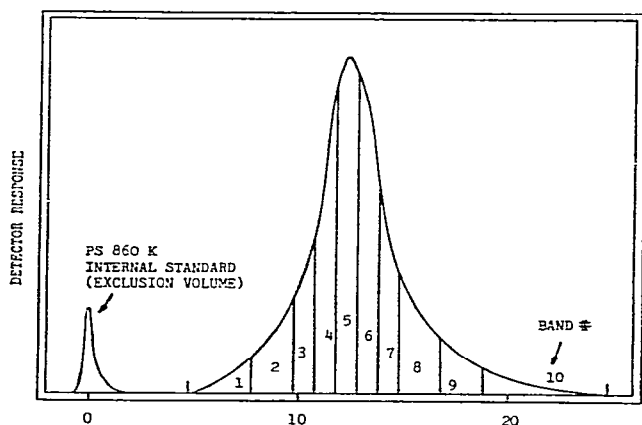


Fig. 3. Chromatogram of deasphalted Iranian Heavy >350°C residue.  $10^4$ ,  $10^3$ ,  $5 \cdot 10^2$ ,  $10^2$  Å column set: THF-MeOH (9:1); 1.0 ml/min; 35°C; 500  $\mu\text{l}$  of 25 mg/ml solution.

vapour phase osmometry (VPO) and the quantity of paraffinic ( $C_P$ ), naphthenic ( $C_N$ ) and aromatic ( $C_A$ ) carbon was determined by nuclear magnetic resonance spectroscopy and elemental microanalysis.

## RESULTS AND DISCUSSION

The principal experimental variable requiring investigation and definition was the nature of the mobile phase. It was required to pass numerous stringent criteria.

- (1) It must readily dissolve the deasphalted residue and the internal standard.
- (2) It must be compatible with the GPC columns.
- (3) It must be relatively polar to suppress adsorption.
- (4) It must be sufficiently volatile to be removed swiftly from the recovered fractions and to ensure efficient removal by the LCM2 solvent stripper.
- (5) It must not be too volatile to ensure that cavitation in the pump is avoided.
- (6) It must be relatively non-viscous to avoid excessive pressure on the columns.
- (7) It must be relatively non-toxic.
- (8) It must be free of high boiling, solid or very polar impurities.
- (9) It must not be prohibitively expensive.

The application of these criteria limits severely the choice of solvent. The initial choice was methylene chloride. However, it failed to practice on two counts. Firstly, it was too volatile to avoid cavitation on the return stroke of the reciprocating pump whose temperature rose to moderately super-ambient levels during operation. To overcome this, forced cooling by circulating ambient air cured the cavitation but destabilized the flow controller which was housed in the same compartment. The result was that an unacceptably high rate of reject runs occurred. Secondly, methylene chloride failed to suppress the adsorption of polar species on the column packing which resulted in anomalously high  $M_n$  values for the "lower" molecular weight bands. The consequences of this effect are illustrated in Fig. 4 (an Iranian Heavy deas-

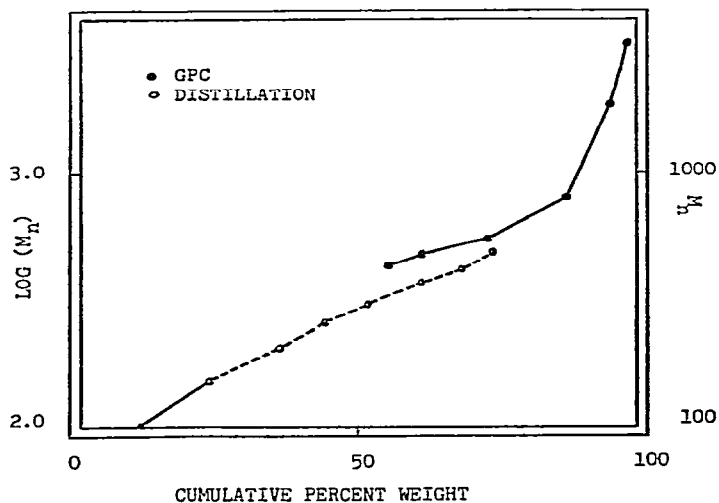


Fig. 4. Molecular weight distribution of deasphalted Iranian Heavy  $>400^\circ\text{C}$  residue.  $10^4$ ,  $10^3$ ,  $5 \cdot 10^2$ ,  $10^2$  Å column set: methylene chloride; 1.0 ml/min;  $35^\circ\text{C}$ ;  $500 \mu\text{l}$  of 25 mg/ml solution. Distillation data derived from whole crude.

phaltned  $>400^{\circ}\text{C}$  residue) where the gap between distillation and GPC derived data in the region of overlap (corresponding to  $400\text{--}550^{\circ}\text{C}$ ) is up to 90 daltons (molecular weight units) *i.e.* *ca.* 25% high. The magnitude of the discrepancy engenders little confidence in the GPC data lying beyond  $550^{\circ}\text{C}$ .

The second choice of mobile phase, redistilled tetrahydrofuran (THF)–redistilled methanol (MeOH) (9:1), produced significant improvements on both fronts. The mobile phase flow-rate stabilized and the number of reject runs diminished. Anomalous retention of polar compounds was reduced by a factor 2 to 3 compared with methylene chloride (Fig. 5).

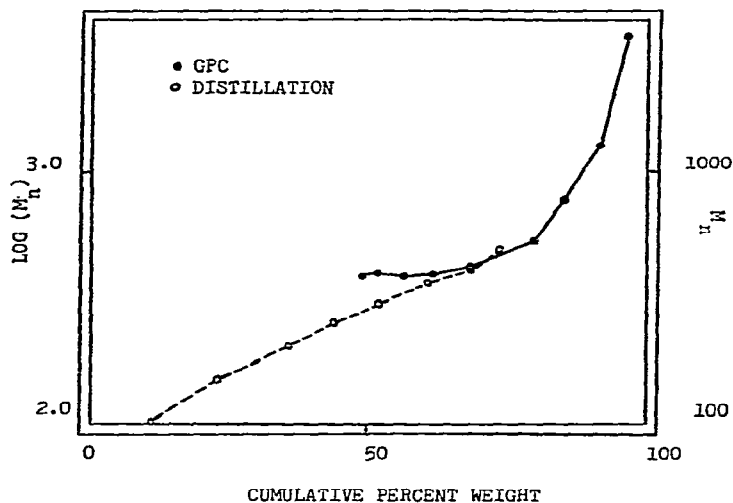


Fig. 5. Molecular weight distribution of deasphalted Iranian Heavy  $>350^{\circ}\text{C}$  residue. Distillation data derived from whole crude. Other conditions as in Fig. 3.

The results of the analysis of 4 deasphalted crude residues; Iranian Heavy  $>350^{\circ}\text{C}$ , Arabian Light  $>370^{\circ}\text{C}$ , Forties  $>350^{\circ}\text{C}$  and North American  $>371^{\circ}\text{C}$ ; in THF–MeOH (9:1) are presented in Table I and Figs. 5, 6, 7 and 8, respectively.

The molecular weight analogues of the TBP curve are constructed in the following manner. The lowest  $M_n$  band, as determined by VPO, usually band No. 9, is assumed to approximate to the initial boiling point (IBP) of the residue and the percent weight distilled is calculated from the distillation TBP curve<sup>3</sup>. The recovered weights of each band are converted to percentages of the total deasphalted crude using assay information from the same source<sup>3</sup> and are added sequentially to the percent weight distilled at the IBP of the residue. The midpercentage point of each band is assigned the  $M_n$  value of that band and is used to construct the curves that appear in Figs. 5, 6, 7 and 8. The final tenth band which has an anomalously high molecular weight in each case (*e.g.* Fig. 9) is discounted to ease construction of the curve. It generally represents less than 1% (w/w) of a crude and has little effect on the final shape of the curve.

All four examples demonstrate a satisfying coincidence of data derived from the two techniques. There is particularly close agreement in the upper part of the

TABLE I

## NUMERICAL RESULTS FOR FOUR DEASPHALTENED PETROLEUM RESIDUES

$10^4$ ,  $10^3$ ,  $5 \cdot 10^2$ ,  $10^2$  Å column set: THF-MeOH (9:1), 1.0 ml/min; 35°C; 500  $\mu$ l of 25 mg ml<sup>-1</sup> solution.

<i>Deasphalted residue</i>	<i>Band number</i>	<i>% Weight of deasphalted crude</i>	<i>M<sub>n</sub> (VPO)</i>
Forties > 350°C	1	1.7	2065
	2	7.1	918
	3	7.1	608
	4	8.4	476
	5	7.1	399
	6	4.6	390
	7	2.6	370
	8	3.4	—
	9	1.1	324
	10	0.6	500
Arabian Light > 370°C	1	3.0	1769
	2	6.2	1006
	3	7.2	647
	4	9.2	483
	5	7.5	426
	6	4.6	401
	7	2.8	386
	8	2.9	353
	9	1.3	325
	10	0.7	403
Iranian Heavy > 350°C	1	2.7	3506
	2	6.8	1296
	3	6.1	777
	4	8.1	537
	5	9.2	427
	6	6.3	399
	7	4.0	393
	8	4.3	400
	9	1.9	397
	10	2.5	—
North American > 371°C	1	2.1	3128
	2	8.3	1311
	3	7.0	741
	4	8.9	545
	5	8.5	455
	6	6.3	417
	7	4.2	390
	8	4.2	349
	9	1.4	336
	10	0.8	461

region of overlap corresponding to *ca.* 450–550°C boiling range which engenders an increasing measured of confidence in the data lying above the upper limit of distillation. Anomalous polar retention phenomena have not been entirely eliminated in the *ca.* 350–450°C region of overlap. There is strong evidence to support the hypothesis that pericondensed aromatic compounds are responsible for a major part of the problem<sup>15</sup>.

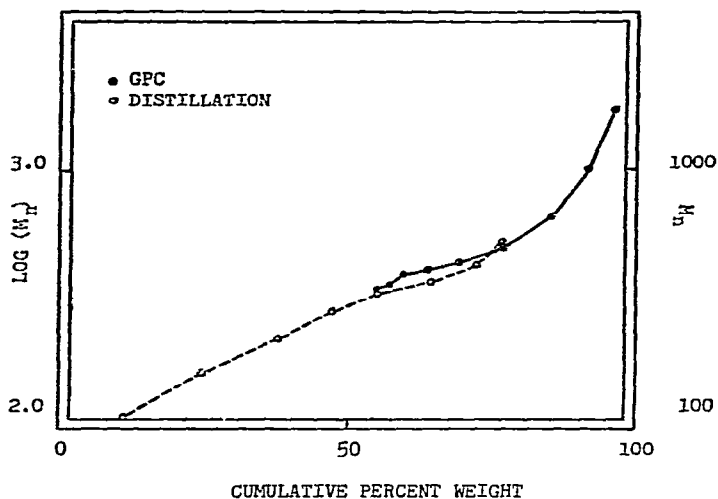


Fig. 6. Molecular weight distribution of deasphalted Arabian Light  $>370^{\circ}\text{C}$  residue. Distillation data derived from whole crude. Other conditions as in Fig. 3.

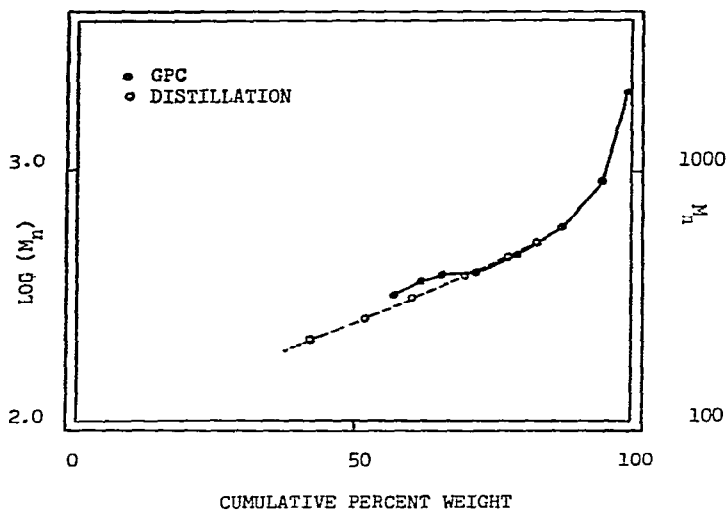


Fig. 7. Molecular weight distribution of deasphalted Forties  $>350^{\circ}\text{C}$  residue. Distillation data derived from whole crude. Other conditions as in Fig. 3.

Fig. 9 illustrates a plot of  $\text{Log } M_n$  against  $V_c$  for the 4 residues. It cannot escape notice that these curves are not even remotely linear. Their deviation from ideal linearity is a function of the factors introduced under *Gel permeation chromatography*. However, they do have some virtue. Although not identical they are very similar in shape and magnitude. Therefore, there is the prospect of constructing one or perhaps a small set of common calibration curves which would fit the majority of crudes according to traditional classifications, e.g. light, heavy; paraffinic; naphthenic; high or low sulphur. This would enable an  $M_n$  distribution to be calculated from a single



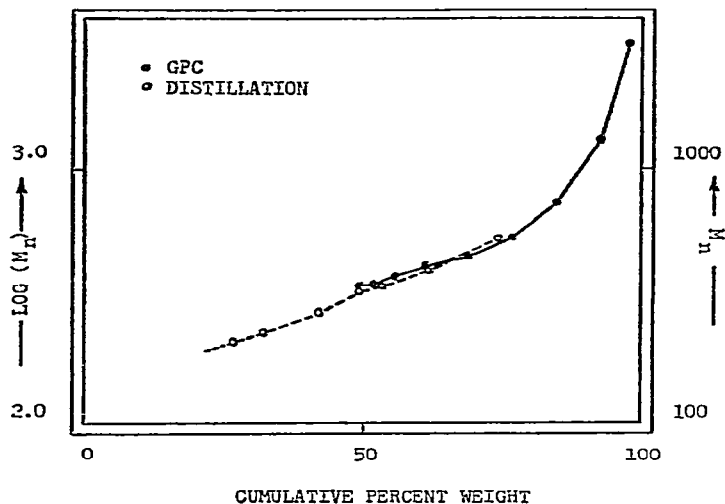


Fig. 8. Molecular weight distribution of deasphalted  $> 371^{\circ}\text{C}$  residue of a North American crude. Distillation data derived from whole crude. Other conditions as in Fig. 3.

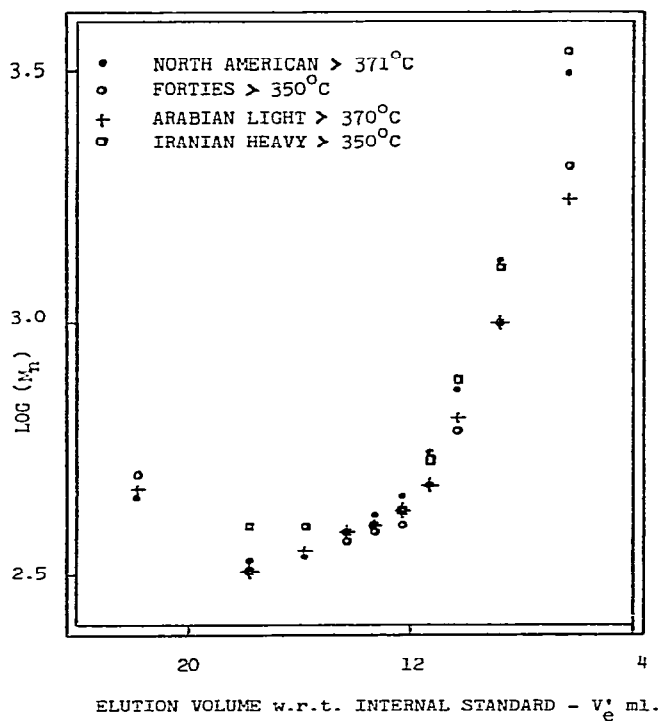


Fig. 9. Plot of  $\log M_n$  versus  $V$  for crude petroleum residues. Conditions as in Fig. 3.

permeogram, thus eliminating the tedious iterative cutting element and the VPO determinations. However, that development must await the accumulation of a greater body of data.

The accuracy of the exercise is presently unknown because there is no independent method of verifying the results that lie above the range of distillation and the use of realistic synthetic standards is precluded. It is for that reason that such importance is attached to securing the maximum coincidence of data between distillation and GPC data between *ca.* 350 and 550°C.

A preliminary estimate of precision has been made by comparing the results of three analyses of Forties >350°C deasphalted residue. The results are listed in Table II. It is apparent that in normal analytical terms that the "precision" of bands 1, 2 and 10 is less than adequate. This is of particular concern in the case of bands 1 and 2 since they define the FBP of the residue which is of particular importance to the TBP curve. Fortunately, the rate of change of  $T_b$  as a function of  $M_n$  diminishes rapidly as  $M_n$  reaches these levels.

TABLE II

## REPEAT ANALYSES OF FORTIES &gt;350°C DEASPHALTENED RESIDUE

$10^4$ ,  $10^3$ ,  $5 \cdot 10^2$ ,  $10^2$  Å column set: THF-MeOH (9:1) 1 ml/min; 35°C; 500  $\mu$ l of 25 mg ml<sup>-1</sup> solution.

Band number	Analysis No. 1 ( $M_n$ )	Analysis No. 2 ( $M_n$ )	Analysis No. 3 ( $M_n$ )	Mean	Relative standard deviation (%)
1	2065	2348	1487	1967	18.2
2	918	1037	—	978	6.1
3	608	648	665	640	3.7
4	476	489	499	488	1.9
5	399	399	419	406	2.3
6	390	378	387	385	1.3
7	370	362	379	370	1.9
8	—	328	343	336	2.2
9	324	302	314	313	2.9
10	500	387	532	473	13.1

*The molecular weight/boiling point relationship*

The matter of defining a satisfactory  $M_n/T_b$  relationship has not been concluded. Simple relationships based on extrapolation of known data below 550°C that do not take account of the hydrocarbon type (paraffins, naphthenes, aromatics) distribution within residues and variations amongst them can only be valid for one crude. Any universal relationship must be weighted according to the different characteristic  $T_b$  trends of at least these three fundamental types.

The avenue presently being explored utilises specific gravity as a link between  $M_n$  and  $T_b$ . On one side  $M_n$  is linked to specific gravity by a close to linear relationship which has been found for narrow boiling fractions below 550°C<sup>1</sup>. It can be extrapolated beyond that point with some confidence. On the other side  $T_b$  is linked to specific gravity through an extensive knowledge of the literature of these two properties of *n*-paraffins above and below 550°C (*e.g.* ref. 16). The equation relating  $T_b$  and specific gravity of *n*-paraffin can be manipulated to fit the much more limited data for naphthenes and aromatics. By this route weightings can be assigned to all three fundamental hydrocarbon types and a composite boiling point can be calculated

incorporating the different boiling point trends. The precise forms of the necessary equations are currently being refined.

## CONCLUSIONS

(1) Although actual boiling point distributions up to the FBP of a crude petroleum cannot be obtained directly, GPC data will materially assist in that direction.

(2) The quantitative characterisation of petroleum residues by GPC is beset by some not insignificant problems, *e.g.* uncertain accuracy, variable precision, time consuming. Nevertheless, these factors do not preclude the use of the technique.

(3) The chromatographic conditions necessary for a significant degree of success have been defined.

(4) The now modest discrepancies between distillation and GPC data in their common region of application are not surprising since the two techniques rely on different fractionation mechanisms.

(5) The method of relating molecular weight and boiling point outlined above is unproven in practice and will require refinement in the light of experience.

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