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Characterization of Crude Oils by Gel Permeation Chromatography*

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Summary

The classical method of dividing crude oil into narrow molecular-weight cuts—distillation—is not practical in the high-boiling region. Thus, gel permeation chromatography was evaluated as a technique for characterizing the high-molecular-weight portion of crude oils. Crude oils, stripped to 180°C, were separated in a dual-column GPC system. The fractions obtained provided information concerning the amounts of material with molecular weights between 400 and 3000. Gross estimates were made of the proportion of ring and nonring carbons in these fractions. The latter estimates were obtained by relating molecular weights determined on the fractions to a calibration plot made up from data on model compounds.

INTRODUCTION

The first step in the characterization of crude oils usually involves separation into molecular-weight ranges by distillation. The cuts thus obtained are then analyzed either superficially or in depth, depending upon capabilities and needs. Considerable effort has been expended to develop analytical techniques to analyze hydrocarbon compound types in fractions boiling below 400°C, and this knowledge has materially aided in the efficient use of the lower-boiling fractions of

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crude oils. The increasing demand for gasoline and jet fuel requires the petroleum industry to convert the higher-boiling residual material into lower-boiling fractions. Thus, a knowledge of the composition of the high-boiling cuts of petroleum—the heavy ends—is of growing importance.

Distillation-based methods for the analysis of crude oils do not separate the heavy portion of the oil; they stop at about 400°C and lump the high-boiling materials in the crude oil (often more than 50%) together as residue. Although some further tests may be performed on these residues, the material is largely uncharacterized. The distillation temperature limit can be extended somewhat by use of special high-vacuum equipment, but the practical limit is not much above 400°C. High temperatures must be avoided because of the thermally sensitive materials that are often present in crude oils. The efficiency of actual distillation usually decreases as boiling point increases; but, even if ideal distillations were possible, the molecular-weight range of the expected cut increases dramatically with increase in temperature. For example, an ideal cut at 200°C would have a spread of 6 carbon numbers, while at 400°C the spread would increase to 18.

Because of the limitations of distillation, it seemed worthwhile to evaluate the capabilities of a relatively new chromatographic technique, gel permeation chromatography (GPC), to characterize crude oils, especially that portion of the oil boiling above 400°C. The development of gels for use in organic solvent systems (*1*) provided an opportunity for work with petroleum samples. Several workers (*2–7*) have applied GPC to distillate fractions, to asphalts and asphaltenes (*8–12*), and to porphyrins (*13*, *14*); but only one attempt has been made to characterize crude oils with GPC (*6*).

GPC has the advantages of high reproducibility of separation runs, short run times resulting in low labor costs, and the ability to fractionate thermally sensitive compounds without exposing them to high temperatures. However, as pointed out by Giddings (*15*), the expected separability is not great because the effective working range is limited by the internal volume of the gel. Therefore, for a highly complex mixture such as crude oil, a gross separation is expected.

This paper describes the separation of crude oils in a calibrated GPC system. The relationship between fraction elution volume and molecular weight provides information concerning the molecular weight spread in the heavy portion of the oil and allows an estimation of the proportion of ring and chain carbons in the fractions.

EXPERIMENTAL PROCEDURES

Materials

The polystyrene cross-linked gels used were Poragel A-1 and Poragel A-3 (Waters Associates, Framingham, Mass.). The molecular-weight exclusion limits for these two gels are 1000 and 3000, respectively; each gel has a particle-size range of 36–75 μ.

Reagent-grade methylene chloride, flash distilled to remove high-boiling impurities and water, was used as the solvent. The gels were swollen for 10 hr the methylene chloride before packing in the columns.

Five crude oils, Wilmington (Calif.), Wasson (Tex.), Red Wash (Utah), Ponca City (Okla.), and Recluse (Mont.), were separated in this study. Before GPC, the material boiling up to an equivalent temperature of 180°C was vacuum stripped from each oil in a Büche Rotovapor apparatus.

The model compounds used in calibration studies were reagent grade or better.

Apparatus and Procedure

The GPC separations were carried out using two water-jacketed glass columns 0.5 in.× 5.0 ft, in series. The first was packed with Poragel A-3 and the second with A-1. Solvent flow was upward under a constant pressure of 15 psig of N_2.

The system had a total volume of 480 ml, an exclusion volume of 100 ml, and an internal volume of 260 ml. About 300 mg of oil was dissolved in 0.5 ml methylene chloride and charged to the column. Three to five charges of each oil were separated to provide sufficient sample for molecular-weight characterization. For model compound studies, about 50 mg of sample was used.

Fractions of 5.2 ml were collected by means of a siphon. Solvent was evaporated, and the sample was weighed. Molecular weights were determined by vapor-phase osmometry, with benzene as the solvent.

RESULTS AND DISCUSSION

Calibration of System

The dual-column system used for the separation was studied using model compounds representative of various types. These calibration data were used to construct the curves shown in Fig. 1, in which the relative elution volume (V_R) (benzene = 1.0) is plotted against the log of the molecular volume (V_m). Line I includes *n*- and isoparaffins,

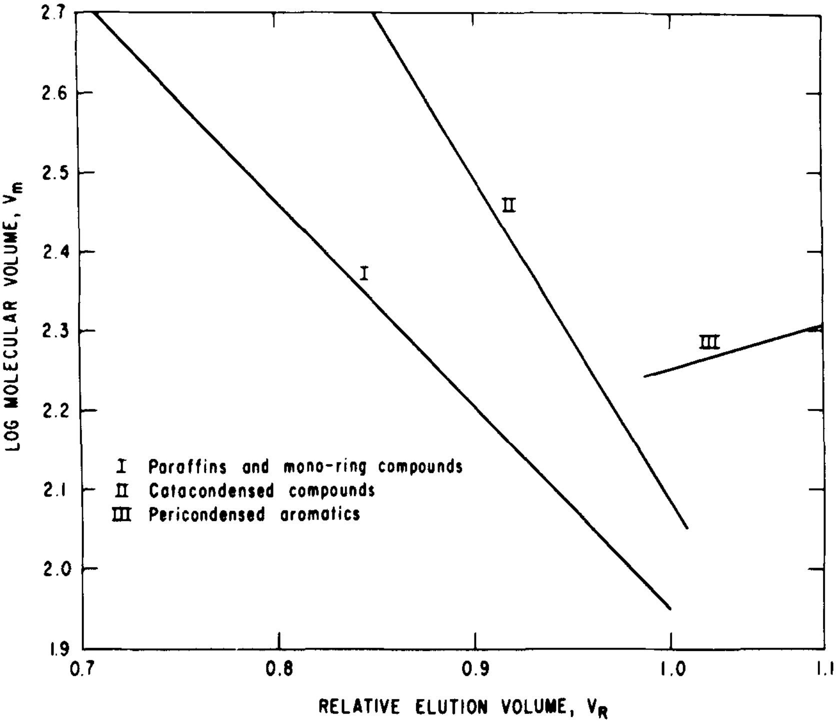

FIG. 1. Model compound data for dual-column system.

mono-ring cycloparaffins, benzenes, and polyaryls; Line II includes catacondensed cycloparaffins and aromatics; and Line III includes pericondensed aromatics.

Figure 1 shows that the elution volume is related to the molecular volume but that the relationship is different for different types of compounds. The difference in types of compounds that are described by the three lines is the amount of condensation. Line I includes branched chain paraffins, mono-ring cycloparaffins, and noncondensed aromatics—no condensed ring compounds are included in this group. All of the catacondensed aromatics and their saturated analogs fall on Line II. The two-ring, three-ring, etc., compounds fall on a straight line as long as condensation is cata (i.e., four carbons are added to two already in the system to form a new ring). If, however, the new ring is formed by pericondensation (i.e., the new rings is formed by adding three carbons to three already in the system), an extreme effect is noted, as shown by Line III. Because types of molecules in the I and II lines differ, not in polarity but in condensation, the difference in slopes is probably not due to sorption effects. Rather, this difference must be due primarily to a variation between the effective size of the molecules in a GPC column and the size of the molecule as determined by the molecular weight/density relationship.

Line III is tentative because it represents only a few aromatic compounds. However, it can be partly justified by the same argument. If the variation in slope of Lines I and II is due to catacondensation, then pericondensation should produce at least an equal change in slope so that Line III might assume an almost vertical position. However, the extreme shift of Line III suggests that factors such as sorption are overruling size effects for these compounds. These types of compounds would emerge much later than the others of the same molecular weight. However, if other compounds having V_R's near or greater than 1.0 are absent from the sample, one can assume that materials eluting in this range are pericondensed aromatics or other, as yet undefined, adsorbed types.

Comparison of GPC and Distillation Separation Data

Because distillation is the classical separation procedure for crude oils and because both distillation and GPC provide separations on a gross-molecular-weight basis, the temptation exists to equate the fractions from the two techniques. To compare the separation parameters of distillation and gel permeation chromatography, the molecular volume data in Fig. 1 have been translated to a carbon-number basis and superimposed on a similar plot for distillation, as shown in Fig. 2.

TABLE 1

Crude Oils Studied

Crude oil	Stripped crude (>180°C) wt% of crude	Residue (>400°C) wt% of crude	Residue (>400°C) wt% of stripped crude
Ponca City	64	12	19
Recluse	67	18	27
Red Wash	99	57	58
Wasson	72	27	38
Wilmington	91	47	52

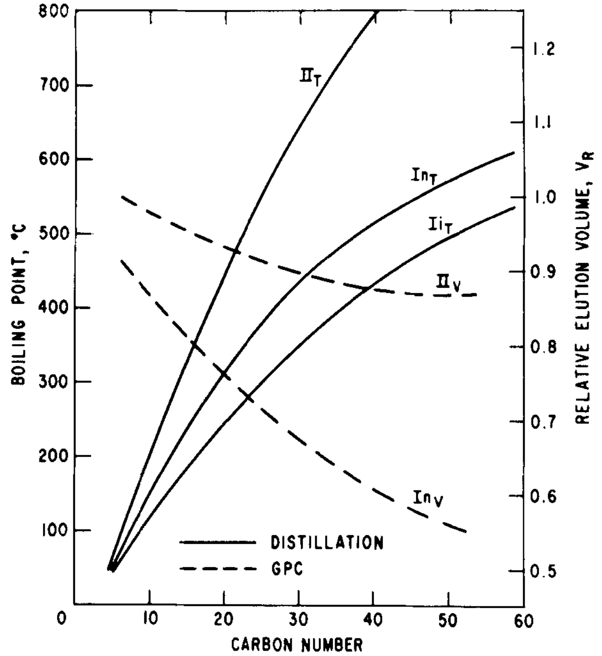

FIG. 2. Correlation of boiling point, relative elution volume, and carbon number for hydrocarbons. Ii = iso-paraffins; In = n-paraffins; II = condensed rings.

The dotted lines represent the limits of GPC and the solid lines the limits for boiling point. The translation from a molecular volume basis to a carbon number basis produces a family of curves or bands. The isoparaffins of increasing carbon number form a band above the n-paraffin line shown. The one-ring compounds lie above this line, then the two-ring, and on up until the limiting line for the most catacondensed systems. The intermediate lines are not shown, simply the limits. Just as Ii_T and II_T are limits for distillation, I_V and II_V are limiting lines for GPC.

If the objective of the separation procedure is to produce fractions with a narrow molecular-weight or carbon-number range, either procedure can be used. Figure 2 shows that for both methods of separation a larger carbon-number spread must be expected as the carbon number increases. The spread for distillation is less than that for GPC so that distillation would be preferable if usable. However, Fig. 2 also suggests that GPC would give some discrimination in the high-molecular-weight region where distillation is impractical or impossible.

Figure 2 demonstrates two differences between the separation techniques—one obvious and irritating, the other less obvious but more important. The data in Fig. 2 are arranged so that, for both techniques, the separation proceeds from bottom to top. Thus in distillation the small molecules emerge first, but in GPC the large molecules emerge first. This reversal in order of emergence is initially troublesome to the distillation-oriented petroleum chemist because he must reverse his thinking. Of considerably more importance, when attempting to equate distillation fractions and GPC fractions, is the difference in the effect of structural variations on the two separation schemes. Examination of Fig. 2 shows that a distillation cut containing the *n*-C_{20} paraffin might also contain isoparaffins up to C_{27} and aromatics down to C_{15}. The *n*-C_{20} paraffin would be approximately in the middle of the

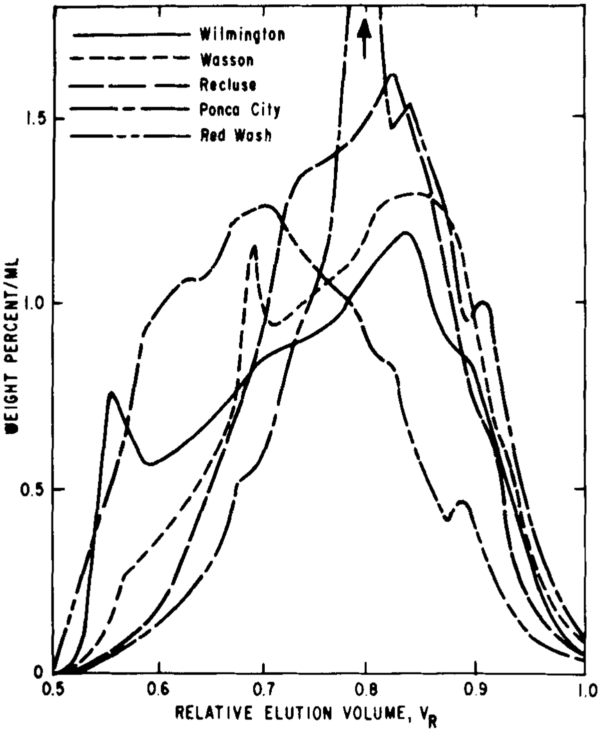

FIG. 3. GPC chromatograms of five crude oils.

carbon-number spread; and one might expect that the average molecular weight of this cut would be near that of the n-C_{20}, or about 280. If condensed molecules predominate in the mixture, the average molecular weight would decrease, with about 200 as the limiting value. The GPC cut in which the n-C_{20} paraffin would be expected would contain no molecules of lower molecular weight but would have isoparaffins and aromatics of higher carbon number; condensed aromatics with carbon numbers over 50 might be included. The average molecular weight of this cut would be well above 300 and, if the condensed rings predominated, could approach 1000. Thus, the types of molecules associated with each other are quite different in fractions from the two procedures.

The difference in the effect of structural variations frustrates a one-to-one comparison of fractions from the two techniques. For example, Fig. 2 shows that a narrow fraction at 180°C (the temperature to which our crude oils were stripped) could contain a C_9 ring compound, a C_{11} paraffin, and a C_{15} isoparaffin. Transferring these carbon numbers to the GPC scale suggests relative elution volumes of .98, .85, and .81. A similar inspection for a fraction at 400°C (the end temperature for a temperature for a practical assay by distillation) shows a C_{18} ring compound, a C_{27} n-paraffin, and a C_{35} isoparaffin. These materials should elute at V_R of .94, .70, and .64. Thus, materials from the 180°C cut will elute from .81 to .98 and will overlap those from the 400° cut, which will elute from .64 to .94. Similar fractions should not be expected from the two procedures.

Crude Oils

The lack of similarity of the GPC and distillate fractions does not negate the promise of GPC for producing usable fractions. Figure 2 suggests that GPC would provide some molecular-weight discrimination in the high-molecular-weight region where distillation is impractical. Five crude oils were stripped of material boiling up to 180°C and separated by GPC. Table 1 shows the relationship that these stripped crudes had to the whole crude oil and also the percentage of each crude that was classified as residue by the Bureau of Mines crude oil analysis.

The GPC chromatograms are shown in Fig. 3, in which weight percent of material per milliliter of eluant is plotted against relative elution volume. These curves show some similarities and some differences among the oils. Four of the oils are quite similar at high-relative

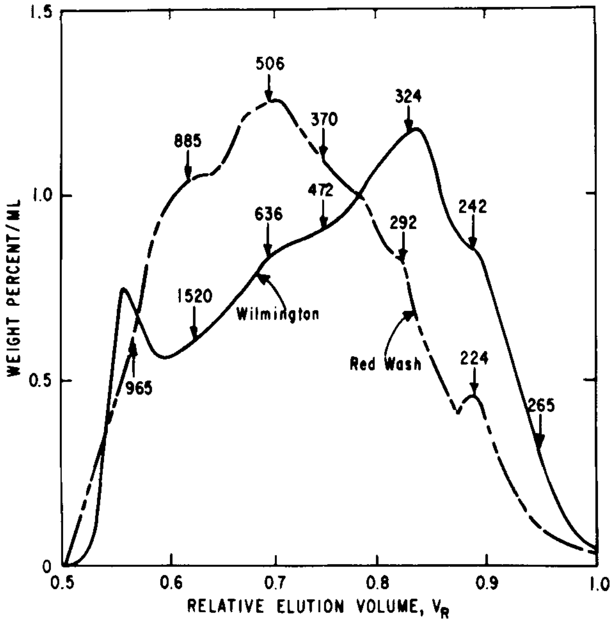

FIG. 4. GPC chromatograms of two crude oils. (Numbers are molecular weights of fractions.)

elution volumes (low-molecular-weight region) and show the maximum concentration of material between the relative elution volumes of .80 and .85. The fifth oil, Red Wash, is deficient in low-molecular-weight material and shows a maximum at .71.

A comparison of the amount of material in the high-molecular-weight portion of the GPC chromatograms (V_R's lower than about .7) and the amount of material in the residues from distillation (Table 1) shows that for these oils each technique arranges the crudes in the same order of increasing residual material—Ponca City, Recluse, Wasson, Wilmington, and Red Wash. However, the magnitude of the variations is different for the oils. For example, the chromatograms show a much greater variation between the Wilmington and Red Wash oils than the difference in their distillation residue contents (52 and 58%, respectively) indicates. This is probably due to major compositional differences between the two oils, which, as discussed earlier, influence the separations by GPC and distillation. Therefore, the correlation observed may not be found when another group of oils is compared.

In Fig. 4 the chromatograms of Wilmington and Red Wash crude oils are repeated, and the molecular weights of several fractions are added to the curves. These oils were chosen for this comparison because they are quite different and may suggest limits within which most crude oils should fall. Wilmington is an asphaltic oil, and Red Wash is very paraffinic. A comparison of the molecular weights of fractions with the same elution volume shows gross differences, particularly in the first part of the separation. The early peak at V_R .55 in the Wilmington oil must be due to large asphaltenic molecules that exceed the exclusion limit of the gel (3000) and emerge as an unseparated peak. Following these large asphaltenic molecules, the separated molecules begin to emerge; from elution volumes of .6 to .85 the amounts increase as the molecular weight decreases. Both the amount and molecular weight then decrease until a relative elution volume of .95. An increase in molecular weight at V_R .95 suggests the presence of adsorbed species such as pericondensed aromatics.

The Red Wash oil begins to elute slightly before the Wilmington, but the molecular weights are much lower. No maximum is observed for the large excluded molecules. The molecular weights decrease in a slow, orderly fashion across the entire curve; while the amounts show a similar distribution on both sides of the V_R .7.

Thus, these two stripped crude oils, which have similar amounts of distillation residue and similar average molecular weights (Wilmington 381, Red Wash 433), are shown by GPC to be quite different in the high-molecular-weight region. If amounts were plotted vs molecular weight, Wilmington would show 20% of the oil in a long tail, with molecular weights from 1500 to above 3000. The Red Wash has only 5% of material with molecular weights above 1000; 70% of its molecules have molecular weights from 300 to 900.

Compositional Estimations

The differences in average molecular weight at similar elution volumes are caused by differences in composition. An understanding of these differences should provide compositional information. Some insight can be gained by examination of the calibration plot for the effect of different types of molecules. In Fig. 5 the data for the Wilmington and Red Wash oils are plotted on the calibration plot for our GPC system. For the purpose of this plot, the molecular weights were divided by 14 to obtain an estimated average carbon number for each fraction. A gross interpretation of the calibration data suggests

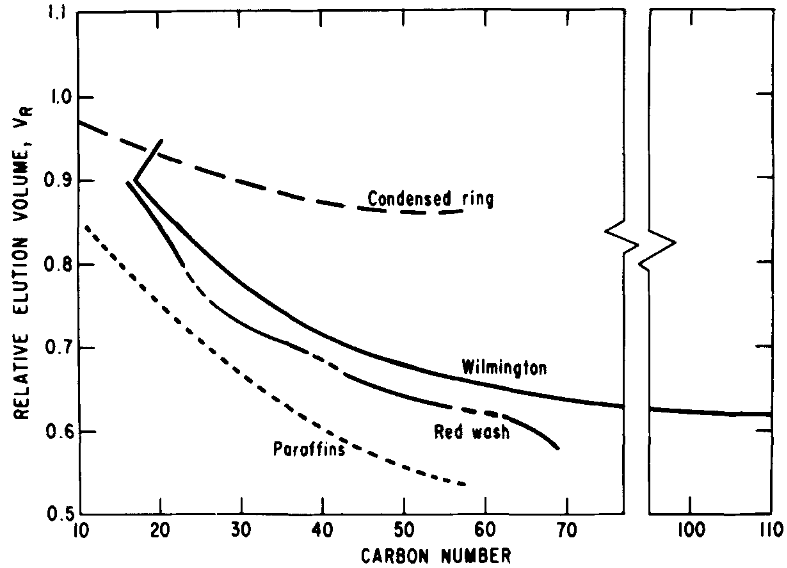

FIG. 5. Carbon number data for two oils as compared with GPC calibration data.

that the position of the fraction between the two calibration lines is related to the amount of ring vs nonring carbons. The position of the Wilmington curve is somewhat above the Red Wash curve and nearer to the limiting curve for completely condensed compounds. This shows that the Wilmington fractions are rich in ring carbons, as would be expected in this asphaltic oil. The position of the Red Wash curve—near the I or nonring-carbon line—shows that the Red Wash fractions contain predominantly nonring carbons. Although not shown in Fig. 5, the curves of Ponca City, Wasson, and Recluse fall between the Wilmington and Red Wash curves.

The above data show that by using molecular weights and a GPC calibration plot, one can obtain some information on the size and type of the molecules present in GPC fractions.

CONCLUSIONS

GPC was used to separate several crude oils, especially the high-molecular-weight portion of those oils. The relationship of fraction elution volume and molecular weight provides information on the proportion of ring and nonring compounds in the fractions. Comparison of GPC and distillation separation data shows the difference between the two techniques and that similar fractions will not be obtained using these two procedures. GPC provides discrete fractions in the molecular-weight range from 400 to 3000 using the system described.

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Mention of specific models of equipment or brand names of materials is made to facilitate understanding and does not imply endorsement by the Bureau of Mines.

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