

## ACKNOWLEDGMENTS

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# Review of the Application of High-Pressure Liquid Chromatography to Pavements

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High-pressure liquid chromatography has been promoted as a technique for determining the molecular size distribution and suggested as a method for determining the composition of asphalt cement. However, some authorities have expressed reservations about the interpretation of data obtained with this technique. The purpose of this paper is to review the data available in the literature to determine the significance of the conclusions that can be drawn from it. The literature indicates that there are several test parameters that must be carefully controlled to ensure interlaboratory comparison of results. The technique does produce consistent and repeatable results, differentiating clearly between asphalt cements from a variety of sources. However, correlation between chromatographs,

physical properties, and pavement performance is currently not usable.

Traditional approaches to the design of pavements have separated consideration of the asphalt surfacing mix from the design of the pavement structure. Modern developments in pavement design technology and, in particular, the implementation of mechanistic methodology have highlighted the inadequacy of this traditional separation and have demonstrated the need for a greater understanding of the behavior of asphalt mixes. This need has been reinforced by the development of new paving technology, such as recycling processes, and by the introduction of new products, including specialized additives, into the asphalt industry.

Recycling and the use of additives in mixes have highlighted the lack of knowledge about the bituminous binder. Little information exists on how it will respond in both the short and the long term to chemical changes induced by the presence of additives and the effect that they will have on the performance of the asphalt mix in a pavement structure. It is appropriate to note at this point that considerable effort has been, and continues to be, directed toward analysis of the chemical structure of bitumen. Much of this work has been summarized by Pfeiffer (1) and Barth (2), but it would appear that it is considered impractical. It is not used in the regular practice of asphalt technology and rarely appears in the technical literature. It is probably a measure of the true complexity of the material and of the associated complexity of the structure in which it is used that the connection between the chemical structure of bitumen and the performance of pavements has not yet been made.

Recognition of the gap in the technology just discussed has provided new impetus for studies of the nature of bitumen and relating it to the performance of pavements. A relatively new technique known as high-pressure liquid chromatography (HPLC), originally developed to study polymers, has been used to study bitumen. This technique, after installation, is quick and inexpensive to operate. The Texas State Department of Highways and Public Transportation (SDHPT) is currently investigating the use of the technique as an aid to producing better highways. The work in progress is able to take advantage of the program of test pavements constructed by the SDHPT in collaboration with research workers at the Texas Transportation Institute at Texas A&M University to collect data on field performance for comparison with both physical and chemical data collected in the laboratory.

The purpose of this paper is to contribute to the discussion of the fundamental composition of asphalt and its relation to field performance by presenting the results obtained to date from the study in Texas.

## REVIEW OF HPLC STUDIES

### Description and Discussion of the Technique

HPLC was developed to study the molecular weight distribution of polymeric species, which is achieved by dissolving a sample of the material to be studied in a suitable solvent and passing the solution through a column of porous gel beads. (In the context of this discussion, a suitable solvent is one that releases individual molecules into solution as they pass through the column.) Characteristically, the largest molecules exit from the system first and the smallest exit last. Figure 1 shows the process schematically.

Detection is achieved by determining the difference between the refractive index of the solution, which at this stage carries molecules arranged in order from the largest to the smallest, and a stream of clear solvent, which is used as a reference. It is conventionally assumed that the difference between the refractive index of the solution and the solvent is the same regardless of molecular weight of the solute molecules, and so the response of the refractometer is related directly to the number of molecules being detected. Thus, if the instrument is cali-

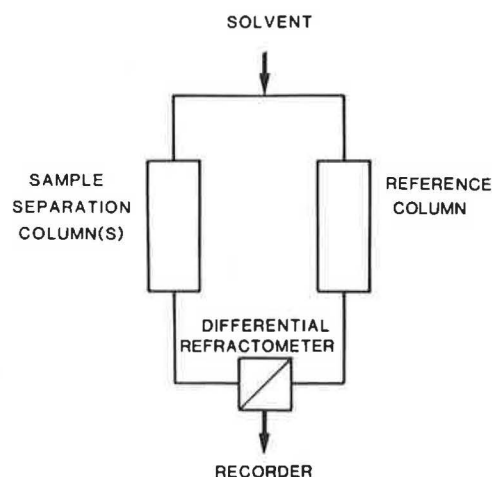


FIGURE 1 Schematic representation of a liquid chromatogram.

brated it is possible to obtain a molecular-weight distribution for the material under test. This would appear as a relationship between relative concentration and molecular size at the recording device.

Several points relating to the use of HPLC made by Petersen are of considerable importance when interpreting HPLC data (3); they will be summarized in the following paragraphs.

The technique, as previously described, separates the molecules on the basis of size and shape. When applied to polymers (for which the technique was developed), there is a close relationship between molecular size and molecular weight because polymers are composed of repeating units of monomeric building blocks. Asphalt is not a classical polymer because the molecular types and size vary widely in both chain and ring shapes; thus there is no consistent relationship between size and weight.

The differential refractometer used in the detection system gives a response that is related to the amount of sample present and to the difference in refractive index between the solvent and the molecules being detected. The molecules of the classical polymer have similar chemical composition, and hence their refractive index is essentially the same regardless of molecular weight. The refractive indices of the chemically different molecules in asphalt vary widely, and thus the detector will have varying sensitivity toward different molecules.

A further point made by Petersen relates to the presence of molecular aggregations in the solution (3). That is, the solvent may not separate some of the aggregations of molecules, and thus something that may be detected as a large molecule could be a group of small molecules.

Petersen's comments lead to the conclusion that the technique does not give an accurate indication of either relative numbers or molecular weights for bitumens. This conclusion is supported by information reported by Barth, who reminds his reader that molecular weight can only be determined for pure chemical substances (2). Barth also reminds his reader that before chemical properties can be determined, narrow fractions have to be obtained, based on selection of a molecular size within a selected group of the hydrocarbon series.

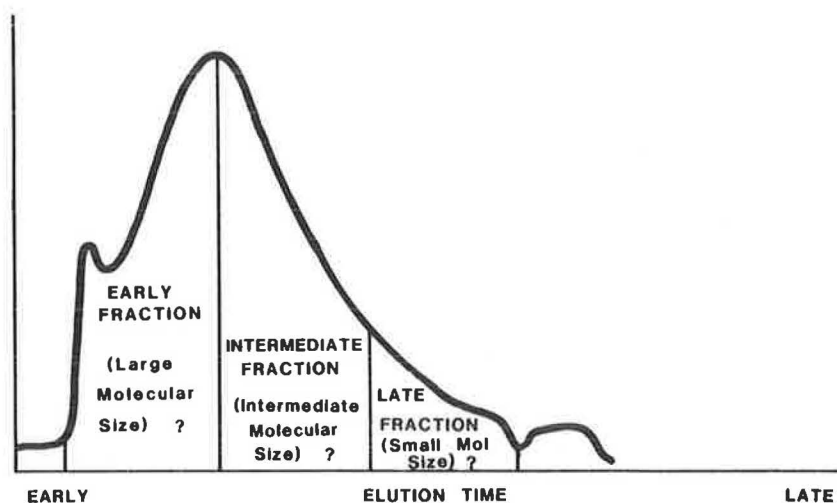


FIGURE 2 Interpretation of a chromatogram.

### HPLC Studies to Date

The literature reporting the results of HPLC studies on asphalt is not voluminous. However, a number of studies have been reported. Before discussing these studies, two important points must be clarified.

First, in view of the reservations reviewed previously about the interpretation of chromatograms, it is considered to be inappropriate to refer to large, medium, and small molecular sizes. It is more correct to refer to molecules that elute early (referred to by some authors as large) and late (referred to by

some authors as small), with the time period in the middle being referred to as intermediate (referred to as mid-size by some authors) (see Figure 2).

Second, it should be noted that different conventions have been adopted when plotting the chromatograms, as shown in Figures 3 and 4. Richman (4), Breen and Stephens (5), Bynum and Traxler (6), Dougan (7), and Hattingh (8) plot their chromatograms with the fractions that are eluted from the columns earliest appearing on the right side of the plot. Jennings (9-11), Button et al. (12), and Jennings and Pribanic (13) plot their chromatograms with the fractions eluted earliest appearing on

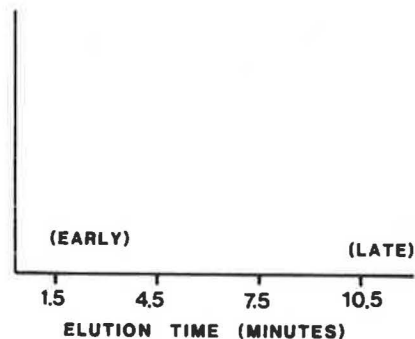
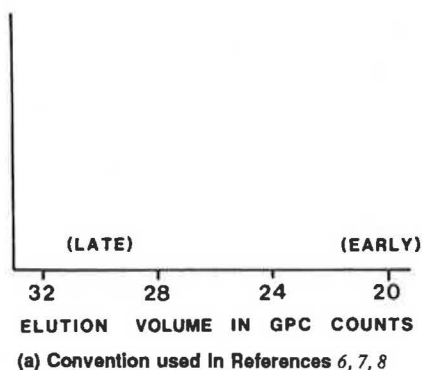


FIGURE 3 Comparison of conventions used in the presentation of chromatograms.

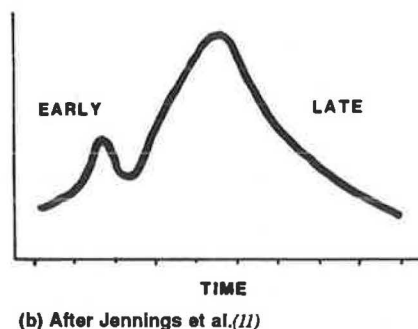
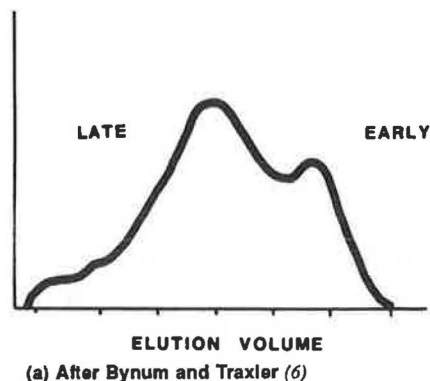


FIGURE 4 Comparison of chromatograms after Bynum and Traxler (6) and after Jennings et al. (11).

the left side of the plot. Because most chromatograms are interpreted on the basis of a visual inspection, it is important to be aware of this difference.

### Consistency of the Technique

One of the principal objectives of Dougan's study was to check the consistency of the GPC technique (7). The conclusion drawn from replicate tests on a single 85-100 penetration grade asphalt was that the test is accurately reproducible. One condition for reproducibility was recommended; that is, the solution should be injected into the instrument as soon as possible after preparation to avoid molecular swelling, a phenomenon also observed by Barth (2). It is not likely that the molecules increase in size with the time of exposure to the solvent. In general, the molecular agglomerations are reduced in size as individual molecules are stripped off by the solvent. Thus it is more logical to extend the time during which the bitumen is exposed to the solvent to ensure that an equilibrium solution has been obtained.

To secure comparability between chromatograms produced by different laboratories, the column system used in the instrument and the solvent used as the mobile phase should be the same. Jennings indicates that difficulties can occur in obtaining adequate separation between an internal standard and the test material if columns with inappropriate pore sizes are used (10). Dougan also mentions the importance of selecting appropriate columns (7).

It has been demonstrated that the solvent used for the mobile phase can have a significant effect on the chromatogram (11). Four solvents and two combinations of solvents were used in the comparative tests. A combination of 15 percent pyridine in tetrahydrofuran (THF) produced a trace containing sharper peaks than did the other solvents, indicating that it is probably more efficient at breaking up the molecular aggregations than are the other solvents. The traces produced by some solvents have the appearance of being smoothed to a significant degree. It should be noted that THF is the solvent most commonly used and produces a trace that is nearly as sharp as the pyridine/THF combination.

The last item that has been discussed concerns the detection of the molecules. Jennings et al. have compared an ultraviolet (UV) detector with the conventional differential refractometer (11). Jennings stresses that the study was not exhaustive, but indicates that the conventional refractometer appears to be more sensitive to components in the early and intermediate fractions, and the UV detector more sensitive to the late fractions (11).

To summarize, it is clear that to achieve consistent results that can be compared in a laboratory, and particularly between laboratories, it is essential to standardize at least column configuration, the solvent, and the detector system, and is probably desirable to control the time between sample preparation and performance of the test.

### Comparison of Asphalts from Different Sources

There is ample evidence in the literature (6, 8-13) that the HPLC technique is sensitive to the difference between asphalts

from different sources. Visual inspection of the chromatograms indicates clear differences between the asphalts. One interesting comparison has been noted from the literature. The chromatographs plotted by Bynum and Traxler generally show a small peak or a plateau in the early fraction (6). Many of the chromatographs published by Jennings and his co-workers show a similar shape but with the peak plateau in the late fractions (9-11, 13) (see Figure 4). This is likely to be due to differences in the source of the asphalt cement. Bynum and Traxler's asphalt cement (6) probably originated in Texas and Jennings and co-workers' asphalt cement in Montana (9-11). Button et al. show both types of chromatograms in their study of asphalt cements from several different sources (12). Data on the difference between different grades of asphalt from the same source have been presented by Breen and Stephens (5). These results are for asphalts of different grades from the same source.

### Determination of the Effects of Mixing and Aging

Both mixing and aging affect the physical properties of asphalt. For example, the viscosity of any given asphalt cement will increase when it is mixed. Aging while in service in a given pavement will also cause viscosity to increase, the rate of change being dependent on many factors.

Bynum and Traxler have presented data obtained from asphalts used on several sites in Texas (6). The data cover tests on original material and asphalt cement recovered after 4 and 24 months of service. For all asphalts tested, the refractometer readings indicate an increase in the quantity of material in the early section of the curve and a decrease in the quantity eluted in the last section of the curve. This trend is supported by Jennings, who also studied the effect of holding the asphalt-aggregate mixture at an elevated temperature for up to 1 hr (10, 11).

While the two studies just reported do indicate that changes through mixing and aging can be detected by comparing chromatograms, it must be pointed out that these changes are of an order of magnitude similar to that of the changes shown between asphalts of different grade from the same source. They are also small compared with the relative changes observed in physical measurements such as viscosity.

Dougan conducted some artificial aging tests and calculated three parameters from this chromatogram: the weight average molecular size (AW), the number average molecular size (AN), and the polydispersity-index (PI) (7). Each of these parameters increases as the sample ages (as shown in Figure 5), which suggests that there could be a relationship between these molecular parameters and time. However, as noted previously, the difficulties experienced in producing proper calibrations for the chromatograms suggest that the molecular parameters, while being arithmetically correct in relation to the chromatogram, may not be molecular parameters.

### Data Relating HPLC to Mechanical Properties of Asphalt Cement and Mixes

To relate mechanical properties to the chromatograms, it is necessary to quantify the plot in some relevant manner. Dougan

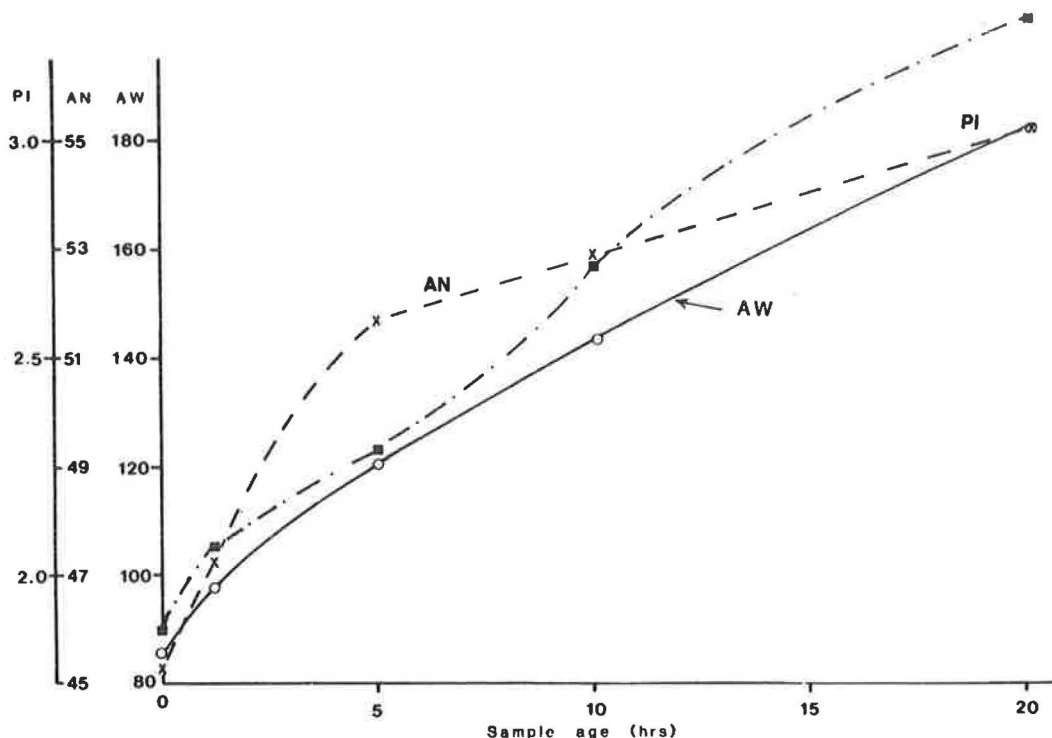


FIGURE 5 Analysis of GPC data after Dougan (7).

used the three parameters described in the preceding section in his artificial aging test (7). The three parameters calculated from the chromatograms have been plotted as a function of penetration. Because few data are available, no conclusions can be drawn concerning the relationship between these parameters. However, it is possible to draw a reasonable curve through the data points, which is encouraging.

Chollar et al. attempted to find a relationship between an early fraction [referred to by Chollar et al. as large molecular size (LMS)] and a combination of ductility, specific gravity, and asphaltene content (14). The attempt was not successful, the authors concluding that "... effects not identified play an important role in the variation of LMS among asphalts."

### Correlation with Pavement Performance

The literature contains opinions but few data that relate chromatograms with performance. None of the data reported exceed 9 yr of service life and the majority is limited to between 2 and 3 yr (6, 8, 9, 14). Also, the performance evaluations used in these studies are limited. Bynum and Traxler limit the assessment to the categories excellent, very good, good, fair, and inadequate, without defining the categories (6). Jennings and Pribanic assess severity of cracking in their study, but it should be noted that there are many potential causes for cracking in asphalt other than a deficiency in the asphalt cement (13). The only comment with respect to performance by Hattingh concerns excessive bleeding of some asphalts (8). It is therefore impossible to correlate the studies in the literature with each other and to draw any fundamental conclusions relating HPLC data to pavement performance.

Both Jennings and Pribanic (13) and Hattingh (8) concur that there is a desirable asphaltene content in an asphalt cement. Jennings and Pribanic (13) tentatively suggest that this content is between 12.5 and 16.5 percent. It must be noted that this asphaltene content cannot be determined from the HPLC chromatograms; it is the heptane-insoluble fraction in the asphalt cement. However, Hattingh also concludes that the asphaltene content alone is not sufficient for the evaluation of the quality of an asphalt (8).

### CONCLUSIONS

There are a number of conclusions that can be drawn about the application of HPLC techniques to pavements.

- Consistent technique regarding column configuration, solvent detectors, and sample preparation is important for consistent results and for interlaboratory comparisons.
- The technique is repeatable and produces notably different traces for asphalts from different sources. It therefore can be valuable with regard to fingerprinting asphalts.
- There is significant doubt about the precision of the calibration of the traces produced for asphalt using the HPLC technique. This indicates that fundamental parameters, such as molecular size and molecular weight determined from HPLC, must be treated as suspect.
- The data obtained by HPLC from an asphalt cement from a particular source are insensitive to the grade of that cement and to changes due to aging.
- The data relating performance to HPLC data are too limited for any conclusions to be drawn.



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