# Use of a Multiwavelength UV-VIS Detector with HP-GPC To Give a Three-Dimensional View of Bituminous Materials

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**High performance gel permeation chromatography (HP-GPC) is being used in the study of asphalt cements. The use of a photodiode array spectrophotometric detector adds to the chemical information that may be obtained from the HP-GPC molecular size distribution by providing chromatograms at multiple wavelengths in the ultraviolet-visible range simultaneously. A three-dimensional image of the asphalt and spectra at various elution times are obtained. The result is improved knowledge of the conjugation/aromaticity of asphalt components of various hydrodynamic volumes. In this study, a group of 19 asphalt cements, from worldwide sources and representing a broad range of properties, was selected for eventual construction of a data base. These materials were sorted into three classes based on their chromatographic shapes. These classes appear to extend to temperature susceptibility (PVN) and aging index as well. Also investigated were a limited number of less common materials to determine the potential utility of the technique. These materials included SARA fractions, viscosity-reduced, air-blown and solvent-deasphalted residua.**

Gel permeation chromatography (GPC), also known as size exclusion chromatrography (SEC), is a method of separating molecules in solution by virtue of their molecular sizes or, more specifically, their hydrodynamic volumes. Used in a high performance (HP-GPC) liquid chromatography system, the technique is widely employed in the quality control of polymer manufacture. Traxler (*1*) reported the use of GPC for analysis of asphalt cements, showing changes in the molecular size distribution (MSD) as a result of pavement construction. Jennings (*2–4*) has published work on the use of HP-GPC to monitor the changes that occur as the result of various processes and to associate molecular size distribution with field performance and the like. Brulé (*5,6*) has also done extensive work, most recently developing associations between MSD and certain physical properties. Others, including Button (*7,8*), and Beazley (*9*), have also explored aspects of the use of HP-GPC of asphalts.

A key element of the HP-GPC system is the detector. Both refractive index and single wavelength ultraviolet-visible (uv-vis) spectrometers have been used. Both give valuable but incomplete information because the detector response is not directly proportional to the mass of material eluting at a given time in either one.

The development of photodiode array uv-vis spectrophotometers has offered a broader spectrum of detection capabilities. Although some asphalt components still escape detection, molecules that absorb radiation wavelengths between 220 and as much as 600 nm (i.e., those with virtually any degree of conjugation/aromaticity) will be detected. It must be emphasized that "aromaticity" is used in this paper to refer to the characteristics of condensed aromatic ring systems, including polynuclear aromatic (PNA) rings.

In an asphalt, the performance arises from its overall chemical composition, a combination of aromatic and nonaromatic hydrocarbons and a variety of functional groups containing heteroatoms (i.e., oxygen, nitrogen, and sulfur) in addition to metals. The information that may be obtained from a combination of HP-GPC and uv-visible absorption characteristics therefore has to do with major components of asphalt, the aromatic and conjugated systems, including those with heteroatoms. Because of the nature of the techniques and the complexity of the asphalt, the information will be of a general nature.

It was in an effort to explore the potential uses of HP-GPC of bituminous materials in general and the utility of a photodiode array spectrophotometer in particular, by a refiner, that the work to be described in this paper was undertaken.

## EXPERIMENTAL

The experimental procedure used was that described by Jennings (*2*), with the addition of the photodiode array detector. The HPLC instrument consisted of the following components: Waters "WISP" automatic sample injector (Model 710B), Gibson pump (Model 303), Hewlett-Packard uv-vis diode array detection system (Model 1040A), Perkin-Elmer interfaces (DCI 2000), Perkin-Elmer computer system with Chromatography Laboratory Automation System (CLAS) Revision 1.7 software, Hewlett-Packard Analytical workstation with operating software—HP 1090M/HP 79994A, and Columns—Licrogel (Merck) PS 4000, 40, and 4.

Analyses were conducted on 50-μL injections of sample at a concentration of 0.5 percent (w/v) in tetrahydrofuran (THF). All THF used was HPLC grade, dry (by NMR), and main-

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tained under helium purge. The flow rate was 1 mL/min. Analysis times were less than 25 min. Columns were thermostated at 26°C.

The diode array detector system was set to acquire chromatograms at eight wavelengths: 210, 230, 254, 340, 380, 410, 440, and 540 nm. The total spectrum range was 200 to 600 nm. Data for two chromatograms (230 and 340 nm) were collected by the Perkin-Elmer system for peak intensity and peak area calculations.

The sample set was selected to include 19 asphalts from a very broad range of crude sources worldwide, as well as examples of viscosity-reduced residua, solvent-deasphalted residua, and air-blown asphalts. The group of 19 asphalts is the subject of a data base that will eventually include a variety of physical data in addition to other chemical characterizations.

In Figures 1 to 6 are examples of the kinds of data that were obtained from the HP-GPC system just described. Figure 1 contains the chromatograms at 230 and 340 nm for an asphalt, normalized to the same peak height. In the chromatograms, larger materials, having eluted first, appear on the left; successively smaller ones appear to the right. Also shown in Figure 1 are the cut points between areas under the curve designated large molecular size (LMS), medium molecular size (MMS), and small molecular size (SMS). These cuts are based on a standard asphalt obtained from Montana State University.

A three-dimensional plot of chromatographic data is also given in Figure 1. These data consist of a series of chromatograms at different wavelengths that are labeled along the left side of the figure (A). The elution time in minutes is printed along the horizontal axis, and the detector response
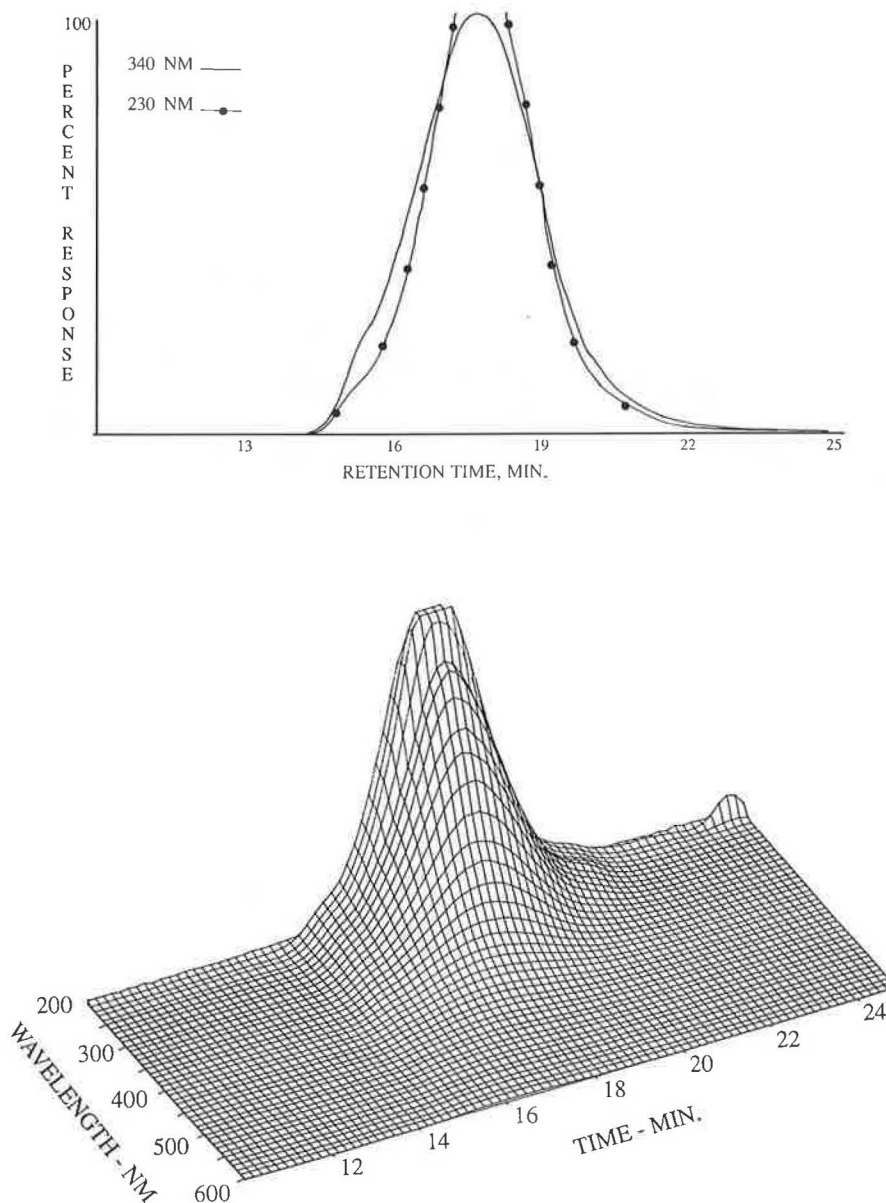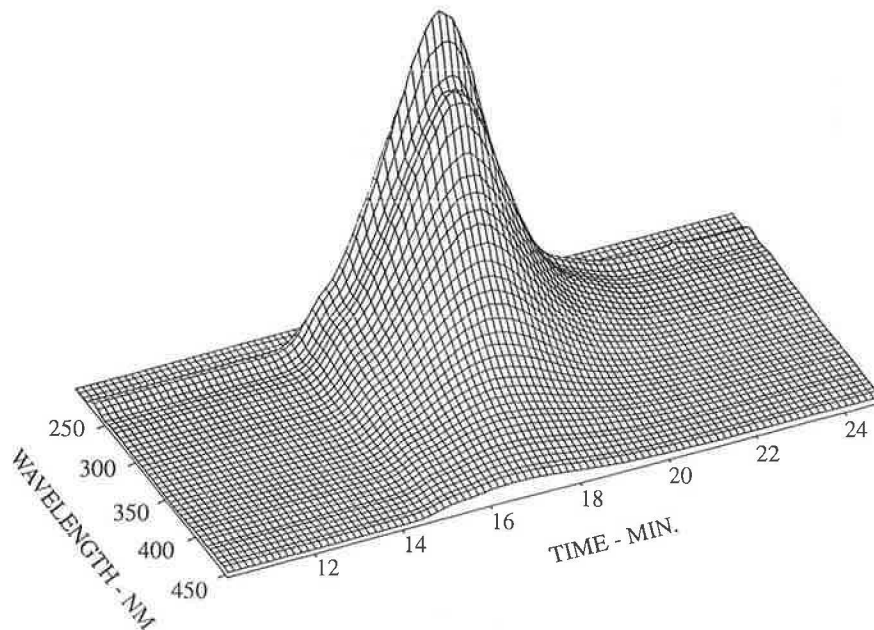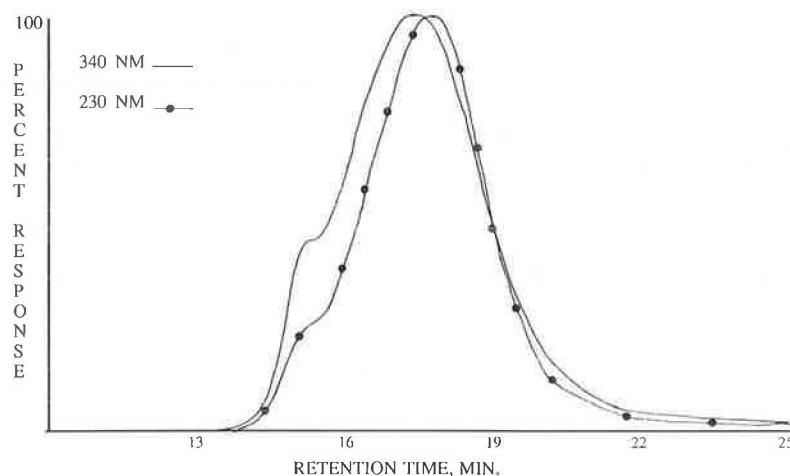


FIGURE 1 Class A Asphalt type.

**FIGURE 2  Class B Asphalt type.**

is indicated by the vertical dimension. A slice perpendicular to the chromatograms at a given time (B) is a spectrum of the molecules that elute at that time. (See Figure 6.)

## RESULTS AND DISCUSSION

Before discussing the results of this work, a few notes about data interpretation are made.

1. Nature of the LMS region. In many, although not all, asphalts, a pronounced shoulder will be found in the LMS region of the chromatogram. It has been shown (3,10,11) that the area of this shoulder for a given asphalt increases as concentration of the sample increases. It is generally accepted that increasing concentration favors intermolecular associa-

tion with the formation of agglomerates or molecular clusters. Brulé has shown (6) that the presence of such clusters in THF can be associated with molecular structuring in the neat asphalt and, eventually, to the rheology of the bitumen.

2. Interpretation of uv-vis data. As mentioned earlier, the wavelength at which a molecule will absorbe ultraviolet and visible light is a function of its structure. In general, but simplified terms, the wavelength increases as the size of the conjugated/aromatic system increases. The intensity of that absorption is a function of the inherent absorptivity as well as the concentration of the molecule. In a complex mixture such as asphalt, it is not possible to distinguish strictly among these contributions. For example, at a given elution time, it is highly unlikely that only one kind of molecule will be present. Therefore, the uv-vis spectrum at that elution time will be the sum of the spectra of the individual components.
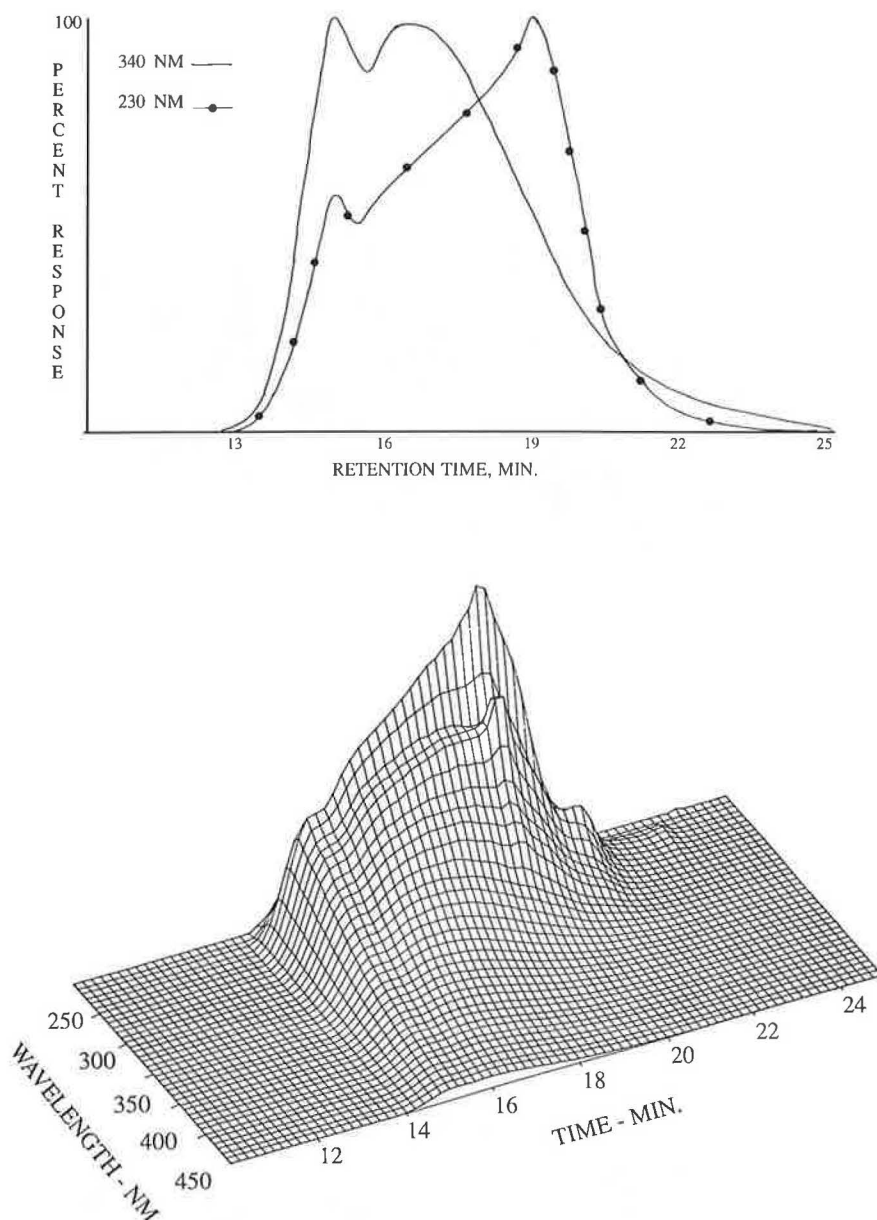
FIGURE 3   Class C Asphalt type.

Nevertheless, because the concentration of asphalt sample and analysis conditions are constant, and because peak shapes, areas, and intensities differ among the samples, it is possible to make comparisons in general terms. For purposes of this paper those asphalts with a more intense absorption at a given wavelength and/or absorption at a longer wavelength are referred to as being more highly conjugated/aromatic.

**The Data Base Asphalts**

The 19 asphalts around which the data base will be built were the first to undergo HP-GPC analysis. Most of these fell into three broad categories by virtue of their chromatographic shapes. Four of the 19 are similar to the asphalt shown in Figure 1 and have been included in Class A. In general, these materials have relatively narrow molecular size distributions and featureless three-dimensional plots. There is no shoulder of consequence in the large molecular size (LMS) region of the chromatograms. Peak maxima of 230 and 340 nm traces occur at approximately the same time.

Class B includes 10 of the data base asphalts (Figure 2). These asphalts have broader molecular size distributions than do Class A materials, and all have a well-defined shoulder in the LMS region. The peak maximum at 230 nm occurs at the same time or only slightly later than that at 340 nm.

Three asphalts are put into Class C by virtue of their broad molecular size ranges and the unusual shapes of their chromatograms at 230 nm. The latter feature is very obvious in Figure 3.

There is some variation within the classes. For example, some Class B asphalts have very clear absorptions at 410 nm
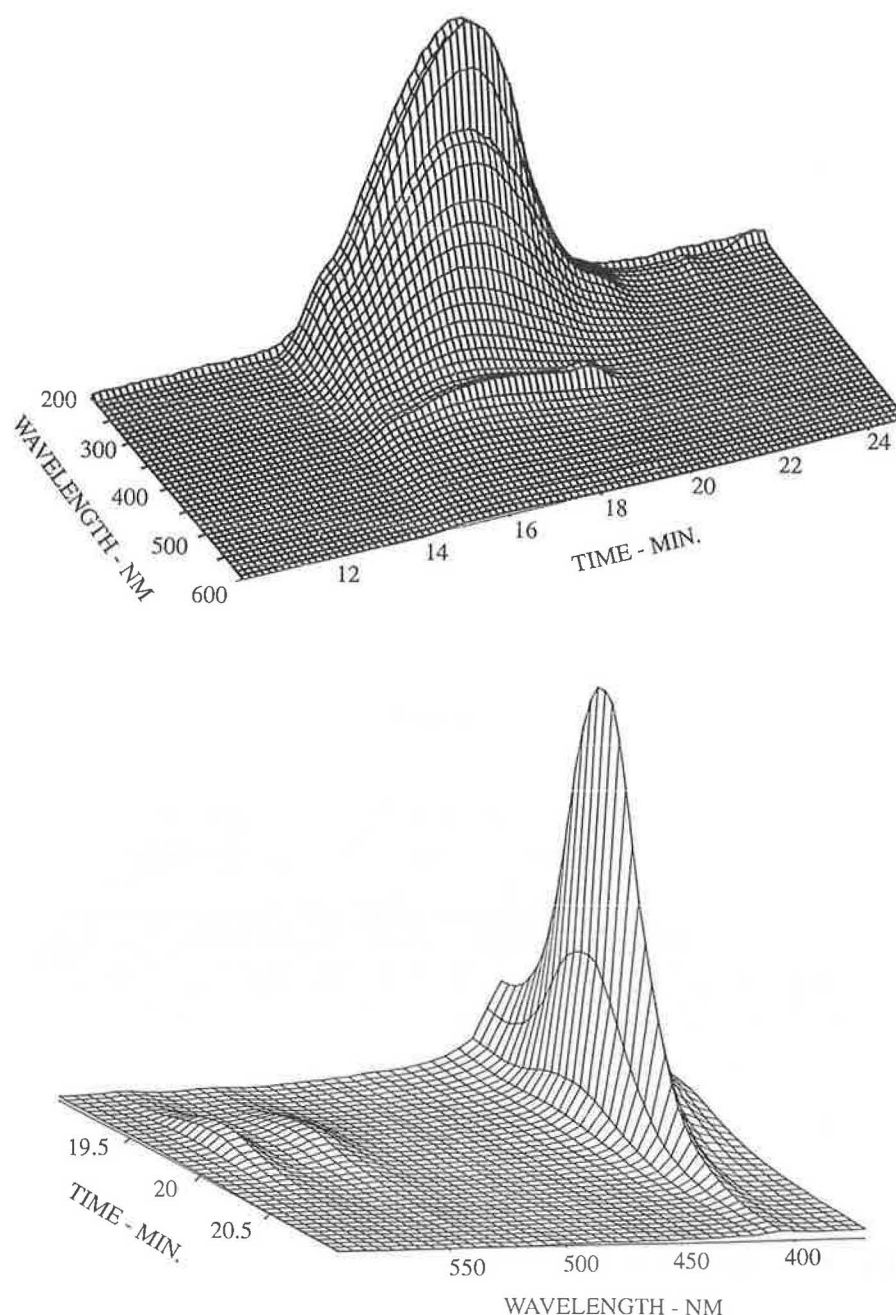
FIGURE 4 Class B Asphalt (Asphalt 3) with apparent vanadyl porphyrin absorptions.

(Figure 4). When the portion of the chromatogram centering about 19.5 min from 410 to 600 nm is isolated and expanded, two more absorbances at ~530 and ~570 nm can be seen. These bands exist for vanadyl porphyrins (*12*). Because Asphalt 3 is from a Venezuelan crude that is known to have a high content of vanadium, these absorptions probably represent those porphyrins, although that has not been exhaustively proven. The entity responsible for the 410-nm absorption is distributed over nearly the entire molecular size range, which would indicate that its apparent molecular size is affected by intermolecular association and/or additional ligands that greatly change its size without changing its absorption. If vanadyl porphyrins indeed play a significant role in the aging of asphalts, this technique offers a quick method of finding concentrations of such materials in asphalt.

There were two asphalts that did not fit easily into any of the classes. Asphalt 12, for example, appears to be a Class A material because of its narrow molecular size distribution (Figure 5), but the three-dimensional plot shows some absorptions between 270 and 300 nm in the SMS region; these indicate the presence there of materials that are somewhat more highly conjugated than are found in any of the other asphalts in the study. This asphalt also contains the lowest percentage of LMS material of the study group (less than 10 percent) and is the most highly temperature susceptible (PVN = -2.1).

The exact crude source and refining history of Asphalt 12 are unknown, but it is believed to be derived from a light crude that cannot be vacuum distilled to yield paving grade asphalt. In such cases, the refiner may harden the residue by air blowing. Air-blown asphalts typically have an intense LMS
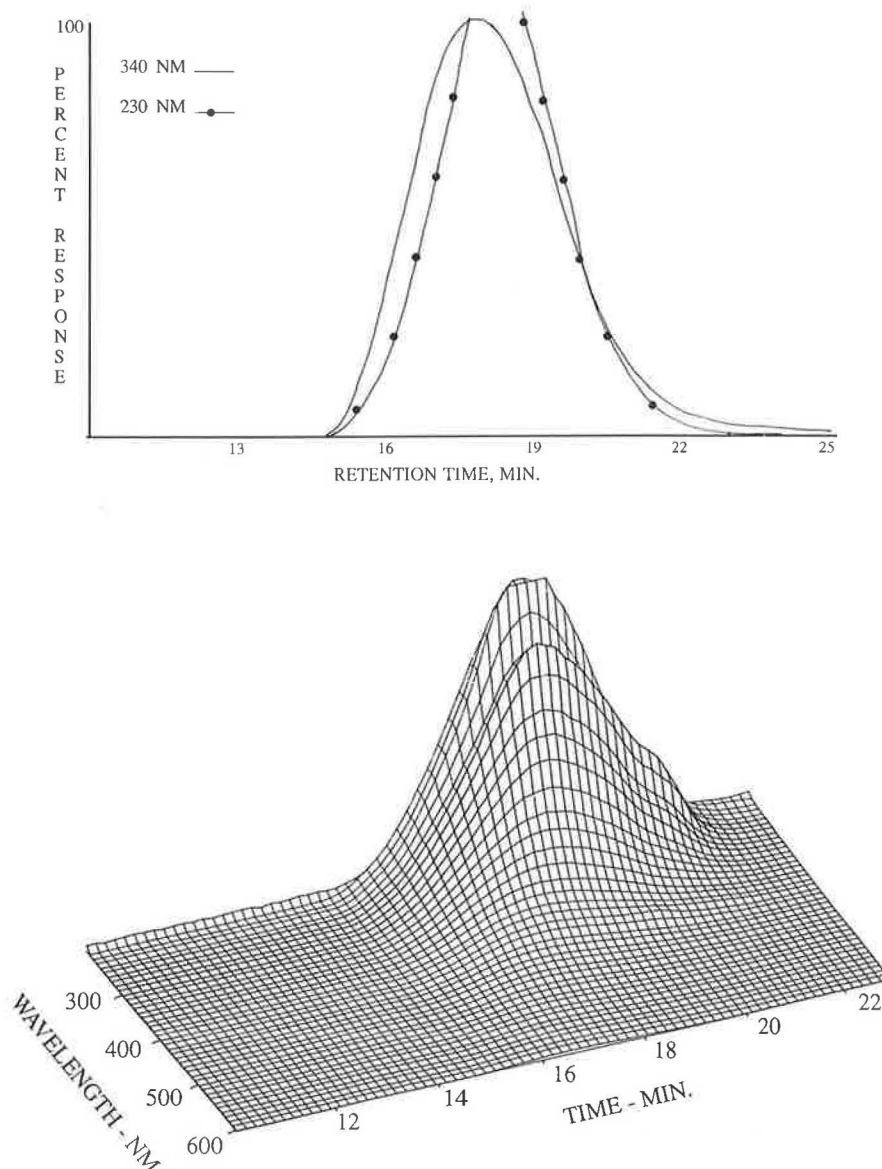
FIGURE 5  Asphalt 12, a nontypical material.

shoulder. Alternatively, solvent refining could be used, giving products with rather featureless three-dimensional plots (solvent-refined asphalts ususally fall into Class A). A third option is thermal cracking or visco-reduction. This process removes aliphatic chains from aromatic rings and yields (among other products) styrenelike products with reduced molecular size and more intense uv-vis absorption. Based on the three-dimensional plot, it could then be theorized that Asphalt 12 contains cracked residues.

Another unusual material is Asphalt 8, which is an important source for northwest Texas. This bitumen contains no precipitable asphaltenes, yet the HP-GPC chromatograms show it to contain a very high level of LMS material. The three-dimensional plot for Asphalt 8 is unusual in that the absorbances at wavelengths above 250 nm are quite different than for other asphalts. This characteristic can be seen clearly by uv-vis spectra taken at various times across the total elution time (Figure 6). These spectra, normalized to the same peak height, were collected at the same times for Asphalt 8 and

for a typical asphalt from Class B. At lower elution times (LMS region), Asphalt 8 is less aromatic/conjugated than the other asphalts (Figure 6, top); as the apparent molecular size decreases, however, the relative aromaticity of Asphalt 8 increases (Figure 6, bottom). Thus, this technique shows chemical evidence that this is a unique asphalt.

Although complete chemical and physical data are not yet available for the 19 asphalts, some trends are visible. Class A asphalts are more highly temperature susceptible (PVN < −1.1) but have low aging indices (about 1.6) when compared with the other classes. They have low asphaltene contents (9–11 percent) and low LMS content (15–17 percent at 340 nm). Three of these asphalts are known to perform poorly in that they undergo early severe transverse cracking.

Class B asphalts seem to be less temperature susceptible in terms of PVN (−0.07 to −0.7), with aging indices between 1.8 and 2.9. Asphaltene contents are higher (11–18 percent), as are percentages of LMS materials (21.5–30.6 at 340 nm). Virtually all of the asphalt cements in the test series commonly
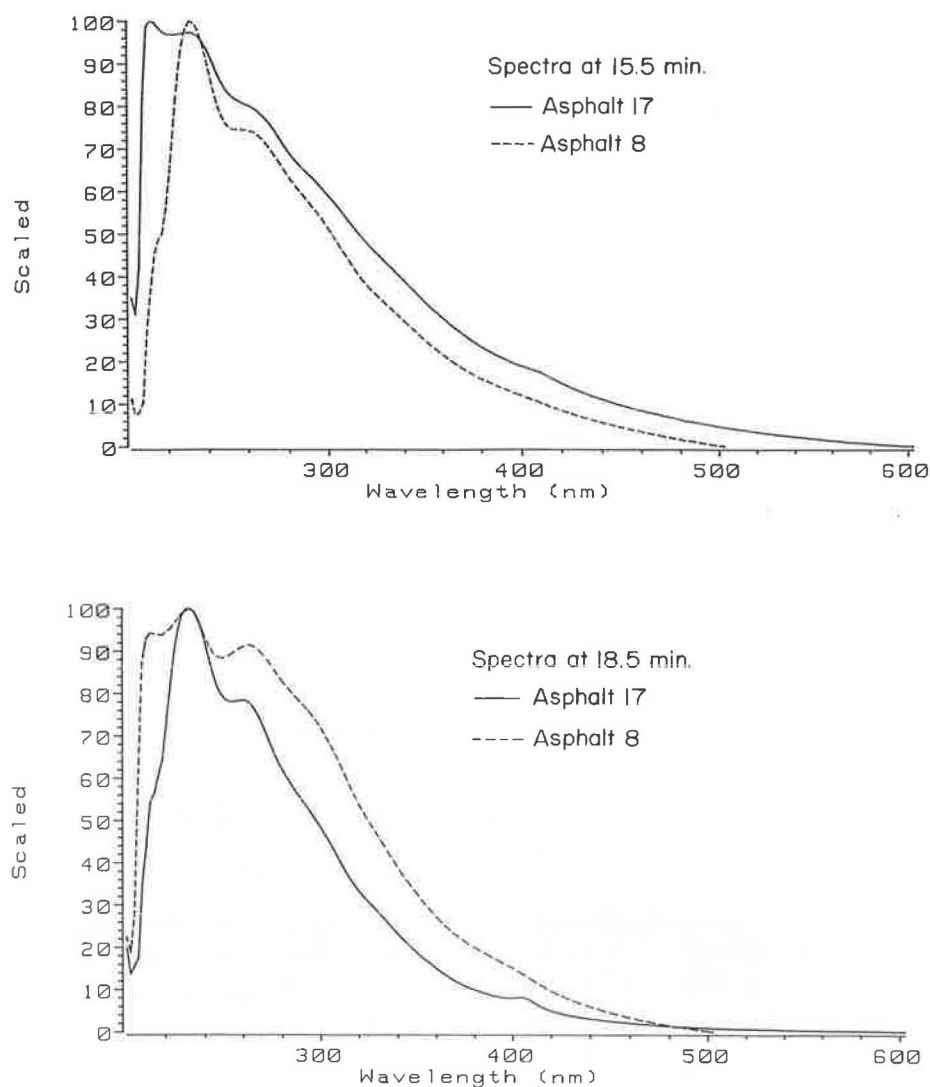
Spectra at 15.5 min.
—— Asphalt 17
---- Asphalt 8

Spectra at 18.5 min.
—— Asphalt 17
---- Asphalt 8

**FIGURE 6 Comparison of uv-vis spectra of Asphalt 8 and a typical Class B Asphalt.**

accepted as high-quality, paving-grade bitumens fall within category B.

Class C asphalts seem to have positive PVN values and high aging indices (3.7 to 7.3), high LMS contents (36–39 percent), and high asphaltene percentages (23–24). Indeed, none of these materials would be expected to meet U.S. standards.

The preceding should not be construed as firm rules but rather as overall trends. In Class C, for example, one asphalt has a lower LMS content than the class at 24 percent; another has a much lower asphaltene content than the others (5 percent).

**The HP-GPC Analysis of Other Materials**

A variety of other bituminous materials were submitted for analysis. These experiments were limited in scope, and efforts to draw conclusions are therefore restricted. However, the work does point out the potential usefulness of the technique and so is described briefly herein.

1. SARA fractionation is a technique similar to the well-known Corbett separation that yields four fractions: (S) sat-

urates, (A) aromatics, (R) resins, and (A) asphaltenes. It was decided that it would be interesting to analyze the fractions from Asphalt 3 to determine whether the material responsible for the 410-nm peak would be preferentially isolated in one fraction. As can be seen in Figure 7, the suspected metal porphyrins can be found in all fractions except the saturates. It is not clear, of course, whether this result indicates truly distinctive forms of the material or lack of specificity in the SARA separation technique.

2. To demonstrate the utility of the HP-GPC technique in comparing products from differing processes, an asphalt from a pilot refinery was compared with a residue from a laboratory distillation thought to mirror the refinery. In this set, the products were found to be dissimilar.

3. The operating conditions of a pentane-deasphalting process were changed to obtain resins with varying softening points from the same vacuum tower residue. The softening point is proportional to percent LMS material at both 340 and 230 nm in this sample set. The spectra and three-dimensional plots show that the extent of conjugation/aromaticity also increases with softening point.

4. Three thermally cracked (visco-reduced) residua representing different crudes and varying process severities were
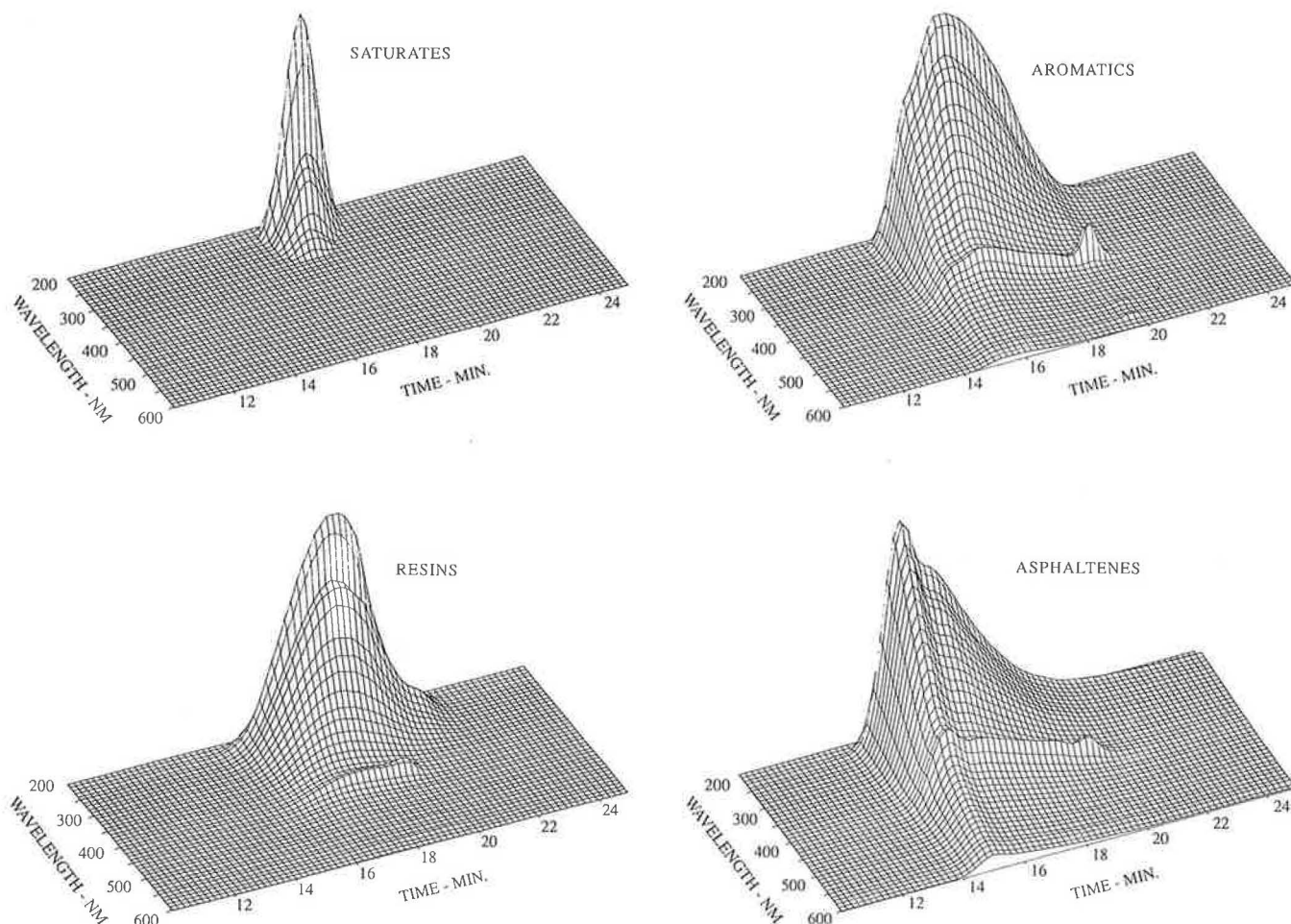
FIGURE 7 SARA fractions from Asphalt 3.

examined by HP-GPC. All showed typical Class A characteristics with low LMS contents. Asphaltene contents range from 9.6 to 19.2 percent, however. The intensities of the absorptions indicate that these materials are highly aromatic.

The 3-D plots show a small shoulder in the SMS region, primarily between 270 and 300 nm, fitting the pattern discussed for Asphalt 12 and thus supporting the theory that Asphalt 12 contains some fairly severely cracked residues.

5. Air blowing causes changes in the HP-GPC chromatograms of asphalts. In particular, there is a strong increase in the height of the leading shoulder and in the percentage of LMS material.

6. A number of experiments in which two bituminous materials were blended supported earlier evidence (2) that the HP-GPC curve of a blend can be predicted from the curves of the component asphalts as a matter of simple proportionality. The refiner can use HP-GPC as a tool that may help in finding ways to use poor-quality crudes and asphalts.

## CONCLUSION

The work presented in this paper was intended to explore the potential uses of high performance gel permeation chromatography (HP-GPC) in the study of bituminous materials by

a refiner. The addition of a photodiode array spectrophotometer for multiple wavelength detection expanded the chemical information obtainable from HP-GPC. This combination provides data on the molecular size distribution of the samples analyzed as well as on their relative conjugation/aromaticity.

A group of 19 asphalts, which will form a data base, was analyzed. These materials were divided into three classes on the basis of their chromatographic shapes. Thus far, associations of the classes have been made in a general way with temperature susceptibility (PVN) and aging index. Two asphalts, both known to be very unusual materials, did not fit the classifications set in this work.

Further explorations included HP-GPC analysis of SARA fractions from an asphalt that contained material absorbing at 410 nm, probably vanadyl prophyrin. The HP-GPC chromatograms show that the material of interest was distributed in all but the saturates fraction.

Other experiments of limited scope were performed to explore a variety of potential applications for this technique.

● Pentane-deasphalted resins from a single feed stock were analyzed. They showed an increase in ring and ball softening point with percent LMS.

● Viscosity-broken residua displayed HP-GPC characteristics similar to Class A asphalts but with an additional small

shoulder between 270 and 300 nm. This evidence was used to help to understand the nature of one of the two asphalts that did not fit the main classifications.

● Air-blown residua showed evidence of an increase in LMS content with increased blowing severity.

This technique potentially is very useful to a refiner producing asphalt products and warrants further exploration. The next step must be to develop a statistical method to characterize the data mathematically. Perhaps techniques such as those developed by Plummer (log Gaussian distributions) or by the French Central Highway Administration (LCPC) laboratories (statistical deconvolution) for two-dimensional curves can eventually be expanded to evaluate these three-dimensional figures.

## ACKNOWLEDGMENTS

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