Use of HPGPC with UV Detection for Determination of Molecular Size Distribution of Asphalt Cement After Quantitative Corrections for Molar Absorptivity Variation and Saturated Oils

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A method is described for calculating molecular size distribution (MSD) of asphalt cement using ultraviolet (UV) detection. A 5-μm, 500Å phenogel column is used to fractionate a known amount of a whole asphalt sample. Tetrahydrofuran:pyridine (95:5) serves as mobile phase. After passing through the UV detector at 345 nm, the eluent is fractionated at arbitrarily selected intervals. The fractions are collected in weighed petri dishes and left to dry. A computer generates a slice report showing percent material eluting at successive retention times. The injection is repeated and eluting fractions collected in volumetric flasks. After removing the column, a known volume of a given fraction is injected and the maximum absorbance reading for each fraction is recorded. The second set of fractions is then poured into the petri dishes containing the fractions from the first injection. Then, the molar absorptivity a is calculated. Using ASTM Method D4124-86(B), the percent saturates is determined. The saturates are injected, a differential refractive index detector is used to get an MSD value, and a computer generates a slice report. The data generated for the whole asphalt sample are treated mathematically, first, to account for variation of a and, second, for undetectability of saturates by UV. For six samples, comparison of data readily available from the slice report with those obtained after treatment reveals differences of up to 65 percent for some fractions. Reproducibility of the system and of the proposed method proved satisfactory. Excluding the separation of saturates, the proposed method consumes 7 to 8 hr; in series less than 4 hr.

The revival of liquid chromatography in its modern version, high-performance liquid chromatography (HPLC), has paved the way for scientists to investigate highly complex organic and inorganic systems. Companies using polymers as raw material rely primarily on high-performance gel permeation chromatography (HPGPC) to fingerprint an incoming batch of polymer. For a batch to be accepted, the molecular size distribution (MSD) profile of the raw material has to match, by overlay, the profile already available for an ideal batch. HPGPC serves as well for quality control of the finished polymer product.

HPLC and HPGPC have been used to study the chemistry of asphalt cement (AC) (1–9). The two techniques, together with other investigations on the rheological behavior of materials (e.g., peeling, viscoelasticimetry, and viscosity of ultrathin films) show that ACs with the same specifications may in fact have substantially different chemical compositions and

rheological behaviors (5). Brule (3–5), therefore, has emphasized the practical application of physicochemical methods such as HPGPC for the characterization of road asphalts.

In the HPGPC study of asphalt, two main types of detection are generally used—namely, the differential refractive index (RI), and ultraviolet (UV) absorption. The RI detector has the advantage of being able to analyze almost all types of organic structures, including the saturated oils (saturates). This advantage, however, is offset by drifting of the baseline, low sensitivity, and, more significant, the lack of reproducibility (4). The UV detector, on the other hand, is characterized by high sensitivity, stability, excellent reproducibility, and a wide range of applicability. For the analysis of road asphalts, however, two difficulties arise.

1. The saturates, which usually constitute 10 to 25 percent of the material, do not absorb UV radiation. Because the UV detector fails to respond to this class of compounds, the slice report, which lists how much material elutes at a given time, does not account for the saturates.
2. Unlike other polymers, any point on the MSD profile is governed by the amount of material eluting from the column as well as by the molar absorptivity (extinction coefficient) of the complex mixture eluting from the column at this particular point (4,8,10). The chemical composition of the asphalt material eluting from the GPC column varies with the retention volume (or time), thus causing the molar absorptivity to be a variable that has to be considered in determining the molecular size distribution of a chemically complex mixture such as asphalt. Unless the molar absorptivity is accounted for mathematically, the percent material reported at a given time will not only be a function of the amount passing through the detector, but also would depend on the molar absorptivity of such material.

These difficulties restrict the usefulness of the slice report and shift the burden of characterization of an asphalt sample to the MSD profile by itself. For many asphalt samples, however, the differences between the corresponding profiles are too subtle to provide decisive answers. Furthermore, two apparently identical MSD profiles can in fact belong to two different asphalts if the molar absorptivity of the constituents is distributed in a manner that tends to minimize the inherent differences.

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A semipreparative GPC column fractionated a whole asphalt sample solution into a number of fractions at arbitrarily chosen time intervals. The slice report generated by the computer determined the percent of material eluting in each fraction. For each fraction, the molar absorptivity was determined in a manner similar to that described by Bishara and Wilkins (*11*). Another sample weight was then analyzed using ASTM Method D4124-86(B) to isolate the saturates; the solvent (hexane) evaporated and the percent of saturates was determined gravimetrically, as usual. After dissolution, an aliquot of the saturates was run across the same GPC column under conditions similar to those used for the whole asphalt sample, but using RI detection. The computer generated a slice report that determined the percent of saturates that eluted in each fraction. From this information, the percent of material in each fraction of the whole asphalt sample was then analyzed mathematically, to account for variation of molar absorptivity and for the undetectability of saturates by the UV detector.

EXPERIMENTAL

Apparatus

A Waters HPLC consisting of a Waters 600 multisolvent delivery system, a U6K injector, a UV-visible liquid chromatographic spectrophotometer (Lambda-Max, Model 481), and a Waters differential refractometer, Model R 401; and a Phenomenex, 5-μm, 500Å phenogel semipreparative column (300 × 22.5 mm) with tetrahydrofuran (THF) as the solvent were used. The data were received by a Waters 840 data and chromatography control station, consisting of a Digital Equipment Corporation (DEC) computer (Professional 380), a DEC LA Printer, and a Waters system interface module (SIM).

Materials

• THF, Optima HPLC-grade, freshly distilled and filtered through 0.2-μm membrane;
• Pyridine, distilled and filtered through 0.2-μm membrane;
• n-Hexane, distilled;
• Helium gas, 99.9 percent pure for sparging;
• Nylon 66 membranes, 47 mm in diameter, 0.2-μm, for solvent and sample purification;
• Whatman Glass microfiber filters, GF/F, 4.25 cm in diameter, for separating the asphaltenes as specified in ASTM D4124-86(B);
• Alumina, activated, chromatographic grade, 80–200 mesh, Type F–20, calcined at 775°F (413°C) for 16 hr, and stored in a desiccator; and
• Toluene, methanol, and trichloroethylene used to elute the asphalt sample solution through the alumina column.

Procedures

Step I—Separation of Saturates

The ASTM method D4124-86(B) was followed to separate the saturates. The rest of the sample, i.e., the naphthene aromatics and polar aromatics, were then eluted out of the column. The percent of saturates was determined gravimetrically, as usual.

Step II—Molecular Size Distribution of Saturates

The saturates were dissolved qualitatively in about 10 mL of THF and filtered through a 0.2-μm membrane. About 150 μL of the solution were injected into the HPLC and a mobile phase composed of 100 percent THF was used at a flow rate of 6.0 mL/min. The phenogel column was maintained at ambient temperature, and the RI detector was activated. A detailed slice report was programmed that showed the percent saturates eluting, e.g., every 0.1 min. From the slice report, the percent saturates eluting within the arbitrary time intervals T_1 (4.5 to 7.5 min), T_2 (7.5 to 8.5 min), T_3 (8.5 to 9.5 min), T_4 (9.5 to 10.5 min), and T_5 (10.5 to 14.0 min) following injection were obtained. Once selected, these intervals had to be maintained throughout the rest of the procedure.

Step III—Molecular Size Distribution of Whole Asphalt

An asphalt sample in the range 2.0 to 2.5 g was weighed accurately (to within 0.01 mg). About 25 mL of THF was added and the mixture was sonified for 15 min at room temperature. The solution was transferred quantitatively to a 50-mL volumetric flask, completed to volume V with THF, and filtered through a 0.2-μm membrane.

1. An exact aliquot (100 to 200 μL) chosen to contain 6 to 8 mg of the asphalt sample was injected. A mobile phase composed of 95 percent THF and 5 percent pyridine was used at a flow rate of 6.0 mL/min. The phenogel column was maintained at ambient temperature. The wavelength of absorption on the UV detector was set to 345 nm. The eluting material was collected in a series of five small, glass, accurately weighed (to within 0.01 mg) petri dishes at the same set of time intervals used in Step II. Petri Dishes 1 to 5 were set aside to allow for the solvent to evaporate. A detailed slice report that showed the percent of material eluting, say, every 0.2 min, was programmed. From this slice report, the percent of asphalt material eluting in each fraction, F_1 through F_5, was determined.
2. Under exactly the same conditions, the injection was repeated using an aliquot equal to that used in Step I. The eluting fractions were collected in a series of five volumetric flasks numbered 1 through 5. Because the fraction volumes were not uniform, each of the first and fifth fractions was collected in a 25-mL volumetric flask; each of the remaining fractions was collected in a 10-mL volumetric flask. The solution volume in each flask was filled to the mark with THF.

Step IV—Determination of Molar Absorptivity of Fractions of Whole Asphalt

To determine the molar absorptivity of each of the fractions collected in Step III, Part 2, the column was removed from the HPLC system and the two lines, originally joined to the column, were connected to each other.

1. Measurement of A. THF was used as the mobile phase at a flow rate of 0.2 mL/min. About 30 μL of the solution in Volumetric Flask 1 was injected. With the wavelength on the UV detector set at 345 nm, the absorbance reading increased, gradually reaching a maximum before declining back to the initial value (0.001). The maximum absorbance reading A_1 was recorded and used to substitute for the absorbance A in Beer's law

$$A = abc \tag{1}$$

where a = molar absorptivity, b = optical path length, and c = concentration. Because the same sample cell was used in all the work, and because relative rather than absolute value of molar absorptivity was sought, the optical path length could be eliminated, and the equation simplified to

$$A = ac \tag{2}$$

or

$$a = A/c \tag{3}$$

The value of the absorbance A was then obtained and recorded for each of the other fractions.

2. Calculation of c and a. The contents of each volumetric flask collected in Step III, Part 2, was poured into the corresponding petri dish from Step III, Part 1, and rinsed quantitatively. The petri dishes were set aside until dry, then heated in an oven at 160°C for 90 min. They were cooled in a desiccator until weight was constant. Setting S = weight in milligrams of saturates in the sample volume injected in Step III, Part 2,

$$S = \frac{W \times 1,000 \times IV \times PS}{V \times 1,000 \times 100} \tag{4}$$

where

W = sample weight (g),
IV = injection volume (μL),
PS = percent saturates (%), and
V = total volume (Step III) (mL).

For example, setting s_1 = weight in milligrams of saturates in Volumetric Flask 1,

$$s_1 = \frac{S \times PS_1}{100} \tag{5}$$

where PS_1 is the percent saturates eluting in time interval T_1 in Step II.

The weight in milligrams of UV-absorbing material in Volumetric Flask 1 is given by

$$X_1 = \frac{W_1}{2} - s_1 \tag{6}$$

where W_1 is the weight in milligrams of material in Petri Dish 1 from Step IV, Part 2.

Therefore,

$$c_1 = \frac{x_1 \times 1,000 \times 30}{v_1 \times 1,000} \tag{7}$$

where c_1 is the concentration of absorbing material in the (IV_1 = 30 μL) injection volume and v_1 is the volume in milliliters of Volumetric Flask 1. Equation 3 was used to calculate the corresponding value of a. Similarly, c and a were calculated for the rest of the fractions.

Calculation

Correction for Molar Absorptivity

For each fraction, the percent material as obtained from the slice report in Step III, Part 1, was divided by the molar absorptivity of the fraction concerned. The result was termed the "interim percent material." In this manner, the effect of molar absorptivity on the apparent value of eluting percent material was nullified (although the sum of the interim percent material for all the fractions was more than 100 percent).

Correction for Saturates

For the whole asphalt sample under consideration, the percent of UV-absorbing material was calculated by subtracting the percentage of saturates (Step I) from 100.0. For each fraction, the interim percent material was multiplied by the percent of UV-absorbing material and divided by the sum of interim percent materials to get the correct percent material in this fraction, i.e., to get the percent of absorbable components present in the given fraction. The sum of correct percent materials of the five fractions was the percent of UV-absorbing material in the given asphalt sample.

RESULTS AND DISCUSSION

Since the introduction of HPGPC as a polymer fractionation method, the technique has proved to be a reliable tool for characterization of polymers (12,13). Although not a polymer in the strict sense of the word, asphalt cement has also been analyzed by this technique. Not many detectors are suitable, and UV detection, though not perfect, is the most advantageous. From the MSD profile obtained, the computer sliced the area under the chromatogram and generated a report (slice report) that listed the percent material that eluted at a given retention time. Unlike polymers (and because of the chemical complexity of asphalt), for these values of percent eluting material to have any significance, the effect of variation of molar absorptivity with retention time had to be offset. Another variable was the undetectability of the saturated compounds by the UV detector.

One approach for addressing these problems was to use a relatively large GPC column that allowed injection of larger sample concentrations, collect the eluting material at different time intervals, generate an MSD profile of the whole asphalt sample, and then determine the molar absorptivity of each

fraction. The saturates were separated, weighed, dissolved, and eventually run through the HPGPC system to obtain an MSD profile.

Development and Limitation

Preliminary investigations to select the highest possible sample load on the column, without much loss of resolution, revealed that a 6- to 8-mg sample, run at a solvent flow rate of 6.0 mL/min, is optimum (Figure 1). As mentioned before, the method depended on fractionizing a whole asphalt sample into a number of fractions. Obviously, the higher the number of fractions collected, the closer would be the results to the actual values. However, the following limitations applied: (a) the maximum sample load allowed, which was a function of the column packing and dimensions, and (b) the capability of the balance used for weighing each fraction. As a tradeoff to these limitations, five fractions were selected as a reasonable number. However, to have fraction weights large enough to be accurately weighed by the balance available at the time of this study, the whole-asphalt sample injection had to be done twice. To facilitate computations, the two injection volumes were identical.

That the time elapsed between dissolution and injection might affect the MSD profile of an asphalt sample was already known. Figure 2 shows three runs for the same sample injected at 1, 2, and 4 hr from dissolution. Curve B demonstrates that after 2 hr the large molecular-weight region ($t_R = 6$ to 7 min) exhibited a slight decrease in detector response that later on (4 hr from dissolution, Curve C) led to a corresponding increase at the small-molecular-weight region ($t_R = 11$ to 12 min). The dissociation of larger molecules into smaller ones over time has been described by Brule (*4*). Therefore, the time interval between dissolution and injection was kept to a minimum, preferably 2 hr.

The time intervals set for collecting the eluent were arbitrarily set to provide a reasonable weight in each fraction. Although the cut times could be altered, once selected they had to be maintained throughout the procedure, or for a whole set of comparative analyses.

In an early stage of this study and to keep the error in weighing a fraction at a minimum, light polythene beakers were used for collection. On drying and heating, however, negative weights were frequently encountered, apparently as a result of the THF partially dissolving the container material to yield volatile by-products. The problem disappeared once glass petri dishes were substituted.

Sonification for 15 min at room temperature proved adequate for quantitatively dissolving any of the samples under investigation. To elute an asphalt sample of 6 to 8 mg out of the 300- × 22.5-mm semipreparative GPC column, a mobile phase of THF flowing at 6.0 mL/min was used at first. But the chromatogram was found to extend beyond the total column void volume, i.e., outside the useful range of separation by GPC. Some of the smaller molecules, particularly the strongly polar ones, are retained within the column by an adsorption mechanism. Use of a mobile phase composed of 95 percent THF plus 5 percent pyridine overcame the forces of adsorption, and enhanced elution.

The importance of asphaltenes in the asphalt macrostructure model of Yen (*14*) is known. Interactions between the

π electrons of the pericondensed polynuclear aromatics provide cohesion for the sheets to form the asphaltene micelles. Under favorable conditions, these combine to form aggregates. Polynuclear aromatics are therefore important, and use of a long wavelength (345 nm) of UV absorption was warranted.

Analysis of Samples

Six asphalt cement samples from five different refineries and covering a wide range of viscosities were selected. Each sample was analyzed by the proposed method, and the results are given in Table 1.

As expected, the results show that the molar absorptivity depends on retention time. For some samples, e.g., Sample 85–1147, the range of variation was 0.1 to about 0.6. This value also varies from one sample to the other. These variations highlight the significance of including the value of molar absorptivity in MSD calculations. For the six samples analyzed, the percent saturates ranged between 10 and 23. Reliable information about the MSD of an asphalt sample using UV detection should account for the amount as well as the MSD of the saturates themselves within the sample in question.

Comparison between the treated and untreated data (those readily generated by the computer) in Table 1 reflects the influence that the molar absorptivity and saturates may exercise on the MSD data. Apart from Fraction 5, the difference was detectable for all fractions of the six samples analyzed, and was quite significant for some samples and for certain fractions reaching about −65 percent for F_1 of Sample 88–1043 and about +60 percent for F_3 of Sample 86–4292.

For laboratories where the analysis of asphalt into four fractions according to the ASTM method D4124-86(B) is a routine test, the time required for Steps II through IV of the proposed procedure is approximately 7 to 8 hr. In series, it takes less than 4 hr.

Reproducibility

To test reproducibility of the HPGPC system, a set of six polystyrene standards and toluene, run 11 days apart, were compared (Table 2). In either case, 100 μL of about 0.25

TABLE 2 COMPARISON OF RETENTION TIMES FOR A SET OF POLYSTYRENE STANDARDS AND TOLUENE, RUN 11 DAYS APART

Standard	Molecular Weight	Retention Time (min)	
		1st Day	12th Day
F–2	16,700	5.66	5.66
F–1	10,300	6.16	6.16
A–5000	6,200	6.78	6.78
A–2500	2,800	7.59	7.58
A–1000	950	8.70	8.70
A–300	402	9.75	9.75
Toluene	92	12.28	12.28
Correlation		0.9999176	0.9999195
Standard error of estimate		0.16848	0.16358

TABLE 1   MOLECULAR SIZE DISTRIBUTION OF ASPHALT CEMENT SAMPLES BEFORE AND AFTER CORRECTION FOR MOLAR ABSORPTIVITY VARIATION AND SATURATED OILS

Sample No.	Fraction	Percent Saturates *	Molar Absorptivity**	Percent Whole Asphalt Material		
				Untreated Data	Interim Data	Treated Data ***
	F_1	2.2	0.200	49.3	246.5	31.3
	F_2	6.9	0.098	17.2	175.5	22.3
85-2754	F_3	0.7	0.089	16.7	187.6	23.7
	F_4	0.1	0.184	14.3	77.7	10.0
	F_5	0.0	0.106	2.5	23.6	2.8
	Total	9.9		100.0	710.9	90.1
	F_1	3.2	0.308	44.1	143.2	21.6
	F_2	3.3	0.103	17.7	171.8	26.0
85-1147	F_3	4.1	0.098	17.8	181.6	27.5
	F_4	2.1	0.242	19.4	80.2	12.1
	F_5	0.0	0.572	1.0	1.7	0.3
	Total	12.7		100.0	578.5	87.5
	F_1	4.2	0.210	58.4	278.1	33.9
	F_2	8.5	0.089	17.8	200.0	24.3
85-2357	F_3	3.9	0.096	14.5	151.0	18.4
	F_4	0.0	0.166	9.0	54.2	6.6
	F_5	0.0	0.283	0.3	1.1	0.1
	Total	16.6		100.0	684.4	83.3
	F_1	1.5	0.297	43.7	147.1	21.5
	F_2	10.3	0.124	19.3	155.6	22.7
86-4292	F_3	2.6	0.093	19.3	207.5	30.3
	F_4	0.3	0.238	13.7	57.6	8.4
	F_5	0.0	0.246	4.0	16.3	2.4
	Total	14.7		100.0	584.1	85.3
	F_1	1.4	0.307	23.3	75.9	8.5
	F_2	14.1	0.301	23.0	76.4	8.6
88-1043	F_3	6.6	0.065	23.7	364.6	41.0
	F_4	0.7	0.150	23.0	153.3	17.2
	F_5	0.0	0.397	7.0	17.6	2.0
	Total	22.8		100.0	687.8	77.3

85-3890   See Table 3

*Calculated as percentage of the whole asphalt sample.

**   These are not absolute values.

***   Does not include saturates, i.e., only covers the UV-absorbing material.
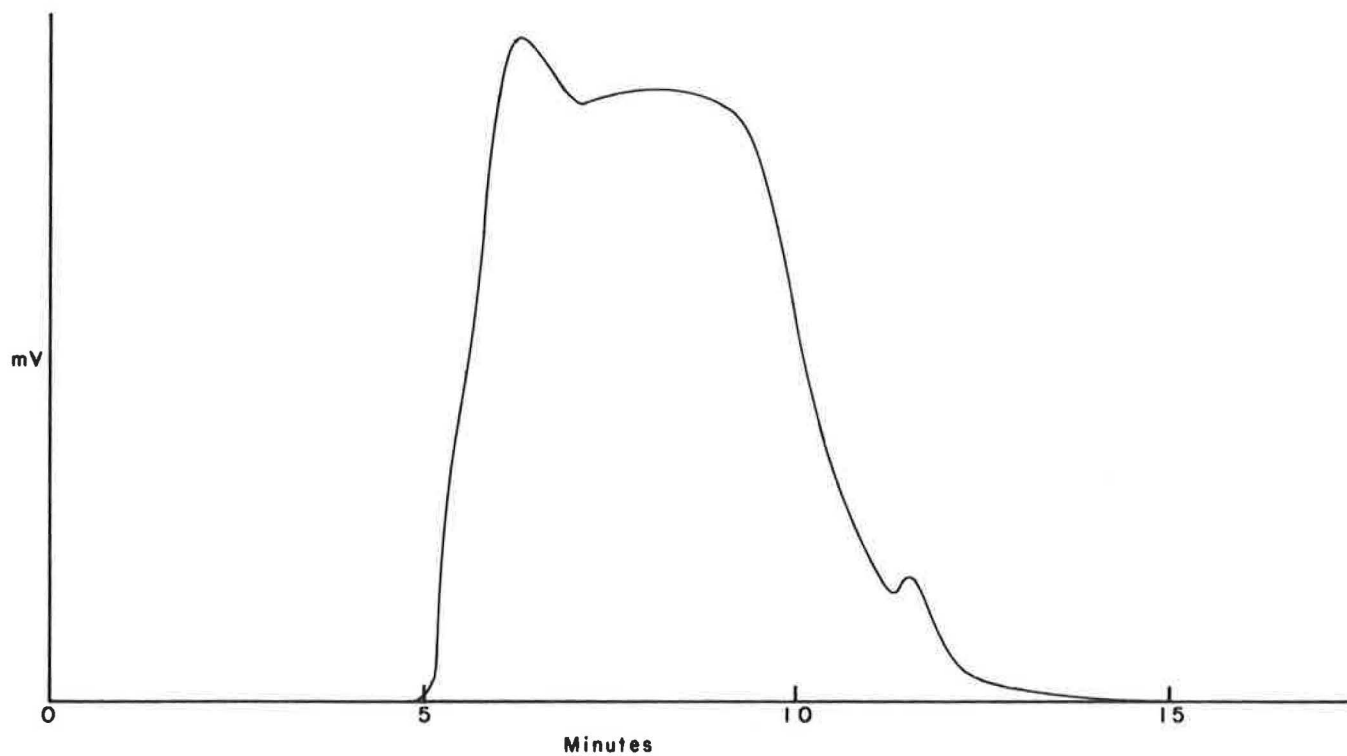
FIGURE 1 MSD profile for 7.99416 mg of Sample 86–4292 using 95 percent THF + 5 percent pyridine at 6.0 mL/min, ambient temperature, and one 500Å phenogel column (300 × 22.5 mm), UV at 345 nm.
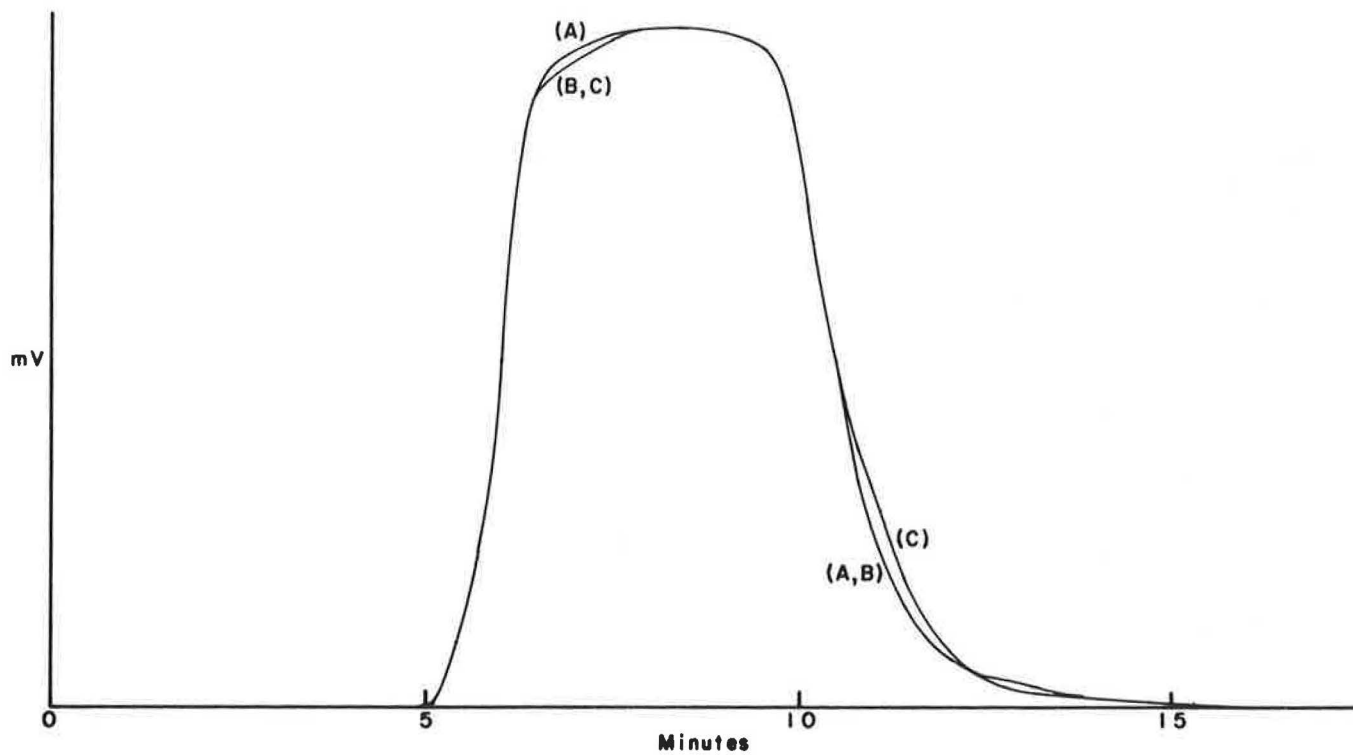

FIGURE 2 Comparison of three runs of Sample 85–3890 at different times from injection; 95 percent THF + 5 percent pyridine used as a mobile phase at 6.0 mL/min, UV at 345 nm, one 500Å phenogel column (300 × 22.5 mm); Curve A, 1 hr; Curve B, 2 hr; Curve C, 4 hr.

TABLE 3   RESULTS OF ANALYSIS OF SAMPLE 85–3890 TWICE, 10 DAYS APART

Frac-tion	Percent Saturates *	Molar Absorptivity ** (i)+	(ii)+	Percent Whole Asphalt Material (i)+		(ii)+	
				Untreated Data	Treated Data ++	Untreated Data	Treated Data ++
F_1	1.2	0.237	0.231	36.7	20.2	37.0	19.1
F_2	2.2	0.124	0.099	21.7	22.9	21.2	25.5
F_3	4.4	0.088	0.079	21.3	31.7	21.1	31.8
F_4	2.5	0.169	0.176	16.9	13.1	17.5	11.9
F_5	0.0	0.256	0.259	3.4	1.7	3.2	1.5
Total	10.3			100.0	89.6	100.0	89.8

*   Calculated as percentage of the whole asphalt sample.

**   These are not absolute values.

\+   (i) Test run the first time; (ii) test run ten days later.

\++   Does not include saturates, i.e., only covers UV-absorbing material.

percent polystyrene solution was injected, one 500Å phenogel column (300 × 22.5 mm) maintained at ambient temperature was used, and THF at 6.0 mL/min served as the mobile phase (the inclusion of 5 percent pyridine in the mobile phase did not seem to affect the retention time, and therefore was dispensed with). On the first day, the UV detector at 272 nm was used; on the 12th day, the RI detector was used.

To test reproducibility of the proposed method, Sample 85–3890 was tested twice under the same conditions but with 10 days separating the two runs. For each run, however, a fresh sample weight was used. Table 3 presents the two sets of measurements. All of the figures, with one exception, revealed a satisfactory level of reproducibility. Only Fraction 2 showed a deviation of 2.6 percent (absolute). This deviation occurred although the fraction weight was practically the same for the two tests (4.45 mg for the first run compared with 4.58 mg for the second run, with a relative error of 2.9 percent). The injected sample weights were also practically identical (16.55 and 16.54 mg, respectively, with a 0.06 percent difference). The difference in the values of A, however, was unexpectedly high, with 25 percent relative error (Table 3). Therefore, the deviation of the results of Fraction 2 was attributed to an odd reading of the absorbance.

CONCLUSION

In the study of the MSD of asphalt cement using HPGPC with UV absorption for detection, two difficulties have to be considered. First, the saturated compounds (usually 10 to 25

percent of sample) do no absorb electromagnetic radiation in the UV region. Second, because of the chemical complexity of asphalt, the molar absorptivity varies with the retention time. The data provided by the slice report depicting the percent material eluting at successive retention times (and correspondingly of decreasing molecular weights) has to be treated mathematically to account for these difficulties. To achieve this, a whole asphalt sample is fractionated, and the molar absorptivity determined for each fraction. The saturates are separated, and their MSD is determined.

ACKNOWLEDGMENTS

REFERENCES

1. C. Such, B. Brule, and C. Baluja-Santos. Characterization of Road Asphalt by Chromatographic Techniques (GPC and HPLC). *Journal of Liquid Chromatography*, Vol. 2, 1979, pp. 437–453.
2. H. V. Drushel and W. W. Schultz. Effect of Solvents and Temperatures on the Separation of Asphaltenes by Gel Permeation

Chromatography. Presented at Symposium on Techniques for Characterization of Residual Fuels. American Chemical Society, San Francisco, Calif., 1980.

3. B. Brule. Characterization of Bituminous Compounds by Gel Permeation Chromatography (GPC). *Journal of Liquid Chromatography*, Vol. 2, 1979, pp. 165–192.

4. B. Brule. Contribution of Gel Permeation Chromatography (GPC) to the Characterization of Asphalts. In *Liquid Chromatography of Polymers and Related Materials II*, (J. Cazes and X. Delamare, eds.), Marcel Decker, New York, 1980, pp. 215–248.

5. B. Brule, G. Ramond, and C. Such. Relationships Between Composition, Structure, and Properties of Road Asphalts: State of Research at the French Public Works Central Laboratory. In *Transportation Research Record 1096*, TRB, National Research Council, Washington, D.C., 1986, pp. 22–34.

6. L. Caylor and T. Sharp. Asphalt Characterization and Performance Study. *Report No. 8301*, Georgia Department of Transportation, Atlanta, March 1987, pp. 1–64.

7. G. R. Donaldson, M. W. Hlavinka, J. A. Bullin, C. J. Glover, and R. R. Davison. The Use of Toluene as a Carrier Solvent for Gel Permeation Chromatography Analysis of Asphalt. *Journal of Liquid Chromatography*, Vol. 11, 1988, pp. 749–765.

8. J. A. S. Pribanic, M. Emmelin, and G. N. King. Use of Multi-wavelength UV-VIS Detector with HP–GPC to Give a Three-Dimensional View of Bituminous Materials. In *Transportation Research Record 1228*, TRB, National Research Council, Washington, D.C., 1989, pp. 168–176.

9. A. S. Noureldin and L. E. Wood. Variations in Molecular Size Distribution of Virgin and Recycled Asphalt Binders Associated with Aging. In *Transportation Research Record 1228*, TRB, National Research Council, Washington, D.C., 1989, pp. 191–197.

10. L. R. Snyder. Determination of Asphalt Molecular Weight Distributions by Gel Permeation Chromatography. *Analytical Chemistry*, Vol. 41, 1969, pp. 1223–1227.

11. S. W. Bishara and E. Wilkins. Rapid Method for the Chemical Analysis of Asphalt Cement: Quantitative Determination of the Naphthene Aromatic and Polar Aromatic Fractions Using High-Performance Liquid Chromatography. In *Transportation Research Record 1228*, TRB, National Research Council, Washington, D.C., 1989, pp. 183–190.

12. J. J. Cazes. Chemical Instrumentation. Gel Permeation Chromatography. *Journal of Chemical Education*, Vol. 43, 1966, pp. A567–A568 and A625–A626.

13. J. J. Cazes. Current Trends in Gel Permeation Chromatography. Part Two: Methodology. *Journal of Chemical Education*, Vol. 47, 1970, pp. A505–A514.

14. T. F. Yen. Chemistry of Asphaltenes (J. W. Burger, ed.). *ACS Series*, Division of Petroleum Chemistry, American Chemical Society, Washington, D.C., 1981.