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HP-GPC and Asphalt Characterization Literature Review

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ABSTRACT

This report is one of several that resulted from a literature review performed as part of SHRP Contract A-003A, "Performance Related Testing and Measuring of Asphalt-Aggregate Interactions and Mixtures." The objective of the literature review was to assimilate information in the technical literature relative to chemical and physical properties of asphalt to field pavement performance, as defined by fatigue cracking, permanent deformation, thermal cracking, aging and water sensitivity. This report focuses on the use of High Pressure Gel Permeation Chromatography (HP-GPC) to characterize asphalt properties and the relationship of HP-GPC parameters to pavement performance.

The state-of-the-literature has been synthesized with respect to HP-GPC and its use in asphalt characterization. Although much information on HP-GPC is available, the focus has been on reports with information on pavement field performance. This report is not intended as a technical review or critique of them or principles applicable to HP-GPC technology.

Some the of difficulties with the HP-GPC procedure are also documented herein. Three basic conclusions on the use of HP-GPC can be made: 1) the molecular size distribution has a definite effect on the physical properties (penetration, viscosity, ductility, etc.) of asphalts. However, these effects are not easily characterized; 2) there are conflicting results on whether HP-GPC analysis can help to identify the performance of asphalt-aggregate mixtures; 3) HP-GPC can be used to identify differences in crude sources between various asphalts, between asphalts of the same grade but with different aging characteristics, and between asphalts from different refinery processes.

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1.0 INTRODUCTION

This report is one of several that resulted from a literature review performed as part of SHRP Contract A-003A, "Performance Related Testing and Measuring of Asphalt-Aggregate Interactions and Mixtures". One of the project objectives is to assimilate information in the technical literature relative to chemical and physical properties of asphalts to pavement performance. In particular, the key focus was on relationships to field pavement performance as defined by fatigue cracking, permanent deformation, thermal cracking, aging and water sensitivity.

During the literature review, it became apparent that there was a body of research available that characterized asphalt using High Pressure Gel Permeation Chromatography (HP-GPC) and which also had information related to field performance. This body of information was deemed important enough to be included in the literature review. However, the information and procedures used were sufficiently different from the more typical asphalt tests (e.g., viscosity, penetration, etc.) that a decision was made to summarize the results in a separate report dedicated to the relationship of HP-GPC products to pavement performance.

In accordance with the project objective cited above, this report is intended to synthesize or summarize the state-of-the-literature on the use of HP-GPC for asphalt characterization and any relationships established with field performance. Although much literature is available on HP-GPC in general, the majority does not relate to field performance, and therefore, have not been included in this review. This report is not intended as a technical review or critique of theories or principles applicable to HP-GPC technology. It is intended to summarize information which has been shown to relate HP-GPC products to the performance of selected asphalt-type pavements included in the respective studies.

Several investigators have studied the subject in detail in recent years, most notably Jennings et al. (1985a & 1985b) in the expanded Montana Asphalt Quality Study. In addition, Kinnison (1986) and Zenewitz & Tran (1987), have further analyzed the data from the Montana study. Three other reports are also reviewed: Glover et al. (1987), in Texas; Chollar et al. (1985), and Garrick & Wood (1988, 1986). Each of these reports incorporates some information on field performance. The reviews are in Chapter 2. Six other reports--Bynum & Traxler (1970), Hattingh (1984), Brûlé et al. (1986), Ishai et al. (1988), Price & Burati (1990), and Garrick & Biskur (1990)--have been included as summaries in Chapter 3. All six studies, in one way or another, were part of a larger research effort. Only those portions in which HP-GPC analysis was related to actual field performance of the pavements have been included for review. Information in Chapter 3.0 is presented in chronological order and supplements the reviews in Chapter 2. Information not related to HP-GPC in these studies has been omitted, e.g., Brûlé et al. (1986) used differential scanning calorimetry (DSC) in addition to HP-GPC to determine the composition of the asphalts; this information is not included in these summaries.

In addition to reports dealing with specific project data, a number of reports are referenced which represent discussions of the HP-GPC procedure and its possible applications to asphalt technology. These are reports which we consider to be significant to our understanding of the concepts and applications relative to HP-GPC.

1.1 HP-GPC BACKGROUND

HP-GPC involves the separation of asphaltic materials into their components according to molecular size. Chromatographic separation for asphalt compositional analysis may be performed using several different methods such as the following:

- Gas Chromatography
- Inverse gas-liquid chromatography
- Liquid Chromatography
    - Absorption
    - Ion exchange
    - Coordination
    - Thin layer
    - Size exclusion (Size exclusion chromatography, mostly HP-GPC: Jennings et al., 1985; Chollar et al., 1985; Garrick et al., 1986; Kinnison, 1986; Zenewitz & Tran, 1987; Glover et al., 1987.)

Size exclusion chromatography (HP-GPC) separates components of the asphalt based on the apparent size (hydrodynamic volume) of molecules and molecular aggregations/associations in dilute solution. The chromatogram describes the molecular size profile of an asphalt.

1.2 HP-GPC PROCEDURES

For the purpose of HP-GPC determination, the asphalt sample is introduced into a solvent (typically tetrahydrofuran (THF) or toluene) flowing at high pressure through a column packed with a highly porous, solid material. The liquid transports the asphalt through and around the porous packing material in the column and as a result smaller size molecules in the asphalt can enter freely into all the pores of the column packing while very large molecules can enter none of those pores.

Molecules of intermediate size have access to varying amounts of available pore volume. Therefore, the larger molecules move through the column more rapidly than the smaller ones. The Large Molecular Size (LMS) portion of the asphalt leaves the column first, followed by the medium-size (MMS) and then the small-size (SMS) components. A detector measures the amount of each component (Figure 1-1). The resultant chromatogram (Figure 1-2) represents the relative amount of material (vertical axis) appearing at a given elution time (horizontal axis). Large molecules and aggregations are seen first on the left of the trace and successively smaller ones follow to the right. This is referred to as the molecular size distribution (MSD) or molecular size profile. The precise elution times and shapes of profiles are functions of column packing, length of pathway, flow rate, etc.; but are relatively constant for a given, carefully controlled system for a specific asphalt (Jennings et al., 1985; Chollar et al., 1985; and Gouw, 1972).

In HP-GPC analysis, molecules that aggregate emerge before unassociated molecules of the same or larger size. For example, Figure 1-3 shows the chromatogram of the original asphalt, as well as the chromatograms of ASTM D 2007 ("clay gel" procedure) fractions obtained from the original asphalt. Notice that the short retention time (larger molecular size) material apparent in the D 2007 fractions is not seen in the original asphalt. Apparently the D 2007 procedure forces molecular associations which are not dissociated by the tetrahydrofuran (THF) solvent used in the HP-GPC. The reconstructed chromatogram (based on the sum of the D 2007 fraction chromatograms) is different from the original asphalt's chromatogram (Goodrich et al., 1986). HP-GPC profiles reflect the apparent molecular size distribution and not the true distribution of sizes in the asphalt. Another explanation (Glover et al., 1987) for this could be that some of the apparently smaller molecular size material is actually of larger size, but because of its polarity is weakly absorbed on the column, resulting in an increased retention time. The hypothesis here is that a part of the molecules that elute at later times (i.e., in the SMS region) are actually larger polar molecules that get weakly absorbed on the column. Hence, the "apparent" molecular size will vary with the following factors: solvent type, detector used, solution temperature (Montana Dept. of Highways, 1983), asphalt concentration in the solvent (Jennings et al., 1982; Winniford, 1960). However, most researchers (Montana Dept. of Highways, 1983; Jennings et al., 1982; Kinnison, 1986; Goodrich et al., 1986) do not give any data to quantify the influence of these problem factors. These and other problems in interpretation of GPC results are discussed in the following section.

1.3 PROBLEMS WITH HP-GPC

There are some problems associated with the use of HP-GPC for analyzing asphalt cements. For example, paraffinic molecules in asphalt are larger than the aromatic molecules of the same mass; consequently, during HP-GPC analysis, paraffinic molecules emerge before aromatic

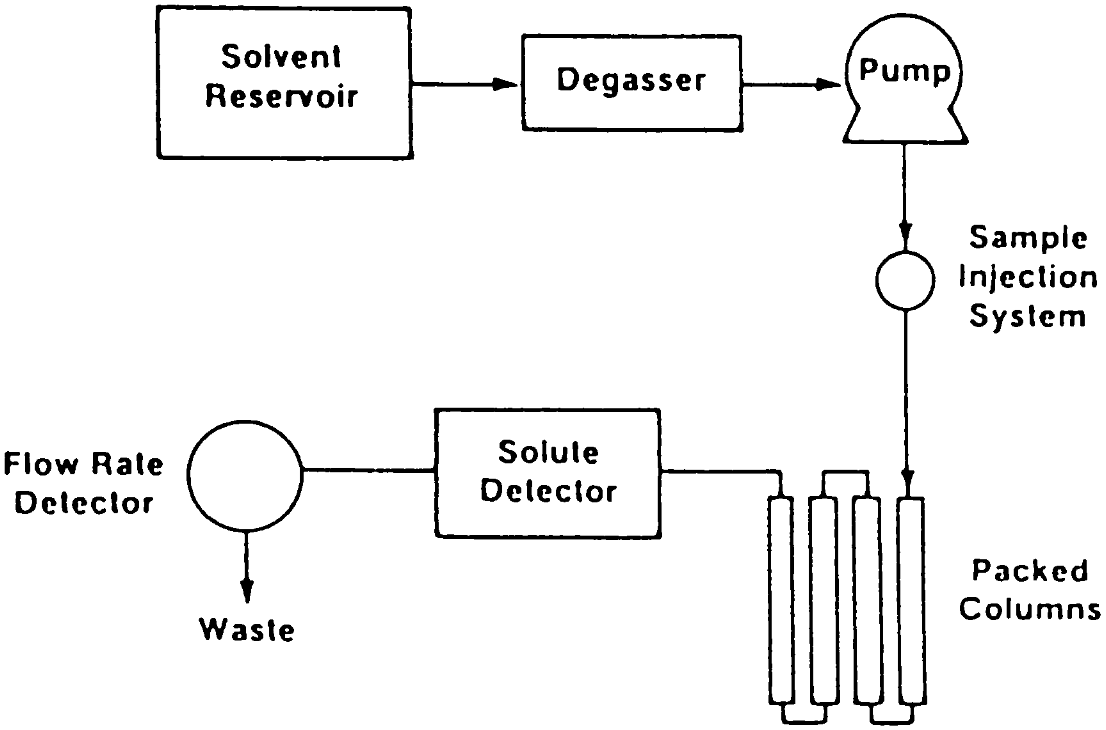
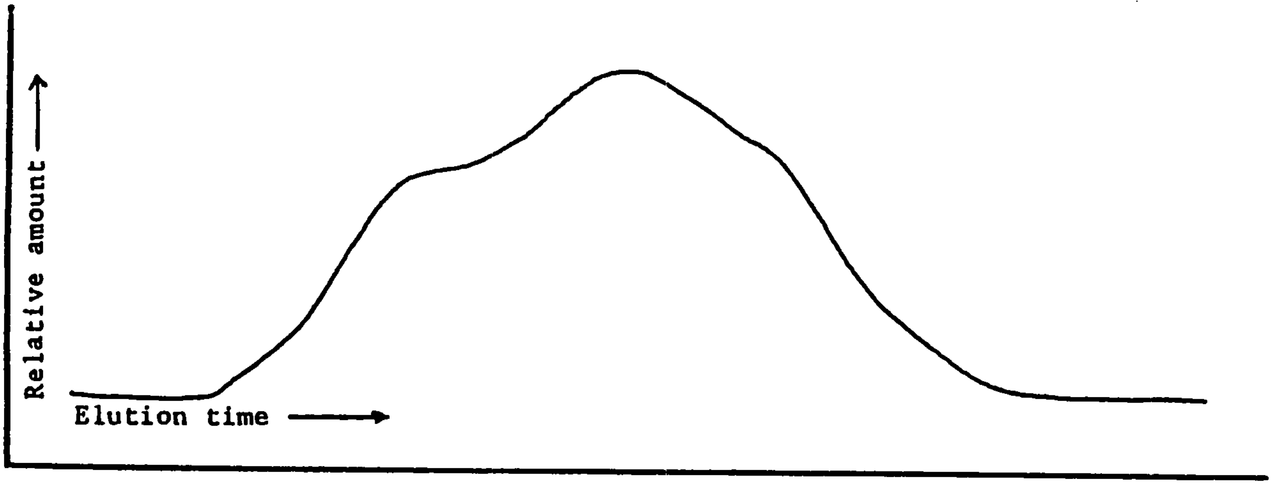
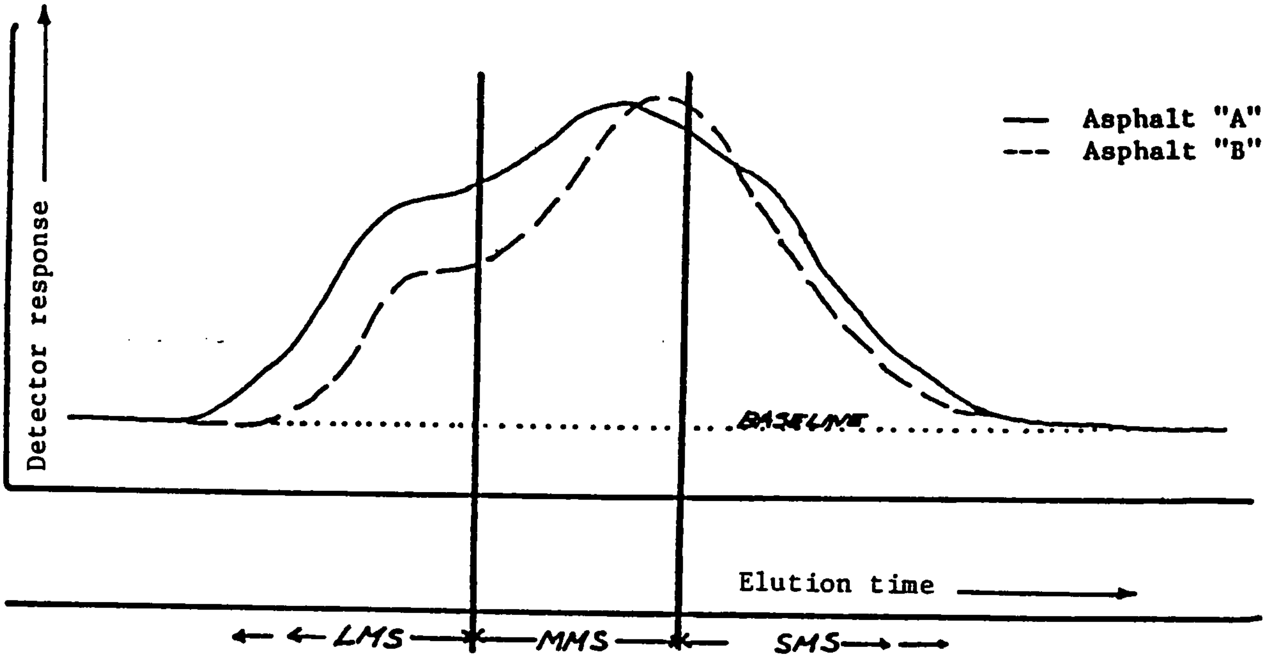


Figure 1-1. Size exclusion chromatography (gel permeation chromatography, e.g., ASTM D 3593) (Goodrich et al., 1986).



i. Sample Asphalt Chromatograph



ii. Means of Comparing Data

Figure 1-2. HP-GPC chromatogram (Jennings et al., 1985).

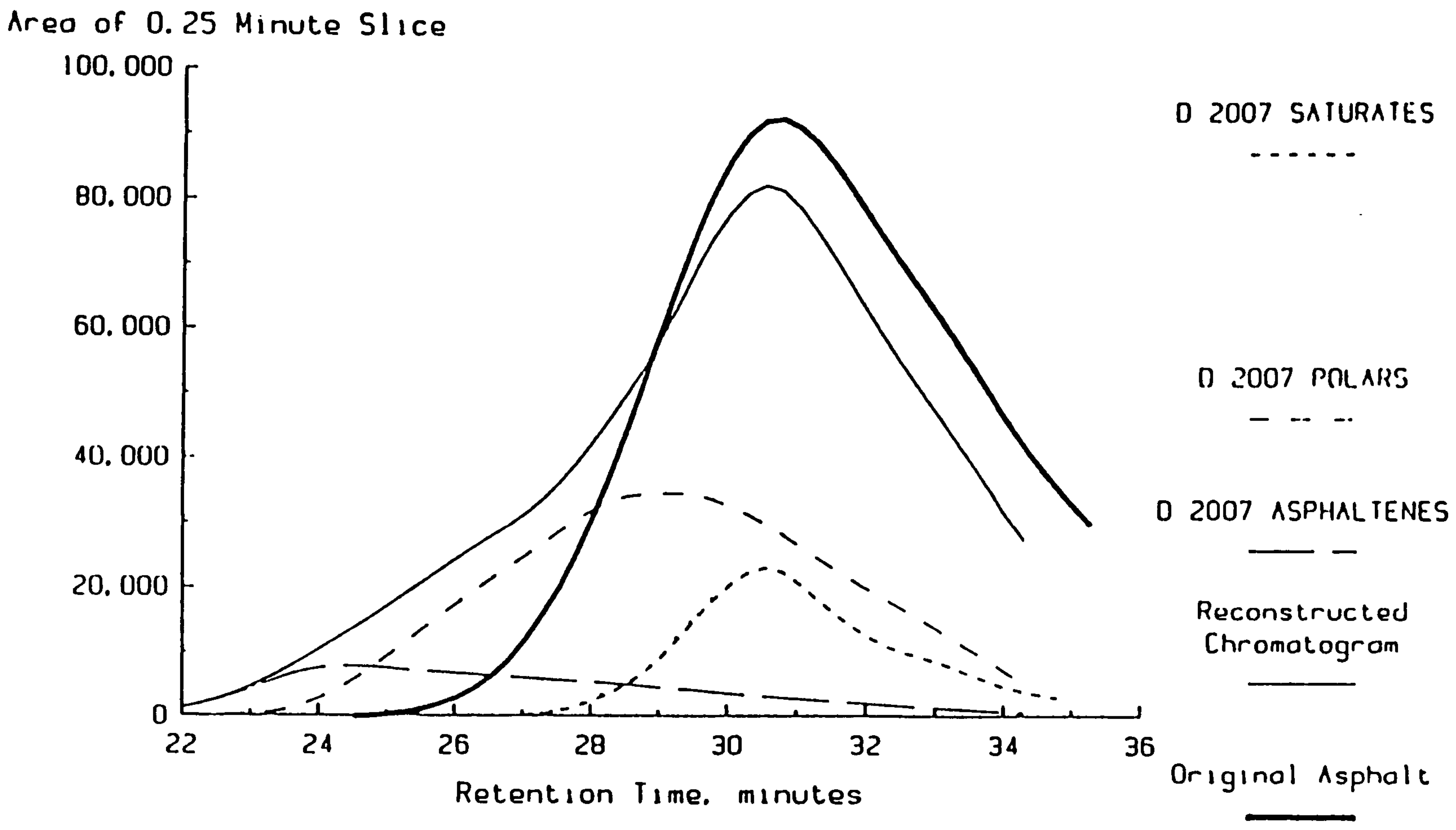


Figure 1-3. HP-GPC chromatograms of D2007 fractions (Goodrich et al., 1986).

molecules of the same mass. The comparison of HP-GPC profiles for asphalts from aromatic sources with those from paraffinic sources may be complicated by this factor.

The discussion that follows is partly extracted from Goodrich et al. (1986) and Glover et al. (1987), which present an excellent summary of size exclusion chromatography techniques.

1. The extent to which molecular associations form depends on several variables, including: the solvent and solution concentration used (Jennings et al., 1982); the solution temperature; the age of the solution, i.e., the time spent in the gel columns; and the unique molecular mix originating from the crude. For example, two different solvents, THF and toluene will give different chromatograms (Glover et al., 1987). Other solvents that have been used include chloroform, trichloroethylene, methylcloride, benzene, tetralin and benzonitrile. Solvent flow rates will also have an effect, with higher flow rates resulting in more association in the LMS and, hence, the LMS portion of the chromatogram will be larger.

2. Condensed aromatic or polar molecules may have a smaller hydrodynamic volume than saturated hydrocarbons of equivalent molecular mass (Bynum & Traxler, 1970). Thus, high molecular weight polar compounds may elute at the same time as low molecular weight saturates.

3. The response of the detector to the compounds being eluted from the column depends on the detector type (Bynum and Traxler, 1970). Jennings et al. (1985) have used both a refractive index (RI) detector and an ultraviolet (UV) detector and found that the refractive index detector responds to molecules which change the refractive index of the mobile phase. The UV detector at 340 nm, responds to molecules which are aromatic (e.g., polynuclear aromatics) or which contain conjugated double bonds. As a result, the two detectors give different information (Figure 1-4), but fortunately, both detectors for an identical sample of asphalt will exhibit the same trends. As can be seen from Figure 1-4, the LMS portion of the RI chromatogram is less pronounced than the LMS portion of the UV chromatogram. UV detection at different wave lengths will also affect the chromatogram obtained.

According to Jennings et al., the UV detector has advantages over the RI detector. Primarily, UV detectors are not as sensitive to temperature fluctuations, hence a flat and consistent baseline is obtained. RI baselines are subject to drift and require close monitoring. Furthermore, the UV "sees" more material in the important LMS region. Water is not detected by UV @ 340 nm, so interference from any water present is eliminated.

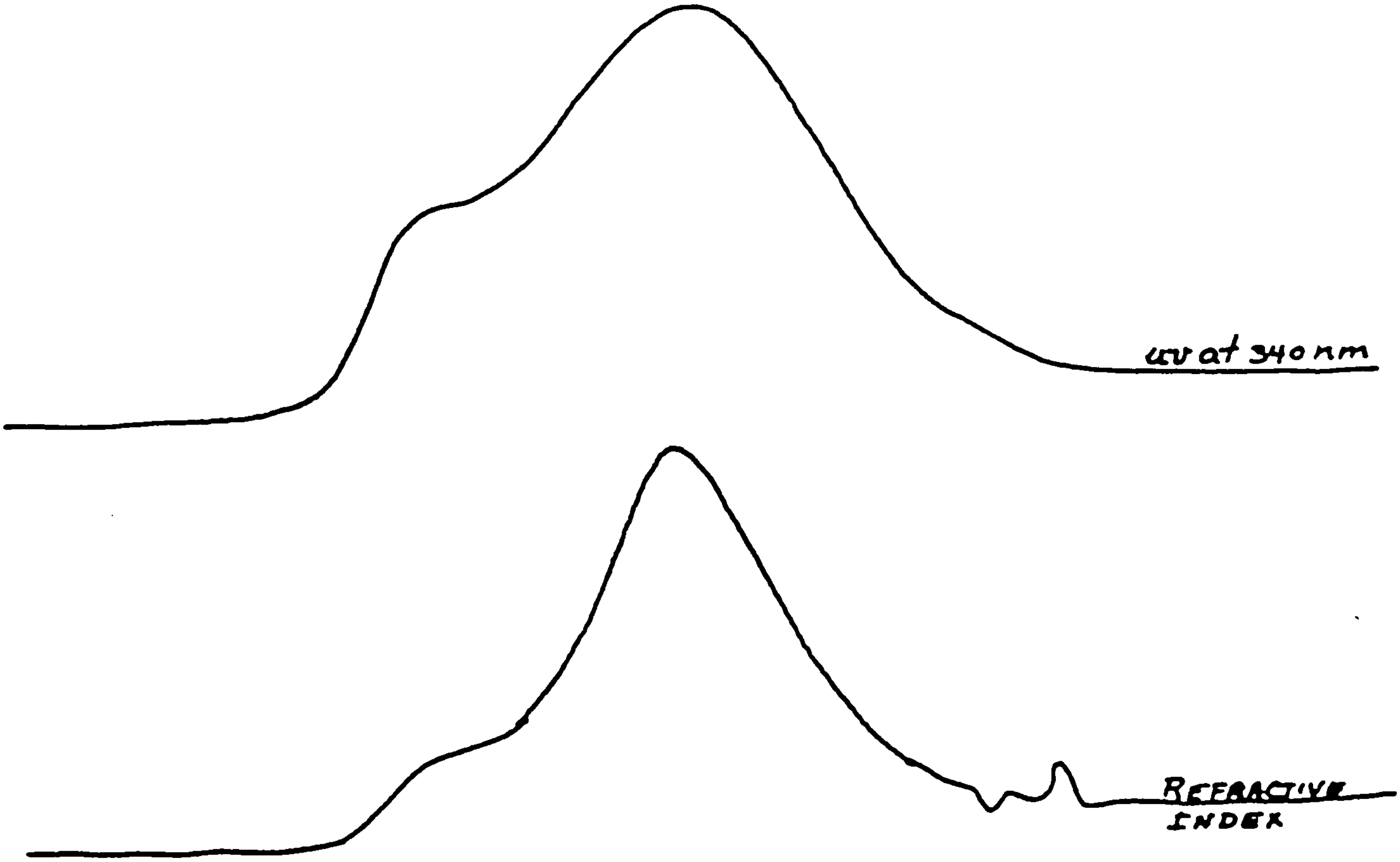


Figure 1-4. Comparison of data by UV @ 340 nm with that by refractive index for an asphalt (Jennings et al., 1985).

Unfortunately, neither detection system is useful in monitoring small, simple hydrocarbons which may exist in the SMS region. Such materials will affect penetration or viscosity, but cannot be detected by HP-GPC as used by Jennings et al.

4. Adsorption of certain compounds on the column can influence the order in which they are eluted from the column. Some of the "apparently" smaller molecular size material is actually of larger size but, because of its polarity, is weakly adsorbed on the column, resulting in an increased retention time (Glover et al., 1987). Glover et al. hypothesize that a part of the molecules that elute at later times (i.e., in the SMS region; hence, the word "apparently" smaller molecular size material) are actually larger polar molecules that get weakly adsorbed on the column.

5. The selection of GPC columns may have a large effect on the GPC profiles. Brûlé et al. (1986), for instance, used different sized columns in their "fast" and "ultra-fast" set-ups, and consequently obtained different chromatograms. Conventional GPC (using a set of several columns with typical particle sizes from 37 to 75 μm on very diluted solutions) do not differentiate between molecular weight distribution greatly. In other words, it is difficult to distinguish between chromatograms of the original asphalt and of the same asphalt after aging (natural or artificial). This is because such a GPC operates slowly enough so that dissociations have time to develop, i.e., the aggregations developed during the aging process dissociate (Brûlé et al., 1986).

6. Defining asphalt GPC fractions as large, medium or small based on calibration with polystyrene standards are dependent as particular GPC columns and may be technically misleading. The GPC measures the size of molecular associations of asphalt components and not the true molecular size.

2.0 REVIEW OF HP-GPC STUDIES

This chapter summarizes information from six HP-GPC studies that were reviewed in detail. These six studies were selected because they provide information on potential relationships between HP-GPC characteristics and pavement performance. Section 2.1 describes studies by three separate groups of researchers based on data from highways in Montana and seventeen other states. The first two studies discussed are the works of Jennings et al., from 1980 and 1985. The third and fourth studies by Kinnison (1986) and Zenewitz & Tran (1987) are statistical treatments of the 1985 report by Jennings et al. Section 2.2 describes a study by Chollar et al. (1985), to compare the results of Jennings et al.'s 1985 data with selected properties of the asphalt binder. Also, other asphalt cements were analyzed. Section 2.3 summarizes work by Adams & Holmgreen (1985), and Glover et al. (1987), on HP-GPC and the performance of highways in Texas. Finally, Section 2.4 discusses research by Garrick & Wood (1988, 1986) on relationships between HP-GPC and the penetration and viscosity of asphalt cements blended from products of a residuum oil superextraction (ROSE) refinery unit and other asphalts.

2.1 MONTANA ASPHALT STUDIES

2.1.1 Jennings et al., 1980

Description: Preliminary work on using high pressure liquid chromatography (HPLC) as a tool for asphalt characterization was first done by Jennings in 1977. Using gel permeation columns, which separate components of a mixture by molecular size, Jennings analyzed a range of asphalt cements obtained from diversely performing roadways. Each asphalt, as a result of high pressure gel permeation chromatography (HP-GPC), yielded a distinct molecular size distribution (MSD). The 1977 study concluded that HP-GPC can "fingerprint" an asphalt. In an attempt to couple this information with the performance of these asphalts in-service, Jennings et al. conducted a new study in 1980 with the following objectives:

a. Refine the HP-GPC procedure to characterize asphalts and develop a repeatable method of analysis;

b. Conduct a broader study of established roadways and determine the characteristics of asphalts from roads with good performances;

c. Determine the ways in which less successful asphalts (in terms of pavement performance) differ in these characteristics;

d. Estimate the effects of asphalt aging;

e. Characterize a model for well-performing asphalts, and apply the model to other asphalts to predict their field performance.

The following GPC system was used in the 1980 study:

HPLC Instrument: Waters Associate
Detector: Model R401 differential refractometer.
Column Type: 5 μ-styragel columns: one 10^3 Å, three 500 Å, one 10^5 Å, one 100 Å.
Solvent: UV grade tetrahydrofuran (THF)

A condition survey of the roads where cores were taken was also performed, and a rating system was established to determine their performance as follows:

Excellent	Older than 14 years and little cracking.
Good	Newer than 14 years and few cracks.
Poor	Newer than 10 years and cracking.
Bad	Newer than 10 years and extensive cracking.

The types of cracking observed were primarily transverse cracking, with some longitudinal and alligator cracking also noted. Unfortunately, no information on traffic or structural sections were included in the report.

A total of 37 roads were selected for study (Table 2-1). The roads selected included asphalt cements in each of the penetration classes (85-100, 100-120, 120-150, 150-200, 200-300), represented the four Montana refineries, and were of varying ages and conditions. Refineries A and B produced asphalts with relatively small amounts of LMS materials; C had higher amounts; and D, yet higher proportions. In addition, all refineries had different refining processes. Three cores were taken from each roadway in the right wheel path. Efforts were made to exclude projects that may have failed from factors other than asphalt, such as base or subgrade failures.

<u>Results</u>: Jennings et al. (1980) discovered differences between the MSDs (as indicated by HP-GPC chromatograms) of the asphalts taken from Montana's best performing roadways (with respect to cracking), and the asphalts taken from the cracked pavements in Montana. A nineteen year old road in excellent condition (Gallatin-Gateway South) was chosen and used as the standard or "model". The trend in all the chromatograms showed that the greater the disparity between a given asphalt and the standard, the poorer the

Table 2-1. Physical properties and condition of roadways studied in Montana (Jennings et al., 1980).

Identification	Age at Sampling (years)	Condition	Pen^a 77°F	Ductility cm. 40°F	Filler	Plant Type	Refiner	Percent Asphaltenes^j
<u>85-100 Design Penetration</u>								
1. Big Timber-Harlowtown F 45(12)U1	9	Bad (cracked after 2 yrs.)	49	5.5	1.5% lime	Pioneer C. F.^{h}	B	16.2 (+0.7)
2. Terry-Fallon I 94-5(10)174	10	Bad TC, LC+++^{d,e}	44	10.25	limestone dust	Barber-Greene C.F.	B	16.8 (+2.8)
3. Toluca-East I 90-9(30)483	9	Bad TC+++	58	6.0	?^{m}	?	B	18.1 (+4.9)
<u>100-120 Design Penetration</u>								
4. Alzada-Ekalaka-1 S 318(4)	15	Bad-AC^k TC, LC+++	38	1.5	-^{n}	Batch	B	21.0 (-1.1)
5. Circle-Glendive-1 F 246(13)	15	Poor TC+++	44	2.0	mineral filler	Batch	B	20.0 (-4.0)
6. Terry-Brockway S 302(19)	13	Good TC++^{f}	49	6.25	mineral filler	Pioneer C.F.	C	13.7 (-0.4)
7. 27th Street to Highway 87 I-IG 90-8(23)447 U2	13	Bad AC, TC, +++	28	0.5	limestone dust	C.F.	B	22.9 (+3.0)
8. Twodot-South S 18(6)	14	Excellent	62	9.0	-	Pioneer C.F.	C	17.9 (-2.1)
9. Wibaux-E & W^g I 94-7(4)233 U1	15	Bad^g	51	15	-	Cedar Rapids Batch	C	19.2 (+0.7)

a-Penetration of recovered asphalt
b-TC-Transverse Cracks
c-+ some cracking
d-LC-Longitudinal Cracks
e-+++-extensive cracking
f-++-moderate cracking
g-aggregate failure; asphalt recycled
h-C.F.=continuous flow plant
j-( )=difference between total asphaltenes & solubles recovered and 100%
k-AC-Alligator Cracking
m-?-unknown
n-not present

Table 2-1. Continued

Identification	Age at Sampling (years)	Condition	Pen 77°F	Ductility cm. 40°F	Filler	Plant Type	Refiner	Percent Asphaltenes
120-150 Design Penetration								
10. Alzada-Ekalaka-2 S 347(14)	9	Good TC+	-	-	Hydrated lime	Cedar Rapids Batch	C	13.4 (+5.7)
11. Circle-Glendive-3 F 246(21)	3	Poor TC++	-	-	-	Batch	B	-
12. Crow Agency-Broadus F 334(18)	10	Good TC+	111	-	-	Batch	C	17.1 (+1.4)
13. Crow Agency-Hardin I 90-9(31)489	8	Good	138	70.5	fly ash	Barber-Greene C.F.	C	11.9 (-4.5)
14. Dawson Co. Line-East I 94-6(21)191 U1	6	Good TC++	92	42.5	fly ash	Batch	B	15.5 (+0.2)
15. Divide-North I 15-2(34)103 U3	3	Good TC+	62	4.5	?	Batch	B	12.5 (+1.6)
16. Judith Gap-East-1 S 174(5)	10	Good	68	9.5	Hydrated lime	Pioneer C.F.	C	16.3 (+0.4)
17. Judith Gap-East-2 S 174(4)	10	Good TC+	103	55.25	Hydrated lime	Cedar Rapids Batch	A	17.6 (+3.1)
18. March-Glendive S 359(11)	8	Good TC++	90	30	-	C.F.	B	15.3 (+3.2)
19. Musselshell River-E & W F-RF 256(36)U1	6	Good	105	68.5	fly ash	Barber-Greene Batch	C	13.0 (-3.2)
20. Prairie Co.Line-East I 94-5(11)166 U4	8	Bad, AC++ TC++	72	15	-	Standard Batch	B	12.1 (-3.7)
21. Rosebud-South S 252(3) U1	8	Good TC+,AC+	57	8.25	-	Cedar Rapids C.F.	B	14.4 (+1.2)
22. Wolf Point-Hungry Creek S 429(3)	10	Bad TC++	35	4.0	Hydrated lime	Cedar Rapids 6-60	F	22.9 (+1.5)

Table 2-1. Continued

Identification	Age at Sampling (years)	Condition	Pen 77°F	Ductility cm. 40° F	Filler	Plant Type	Refiner	Percent Asphaltenes
150-200 Design Penetration								
23. Billings-South S 132(3)	19	Poor TC+, AC+	22	0.25	-	?	B	23.8 (-3.8)
24. Chester-Gildford F 132(7)	15	Bad AC, TC+++	70	12.0	-	Madsen Batch	F	21.6 (-1.8)
25. Circle-Glendive-2 F 246(9)	18	Bad TC, AC+++	65	3.25	-	Cedar Rapids Batch	B	23.3 (+0.5)
26. Drummond-East I 90-3(3)157 UI	19	Bad TC, AC+++	34	3.5	-	?	A	17.4 (-1.1)
27. Gallatin Gateway-Bozeman F 203(7)	19	Excellent	120	52.5	?	Pioneer C.F.	C	15.6 (+0.3)
28. Gallatin Gateway-South F 76(6)	19	Excellent	113	45.75	?	Pioneer C.F.	C	13.3 (-3.9)
29. Glendive-Richey S 32(9)	20	Poor TC, LC++	58	8.0	-	C.F.	G	14.1 (+0.3)
30. Hardy Creek-Cascade Old I 15-5(13)239 UI	16	Bad TC, AC+++	75	8.5	-	Standard Batch	D	22.2 (-0.5)
200-300 Design Penetration								
31. Brandenberg Ashland RS 45(14)	4	Good	210	100+	fly ash	Boeing Drum	C	13.8 (+1.1)
32. Busby-Lame Deer-1 RF-FLH 334(21)UI	5	Good TC+, rutting	191	-	-	Pioneer C.F.	B	14.4 (+2.9)
33. Busby-Lame Deer-2 RF-FLH 334(24)	4	Good	-	-	-	Stansteel	C	9.5 (+0.5)
34. Busby-Lame Deer-3 RF-FLH 334(25)	3	Good	209	-	-	Stansteel	B	15.6 (+1.2)

Table 2-1. Continued

Identification	Age at Sampling (years)	Condition	Pen 77°F	Ductility cm. 40°F	Filler	Plant Type	Refiner	Percent Asphaltenes
35. Columbus-Rapelje RS 129(14)	3	Good	94	21.5	fly ash	Cedar Rapids Batch	A	18.7 (+5.4)
36. Havre-Simpson S 301(17)	6	Good TC+, Deformation	111	21.5	fly ash	Pioneer C.F.	D	14.6 (-3.1)
37. Thompson Falls-West F 7-1(1)	4	Good	200	75.5	-	Cedar Rapids Batch	D	12.9 (-2.7)

performance of that asphalt. This is particularly true with regard to the size and amount of LMS, i.e., asphalts with more and/or larger LMS are likely to crack in Montana.

Jennings et al. (1980) also determined the percent of asphaltenes in the asphalt samples extracted from the Montana roads by heptane solubility. All samples containing more than 19% asphaltenes were from roads performing in the poor or bad range. Eighteen samples with less than 15 percent asphaltenes were from roads in the good to excellent range, with only two exceptions; one road with 17.4 percent asphaltenes rated bad and one with 17.8 percent rated excellent. However, the bad road contained considerably more LMS, as measured by GPC, than the excellent road and the standard. Asphaltene percentages between 16% and 18% were split between good and bad asphalts. The researchers concluded that asphaltene alone may not always accurately predict performance. Penetration and ductility measured from these samples correlated only fairly well with performance; asphaltene content correlated better. The ideal range of asphaltene content is 12.5% to 16.5% Based on all the results of this study, Jennings et al. (1980), made some recommendations for asphalt cements which are summarized in Table 2-2.

It was also observed that processing through either a batch or drum dryer plant causes a twenty to eighty percent increase in the LMS components, and that a substantial increase in LMS components is seen by the use of lime in asphalt mixes.

<u>Conclusions</u>: The following conclusions were drawn for Montana:

1. HP-GPC analysis provides a visual representation of the molecular size distribution in an asphalt. It was possible to characterize the asphalts from the four different refineries.
2. HP-GPC can show the difference between various asphalts and these differences can be related to cracking performance. Recommendations for Montana are provided in Table 2-2 for the model asphalt.
3. Asphaltenes alone do not provide enough data to predict performance.
4. Penetration and ductility did not correlate very well with performance.
5. Common construction processes such as inclusion of fillers (e.g., lime) can change the molecular size distribution (MSD) of an asphalt.
6. Processing through a batch or drum dryer plant may cause increases of 20-80% in LMS components.

However, since these results were limited to conditions in Montana and to asphalts from suppliers to Montana, it was recommended that the study be expanded to include other states so as to verify and extend the results of the 1980 report. To achieve this aim, seventeen states were included in an expanded study and the results published in 1985.

Table 2-2. Recommended molecular size components for Montana (Jennings et al., 1980).

Component	Extracted Asphalt*	Virgin Asphalt*	1990**
LMS	8-10%	6-8%	18.5 ± 1.5%
MMS	46-48%	44-48%	45 ± 1.5%
SMS	44-46%	46-48%	36 ± 1.5%
Asphaltene Content	12.5-16.5%	12.5-16%	---
Penetration	>120 dmm	>120 dmm	---

Note: These are for the State of Montana only.
* These figures are from the 1980 study.
** Pribanic (1990) indicated these are new (as yet unpublished) recommendations.

2.1.2 Jennings et al. (1985)

Description: In this study, 17 states were included. The objective was to analyze the asphalts extracted from roads of known performance using HP-GPC, and then to correlate the results with field performance, specifically transverse cracking. Fifteen out of the seventeen states included in the expanded study submitted performance-related samples. The other two states did not submit any performance data associated with their core samples. The asphalt binder was recovered from 4-inch diameter cores taken from the right wheel path of the designated lane. Table 2-3 summarizes the age, traffic and condition of the selected roadways. In the selection of the cores, the most important factors under consideration were:

- The recovered asphalt were from roadways of known performance, specifically focusing on performance related to transverse cracking;
- Pavements in which cracking performance was likely to have been adversely affected by such factors as subgrade failure, base construction, etc. were not considered;
- If a state is divided by climatic extremes, samples were taken from each of these extremes.

Table 2-3. Field data for cores analyzed (Jennings et al., 1985).

STATE	RANGE OF PAVEMENT AGE (YRS)	CRACKING*					RUT** DEPTH	AVERAGE DAILY TRAFFIC
		T	L	R	A	O	inches	
AK	0 - 29	Y	N	P	P	P	0 - 0.26	198 - 12,000
CO	3 - 21	Y	P	N	P	P	0 - 1.0	820 - 52,300
GA	2 - 13	Y	P	N	N	P	0 - 1.0	200 - 58,800
ID	3 - 22	Y	P	N	P	N	0 - 1.5	1,000 - 7,330
IL	4 - 19	Y	P	P	P	P	0 - 0.44	500 - 17,500
MN	3 - 27	Y	P	P	N	N	0 - 0.45	375 - 12,567
NJ	2 - 18	Y	P	P	P	N	0 - 1.0	6,600 - 122,000
NM	3 - 25	Y	Y	P	P	P	0 - 1.0	3,000 - 22,500
ND	2 - 36	Y	P	P	P	P	0 - 1.0	160 - 2,475
OH	3 - 25	Y	Y	Y	P	N	N/A	570 - 37,260
PA	1 - 14	Y	P	P	P	P	0 - 0.5	2,200 - 46,715
SD	1 - 29	Y	P	P	P	N	0 - 0.63	271 - 4,320
TX	1 - 25	P	P	P	P	N	0	3,150 - 9,175
UT	3 - 12	Y	P	P	N	N	0 - 1.0	3,030 - 24,830
WY	1 - 28	Y	P	N	N	P	0 - 1.0	670 - 7,050

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*The cracking data was broken down into types and extent of cracking by ARE Inc.

Where:
T = Transverse
L = Longitudinal
R = Random
A = Alligator
O = Other

Y (yes) = 50% cracking
P (present) = 11% - 50% cracking
N (no) = 0% - 10% cracking

**Rut depths were not collected by Jennings et al. (1985), but were supplied by the individual states to the FHWA.

Also, samples of neat asphalt cement were obtained from refineries which currently supply asphalt binder to the participating states and these materials were tested and included in the study. The asphalt cements were to be from the same crude source as the asphalts used in construction of the cored pavements. This was, ultimately, not the case, as most states did not have the crude source information. Information regarding definite identification of crude source and refining process were only available for samples from Pennsylvania. Table 2-4 lists the crude sources for asphalts supplied by Pennsylvania.

Asphalts recovered from the cores and those obtained from the refineries were tested using HP-GPC procedures. For Jennings et al.'s 1985 study, the HP-GPC system used was:

Column Type: 3 ultra-styragel columns; one 10^3 Å, two 500 Å
Detector Type: Model R401, refractometer and a two-channel absorbance detector.
Solvent: Tetrahydrofuran (THF)
Sample Concentration: 0.5 percent (w/v)
Injection Volume: 100 µl
Flow Rate: 0.9 ml/min

Results: The HP-GPC versus asphalt performance data collected for this study was first analyzed by Jennings et al. (1985). Kinnison (1986) later performed a statistical analysis on this data, and Zenewitz & Tran further analyzed the data in 1987. The findings of all three reports are presented below.

1. Jennings et al. (1985): Chromatograms were compared visually and area percentages calculated. The optimum concentration of large molecule size (LMS) material for a finished asphalt in a given region was found to be a function of climate; so climate zones were established. The climate zones were based on regionalization of freeze thaw activity (Williams, 1964) and other geographical considerations. A map illustrating the climate zones is shown in Figure 2-1. The results were hence broken down according to climatic zones and further by location, and a summary prepared by climatic zone. The percentages of LMS of the various asphalts tested ranged from 6 to well over 40. The highest percent LMS at which consistent excellent performance was found in a particular climate zone, and the lowest percent LMS at which cracking was found in a particular climate, are shown in Table 2-5. This table also shows the recommended maximum percentage of LMS in asphalt (note that these are recommendations for asphalts extracted from cores) for each zone. As can

Table 2-4. Properties and crude sources of asphalts supplied by Pennsylvania (Jennings et al., 1985).

		%LMS		Pen 77°F		Vis 140° poises		Vis 275 Centistokes			DUC 60°F		DUC 39.
Section	Performance	neat	core	neat	TFO	neat	TFO	neat	TFO	PVN	neat	TFO	TFO
T-3	E	16.9	21.7	72	45	1874	3902	303	556	-0.61	150^+	95.2	4.6
T-6	G	25.1	29.2	80	44	1982	5721	406	575	-0.45	150^+	33.0	12.4
T-2	G	36.9	39.2	64	38	2284	6835	402	569	-0.70	29	7.0	3.
T-4	P	26.7	30.6	65	38	1705	4694	355	527	-0.86	117	12.8	5.
T-1	B	15.1	19.6	42	26	2710	5501	420	563	-1.04	150^+	11.6	3.

Crude Source

T-1 - 49% Sahara, 21% W. Texas, 21% Montana, 9% Kansas - vacuum distillation and propane deasphalting

T-2 - 66.4% Texas Mid-Continent, 33.3% Arabian, - steam distillation

T-3 - 85% Lt. Arabian, 15% Bachaquero - vacuum distillation

T-4 - 75% W. Texas Sour, 25% Texas and Louisiana sour - vacuum distillation

T-6 - Blend of Heavy Venezuelan and Middle Eastern - vacuum distillation

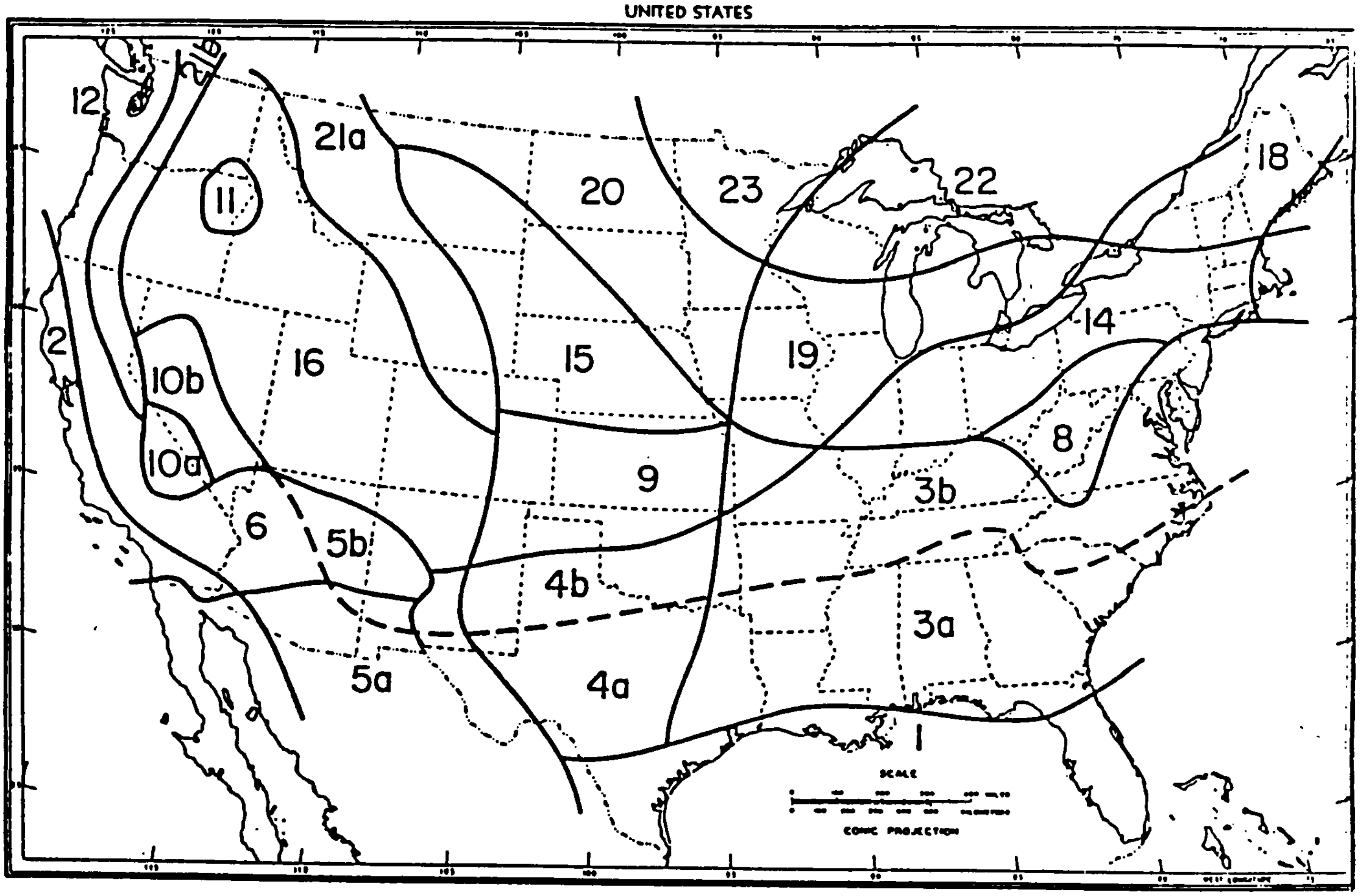

Figure 2-1. Climate zones (Williams, 1964).

Table 2-5. Summary of HP-GPC and performance data by climate zone (Jennings et al., 1985).

ZONE	LOCATION	E(1)	C(2)	NOTES	R(3)
3a	GA	36	37	rutting below 32%	35
3b	NJ	28	31		27
	PA-SE	33	--	young pavement	
	OH-SW	33	34		31
	IL-S	35	--	young pavement	
5a	NM-SW	25	26		24
5b	NM-WC	--	26		23
8	PA-SW	--	28		26
	OH-SC	31	32		29
9	NM-NE	--	26		21
14	PA-N	22	25	young pavement	24
	OH-NC	--	29		24
	OH-NE	--	31		24
	IL-C	37	39	exception, young	24
15	CO-Denver	24	26		23
	WY-E	20	22	exception @ 23%	20
15	SD	23	24		22
16	NM-NW	19	26		20
	CO-W	22	24	exception @ 25%	22
	UT-Mtn	24	26		23
	UT-W	25	29		25
	ID-S	19	21	exception @ 30%	19
	ID-SE	--	18		17
	ID-N	17,28	29	exception @ 28%	29
19	IL-NO	--	26		25
	MN-SE	26,30	31		26
20	MN-SW	--	31		21
21a	CO-Mtn	27	--	exception	20
	WY-Mtn	25	27		
23	MN-N	--	28		20

(1) Highest %LMS at which consistent excellent performance was found in that particular climate zone.

(2) Lowest %LMS at which consistent cracking was found in that particular climate zone.

(3) Highest %LMS recommended for that climate zone, finished asphalt, i.e., asphalt that has been extracted from an in-service pavement.

be observed, the data shows that no asphalt with greater than 36% LMS has given an excellent cracking performance anywhere in the country.

These recommendations were made by the authors (Jennings et al., 1985) based on available in-service performance data (summarized in Table 2-3) and are intended to allow a margin for local climate and other effects. The authors believe that adherence to such guidelines can help to reduce or even eliminate the incidence of long-term transverse cracking.

2. <u>Kinnison (1986)</u>: A purely statistical approach was adopted by Kinnison to analyze the same HP-GPC data that Jennings et al. (1985) collected. The variables investigated were: age, condition, cracking, rutting, traffic, % LMS, and % MMS. The main statistical analysis was a contingency table analysis for association among the variables.

Contingency table analysis is the nonparametric statistical equivalent of regression and correlation, and it is used to determine the significance of nonparametric measures of association between the variables. A nonparametric statistical method was selected because most of the data are classifications (eg., cracking is classified as transverse, longitudinal, etc.) and ranks (eg., condition is ranked as good, poor, etc.) A secondary statistical methodology was also applied, i.e., logistic regression, which is a hybrid between parametric and nonparametric statistical methods. It calculates the probability that a pavement belongs in an age-distress category. Appendix A describes in greater detail these procedures. Table 2-6 summarizes the test of association for all pairs of variables.

The significance levels differ very little between the lift one data and the lift average data, so the same conclusion result from both data sets. The significant associations seem to group the variables into two subsets: 1) age, condition, cracking, rutting & traffic; and 2) %LMS and %MMS. The high association between the two chromatography fractions implies that all the information about these fractions can be obtained from only one and use of both might introduce data dependencies into an analysis. The probabilities fall into two groups, less than 95% and greater than 99%. Those values over 99% are significant and those under 95% are not significant. The closer the chi-squared is to unity, the greater the association between variables. Appendix A provides a glossary of statistical terms.

Table 2-6. Test of associations (Kinnison, 1986).

VARIABLES			CHI-SQUARE ASSOCIATION SIGNIFICANCE	
			LIFT ONE	LIFT AVERAGES
age	vs.	condition	0.9999	0.9999
age	vs.	cracking	0.9999	0.9999
age	vs.	rutting	0.1040	0.0000
age	vs.	traffic	0.9930	0.9915
age	vs.	%LMS	0.4950	0.6805
age	vs.	%MMS	0.6970	0.6805
cond.	vs.	cracking	0.9999	0.9999
cond.	vs.	rutting	0.0000	0.1420
cond.	vs.	traffic	0.9125	0.9255
cond.	vs.	%LMS	0.1007	0.1037
cond.	vs.	%MMS	0.8458	0.5838
crack	vs.	rutting	0.9660	0.9585
crack	vs.	traffic	0.9999	0.9999
crack	vs.	%LMS	0.0908	0.1329
crack	vs.	%MMS	0.9254	0.7697
rutting	vs.	traffic	0.9998	0.9999
rutting	vs.	%LMS	0.8436	0.3913
rutting	vs.	%MMS	0.9505	0.7951
traffic	vs.	%LMS	0.8939	0.9880
traffic	vs.	%MMS	0.7910	0.8852
%LMS	vs.	%MMS	0.9999	0.9999

Note: The closer the chi-square is to unity, the greater the association between variables. Only those probabilities greater than 99% are statistically significant.

Noteworthy is that the chromatography fractions did not show significant associations with any of the three indicator variables (condition, cracking and rutting). According to Kinnison, this obscures one of the original purposes of Jennings et al.'s (1985) study, which was to find an asphalt composition that is associated with durable roads. However, no climatic data was included in the statistical analysis. Also, Kinnison did not perform the analysis on data within any one climatic zone. This may have affected his results.

3. Zenewitz and Tran (1987): Molecular size data for asphalts obtained from Jennings et al.'s (1985) study were further analyzed. Their relation to such factors as pavement condition, rutting, cracking, asphalt lift, age, traffic and climate was studied. A t-test was used to determine significant increases or decreases of average molecular size (i.e., average LMS or average SMS) content using a 5 percent confidence level.

After the initial analysis, the data was broken down into younger (1-16 years of age) and older (17-45[1] years of age) pavements because of the apparent difference in the large and small molecule makeup of the asphalts (Figure 2-2). Note that in this figure, the oldest pavement is only 32-33 years old. Again, it is not known why the older pavements were not included. Table 2-7 shows a t-test comparison of average LMS content (in percent) of asphalts from 16-year old and younger pavements having rutting or various types of cracking with the overall average LMS content for all 576 asphalts from the pavements in the age group.

Another t-test study involved the significant associations of group study variables and pavement failings within each climate category for the 576 younger pavements. A summary of the number reporting from each climatic designation is presented in Table 2-8. Note that the climatic designation used is different from that used by Jennings et al. (1985).

Table 2-9 presents the results of the within-climate category comparisons. An arrow pointing up indicates a significantly larger average value of variable than the overall average for that climatic category. An arrow pointing down indicates a

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[1] According to the data shown in Jennings et al.'s (1985) report, the oldest pavement is 36 years old. It is not known where the 45-year-old pavement in Zenewitz & Tran's (1987) study came from.

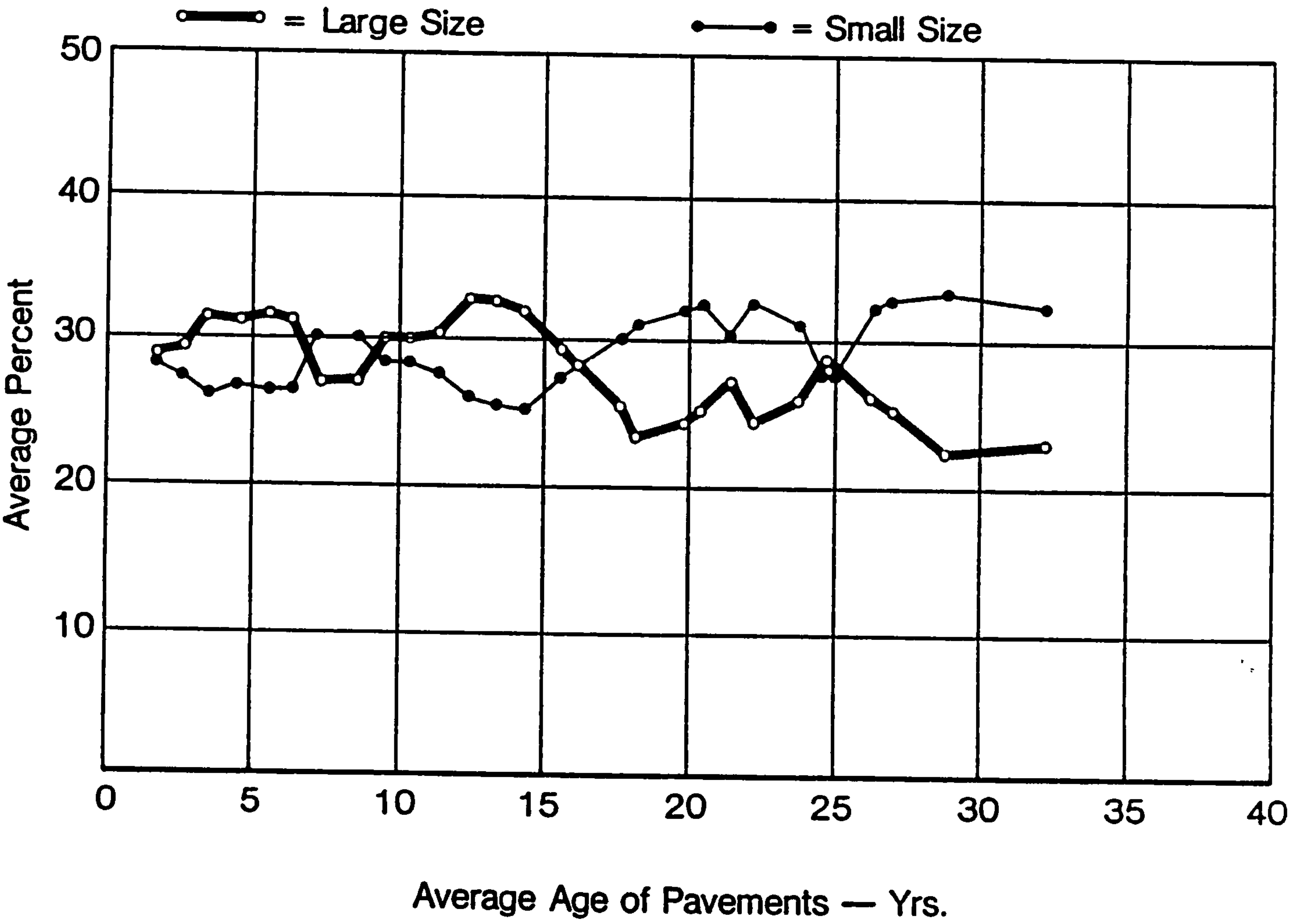

Figure 2-2. Average percent large molecule and average percent small molecule content of asphalts from various aged pavements (Zenewitz & Tran 1987).

Table 2-7. Categorical comparison of average LMS content for asphalts taken from pavements up to 16 years old (Zenewitz & Tran, 1987).

ASPHALTS FROM PAVEMENTS SHOWING	NUMBER REPORTING	LARGE MOLECULE SIZE %	STANDARD DEVIATION %	t-TEST VALUE	% CHANCE OCCURRENCE OF T-VALUE	SIGNIFICANT AT 5% LEVEL?
All up to 16-yr pavement	576	30.184	7.228	--	--	--
No Rutting	500	30.501	7.020	+0.727	47.5	No
Rutting	76	28.100	8.224	-2.324	1.9	Yes
Transverse Cracking	348	32.879	8.654	+2.088	3.5	Yes
Longitudinal Cracking	123	30.195	7.879	+0.015	93.6	No
Random Cracking	98	32.542	5.886	+3.061	0.3	Yes
Alligator Cracking	68	30.703	7.153	+0.560	58.3	No
Other Cracking	14	28.386	9.200	-0.914	36.4	No

Table 2-8. Summary of pavements in different climatic zones (Zenewitz & Tran, 1987).

NUMBER REPORTING	CLIMATE DESIGNATION	ORIGINAL STATES INVOLVED
102	1	Georgia, Illinois, New Jersey, Pennsylvania
46	2	New Mexico, Texas
39	3	New Mexico, Pennsylvania
162	4	Illinois, Ohio, Pennsylvania
94	5	Colorado, S. Dakota, Wyoming
82	6	Idaho, New Mexico, Utah, Wyoming, Colorado
78	7	Illinois, Minnesota, Idaho
66	8	Arkansas, Minnesota, N. Dakota
42	9	Arkansas, Colorado, Minnesota, Wyoming

Table 2-9. Significant t-tests of traffic levels and %LMS and %SMS in asphalt for pavements aged 0 to 16 years (Zenewitz & Tran, 1987).

Climate Group*	1				2				3				4				5				6				7				8				9			
Pavement	100				29				39				116				76				64				73				42				37			
	N	T	L	S	N	T	L	S	N	T	L	S	N	T	L	S	N	T	L	S	N	T	L	S	N	T	L	S	N	T	L	S	N	T	L	S
No Rutting	92	-	-	-	26	-	-	-	30	-	-	-	91	-	-	-	62	-	-	-	53	-	-	-	73	-	-	-	42	-	-	-	31	-	-	-
Rutting	8	-	-	▲	3	▲	-	-	9	-	-	-	25	-	-	-	14	-	-	-	11	-	▼	▲	0	-	-	-	0	-	-	-	6	-	-	-
Transverse Cracking	45	-	▲	▼	12	-	-	-	20	▲	-	-	74	-	-	-	42	-	-	-	29	-	-	-	64	-	-	-	37	-	-	-	25	-	-	-
Longitudinal Cracking	16	-	-	-	14	-	-	-	5	-	-	-	46	▼	-	-	7	-	-	-	18	-	-	-	8	-	-	-	3	-	-	-	6	▲	-	-
Random Cracking	13	▲	▼	-	4	-	-	-	3	-	-	-	56	-	-	-	3	-	-	-	8	-	▲	-	6	-	-	-	5	-	-	-	0	-	-	-
Alligator Cracking	10	-	-	-	3	-	-	-	0	-	-	-	13	▼	-	▲	4	-	-	-	0	-	-	-	31	-	-	-	6	-	-	-	0	-	-	-
Other Cracking	1	-	-	-	2	-	-	-	2	-	-	-	0	-	-	-	2	-	-	-	0	-	-	-	3	-	▲	▼	3	-	-	-	0	-	-	-

*This climate group is defined by Zenewitz and Tran (1987) in Table 2-8.

Legend:
N = Number Reporting
T = Traffic per Day
L = Large Mol. %
S = Small Mol. %
▲ = A significantly greater average than the overall climate group average.
▼ = A significantly lesser average than the overall climate group average.
Pavement = Number of pavements reported in that climate group (total number of pavements in all pavement groups = 576).

significantly lesser average variable than the overall climatic category average of that variable. For example, the average %SMS of the asphalts associated with the eight reports of rutting is significantly greater than the average %SMS of the 100 asphalt samples from pavements in climate group 1. The 45 reports of transverse cracking show a significantly greater average %LMS and a significantly lesser average %SMS than the average percent of these variables for the 100 reports in climate group 1.

From the results presented in Table 2-9, Zenewitz and Tran concluded that:

1. Rutting:
   - Rutting in moderate climates 1 and 2 may be attributable to a significantly larger-than-average content of small molecules in the asphalts.
   - Rutting in the more severe climate 6 resulted from the significantly greater-than-average SMS content and significantly less-than-average LMS content in the pavement asphalts.

2. Cracking:
   - Transverse cracking in climate 1 is attributable to a significantly larger-than-average LMS content and significantly lower-than-average SMS content. In climate 3, it is mainly attributable to the significantly greater-than-average daily traffic.
   - Random cracking in climate 1 is attributable to a significantly greater ADT than average, rather than the significantly lesser LMS.
   - Alligator cracking in climate group 4 is attributable to a significant decrease in ADT together with significantly higher-than-average SMS content.
   - Other cracking in climate 7 is attributable to a greater-than-average LMS content and a lower-than-average SMS content.

3. There were no significant differences in average LMS or SMS content for the 87 asphalts in the 17 years or older age group.

Conclusions:

1. Jennings et al. (1985): The authors concluded that:
   a. Asphalts with less than 36% large molecular size (LMS) have given excellent performance in the 17 states included in this study.

b. Asphalts with relatively larger amounts of LMS can be used in the warmer areas. Colder areas can tolerate smaller amounts of LMS in their asphalts.

c. Asphalts of a given penetration or viscosity grade may vary widely in molecular size distribution (MSD) between different refineries.

d. Different grade asphalts from the same refinery may be identical in terms of MSD.

e. Guidelines are provided by the authors to assist in asphalt selection based on LMS content.

2. Kinnison (1986): No statistically significant associations were found between HP-GPC parameters and condition. The author concluded that further analysis needs to be done incorporating engineering and pavement performance "know-how". He also recommended using discriminant analysis as a future analysis tool for HP-GPC data.

3. Zenewitz and Tran (1987): According to the authors:

a. HP-GPC could be an acceptable approach for quality control of asphalts for maintaining chemical consistency for a particular crude source.

b. HP-GPC could also be used for selections of asphalt derived from various combinations of crude sources.

c. HP-GPC could be a useful tool for monitoring the actual refining or the asphalt production process.

Zenewitz and Tran do not draw any direct conclusions regarding the HP-GPC results and their association with the discussed performance parameters. They do suggest that a possible application of this technique would be the incorporation of HP-GPC parameters (LMS or SMS) into specifications for purchase of paving asphalts. For example, specifying percentage of LMS for purchase of paving asphalts for particular climates or traffic conditions in order to prevent rutting or certain types of cracking. However, no guidelines for such specifications were recommended.

2.2 FHWA

Description: After Jennings et al. (1977, 1980, 1985) published their findings for the expanded Montana study (see Section 2.1), researchers at the Federal Highway Administration's

(FHWA) Turner-Fairbanks Highway Research Centre attempted to correlate the HP-GPC properties of asphalts and their physical properties (Chollar et al., 1985). A study was initiated to measure the HP-GPC properties of asphalts under the same conditions as used by Jennings et al. in Montana, and to compare the LMS results with selected properties of the asphalts.

Briefly, a series of 10 asphalts were analyzed using HP-GPC, and the LMS of these asphalts was determined using different data slice combinations of the chromatograms. Next, five asphalts from the Montana study were analyzed, and the LMS content calculated and compared to the Montana value to ensure that they agreed. Finally, the LMS content of another series of 28 asphalts was then determined and the correlations between the LMS content and physical properties of the asphalts were calculated. The physical properties measured for these asphalts included the following:

- ductility at 45°F and at 77°F
- specific gravity
- shear susceptibility
- asphaltene content (%)
- refractive index
- limiting stiffness temperature

These 28 asphalts were obtained by the Bureau of Public Roads (now FHWA) in the 1960s. They were a sampling of the asphalts available nationwide and came from a variety of sources which were not identified. The asphalts in the original study ranged from AC-5 to AC-40 grades and some were special products.

The HP-GPC system for Chollar et al.'s study utilized five μ-styragel columns. Details of the test procedure are outlined below:

Solvent: Dry Tetrahydrofuran (THF)
Sample Concentration: Solution of 2% asphalt
Flow Rate: 2.0 ml/min
Column Type: 5 μ-styragel arranged in the order: three 500 Å, one 1000 Å, one 100 Å.
Detector: Ultraviolet and visible wavelength spectrophotometric detector at 340 mμ.

Note that the early studies (Jennings et al., 1985) at Montana used a detector wavelength of 254 mμ, but this was later increased to 340 mμ to make more precise LMS measurements. In addition, Jennings used ultra-μ-styragel columns in their later studies. Chollar et al. (1985) uses

μ-styragel columns with the same pore diameter.

Results: For the five asphalts obtained from Montana, the Chollar et al. (1985) analysis calculated LMS percentages using 19 out of 59 data slices. Then t-tests were run to compare these values with the Montana values--there was no significant difference between the results when tested against the appropriate t-value at the 99% probability level. All subsequent LMS calculations were made using 19 out of 59 data slices for LMS content.

Table 2-10 lists the resulting LMS and physical properties for the 28 asphalts analyzed using HP-GPC. The data from the 28 asphalts were then statistically analyzed using linear regression techniques. The LMS content was treated as a dependent variable and each of the physical properties as an independent variable.

It was concluded by Chollar et al. that a combination of asphaltenes, specific gravity, and ductility at 77°F (25°C) gave the best model. Even so, the equation describing this model (shown below) only had a correlation coefficient R^2 of 0.386, i.e., only 39% of the variation of the LMS among the 28 asphalts can be explained by corresponding variations in the three independent variables.

$$\text{LMS} = 2.355 - 0.000565\ \text{DUCT 77} - 2.203\ \text{SG} + 0.8817\ \text{ASPH}$$

Where: LMS = Large molecular size content (%)
DUCT 77 = Ductility @ 77°F
SG = Specific Gravity
ASPH = Asphaltene content

Multivariate analysis of this model shows the following probabilities that the variables included in the above equation do not influence the LMS:

- DUCT 77 - 5.60 percent
- SG - 10.80 percent
- ASPH - 0.59 percent

The results of this study indicate that the examined physical properties of the asphalts have only a minor influence on the LMS content. Therefore, other effects not identified play an important role in the variation of LMS among asphalts.

Table 2-10. Chromatography data and physical properties of 28 asphalt cements (Chollar et al., 1985).

ASPHALT NO.	LMS	DUCT45	DUCT77	SG	SHR SUS	ASPH	REF IND	LST
1	32.23	31	130	1.004	0.36	19.0	1.4827	-46
2	32.15	9	221	1.007	0.39	20.5	1.4826	-45
3	27.01	9	200	1.012	0.51	21.6	1.4817	-41
4	12.70	8	250	1.004	0.42	15.5	1.4837	-39
5	9.43	0	250	1.007	0.62	18.1	1.4844	-39
6	23.96	11	160	1.034	0.42	27.9	1.4775	-51
7	17.75	150	155	1.010	0.21	19.3	1.4815	-51
8	17.24	150	250	1.015	0.31	20.2	1.4819	-48
9	15.98	10	241	1.021	0.44	21.6	1.4822	-44
10	8.79	0	215	1.005	0.66	16.5	1.4851	-20
11	15.57	12	230	0.994	0.41	17.8	1.4833	-50
12	23.07	7	205	0.995	0.49	20.1	1.4813	-54
13	26.88	150	245	1.021	0.32	20.8	1.4810	-39
14	14.58	14	250	1.025	0.39	21.6	1.4814	-42
15	16.09	3	152	1.011	0.30	19.5	1.4806	-53
16	12.40	5	250	1.028	0.59	29.3	1.4812	-41
17	12.64	11	210	1.026	0.42	16.7	1.4827	-56
18	16.13	150	250	1.028	0.18	26.1	1.4769	-46
19	11.52	3	250	1.020	0.64	19.2	1.4806	-34
20	22.61	150	140	1.021	0.31	22.4	1.4790	-46
21	16.27	244	167	1.011	0.23	17.3	1.4851	-40
22	18.43	19	250	1.014	0.43	18.6	1.4850	-33
23	14.93	9	250	1.018	0.54	19.7	1.4821	-36
24	14.11	150	205	1.015	0.21	18.1	1.4890	-35
25	11.66	150	145	1.010	0.40	18.0	1.4897	-35
26	6.96	250	171	1.011	0.29	9.7	1.4863	-30
27	16.50	12	250	1.016	0.50	11.0	1.4867	-23
28	3.47	4	250	1.021	0.65	12.2	1.4868	-22

LMS = Large Molecular Size Content (%)

°F = 1.8°C+32

DUCT = Ductility at 45°F and 77°F

SG = Specific Gravity

SHR SUS = Shear Susceptibility @ 45°F (Tangent of viscosity-rate of shear curve between 0.05 and 0.1 sec^{-1})

ASPH = Asphaltene Content

REF IND = Refractive Index

LST = Limiting Stiffness Temperature (°C) (Using limiting viscosity and temperature relationships)

Conclusions: The authors concluded that:

1. The results of this study show that the physical properties of asphalt only marginally influence the LMS content of asphalt.
2. HP-GPC may be useful in asphalt identification.

2.3 TEXAS

Description: In 1981, an investigation of the performance of asphalt cements from several suppliers was sponsored by the Texas State Department of Highways and Public Transportation (SDHPT) as Study Number 287 (Adams & Holmgreen, 1985). Test pavements were constructed in three different locations selected to represent different climatic zones within Texas. Samples of the materials used in Study No. 287 were preserved for future analyses with improved or new techniques. This provided a unique opportunity for on-going studies of asphalt characterization and performance. Virgin asphalt and core samples were retained during the original construction.

In 1987, a report was published by Glover et al. that summarized the results of their study of these materials. Their objectives were to:

1. Perform GPC and other chemical tests on the virgin asphalt and cores;
2. Collect and review physical property data of cores;
3. Evaluate the field performance with regard to tenderness, water susceptibility and rutting; and
4. Relate physical properties and field performance to chemical properties and characterization.

Cores were taken during the performance surveys, with most of these cores being one to two years old. Asphalt cements were collected directly from the respective refineries before construction of the three test sections. In addition, asphalt samples were extracted from laboratory-molded plant mixes. The physical tests on these asphalts included:

- Penetration @ 39.2°F and 77°F
- Viscosity @ 77°F, 140°F, and 275°F
- Thin Film Oven Test (penetration and viscosity parameters were evaluated before and after TFOT).

Compositional analyses of virgin asphalts and asphalts extracted from the pavement cores taken from the test sections included:

- Gel Permeation Chromatography (GPC) using Waters model R401 refractive index detector with 10 μM cell. Two solvents were used: tetrahydrofuran (THF) using one 500 Å and one 50 Å styragel column; and toluene using one 500 Å styragel column.
- Corbett Fraction Analyses
- GPC analysis of the Corbett fractions
- Elemental analyses[2]

In another segment of Glover et al.'s study, the researchers attempted to determine how well asphalt setting rate or tender mix problems could be predicted using an abbreviated version of the Heithaus procedure[3]. (The Heithaus test measures the state of peptization of asphalts. The state of peptization of the asphaltenes play a role in determining the rheological properties of an asphalt and the influence of asphalt composition and environmental factors). This was accomplished by relating flocculation ratio to asphaltene content, rheological properties, compatibility and durability of the asphalt cement (See Appendix B for more detailed information on these test procedures and terms).

Results: Table 2-11 summarizes the results from physical tests related to these three test sections. The results of the chemical analyses may be divided into the following sections:

1. GPC Analysis with THF Figure 2-3 shows chromatograms for two asphalts (AC-20 and AC-10) with GPC profiles for both the virgin asphalt used and the recovered asphalt from pavement core samples. Two noticeable features are the distinct differences in profile between the virgin and aged asphalts, and the increase in large molecular sizes at the expense of small molecular sizes (SMS) as the asphalt ages. This is a characteristic for most of the asphalts.

2. GPC Analysis with Toluene Figure 2-4 shows chromatograms for the same two asphalts as in Figure 2-3. The general increase in LMS with aging is again confirmed. However, for the Dorchester AC-10 sample, the profiles for both virgin and aged asphalts are so similar that the increase in LMS may not be significant. The shapes of the

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[2] This analysis provided the percentages of various elements in the sample irrespective of the type of compound in which the element is present. The elements of interest here were carbon, hydrogen, oxygen and sulfur.

[3] See Appendix B for further details on these terms.

Table 2-11. Physical properties of asphalts obtained at different stages before, during and after construction (Glover et al., 1987)

Asphalt Refinery & Grade	Location of Test Pavement	Directly from Refinery					As Delivered to Construction Site					After TFOT		
		Viscosity*			Penetration		Viscosity*			Penetration		Viscosity*	Penetration	Weight Loss Percent
		77	140	275	39.2	77	77	140	275	39.2	77	140	77	
Dia. Sham AC-10	**	0.66	973	2.76	20	106	-	-	-	-	-	1280	69	0
	Dickens	-	-	-	-	-	1.35	1220	4.51	15	95			
	Dumas	-	-	-	-	-	0.56	958	4.65	16	104			
Dia. Sham AC-20	**	3.55	2240	6.42	-	-	-	-	-	-	-	4680	41	0
	Dickens	-	-	-	-	-	4.00	2180	7.15	8	65			
	Dumas	-	-	-	-	-	1.09	2160	6.39	16	61			
	Lufkin	-	-	-	-	-	1.80	1730	5.05	16	70			
MacMillan AC-10	**	0.22	773	2.76	35	166	-	-	-	-	-	1210	121	0.04
	Dumas	-	-	-	-	-	0.36	691	3.63	39	133			
	Lufkin	-	-	-	-	-	0.76	932	3.63	25	95			
MacMillan AC-20	**	1.55	3010	5.33	26	64	-	-	-	-	-	5010	53	0.04
	Dickens	-	-	-	-	-	1.20	2520	4.64	27	77			
Exxon AC-10	**	0.66	1268	2.85	16	80	-	-	-	-	-	2540	50	0.03
	Dumas	-	-	-	-	-	0.83	1388	3.06	15	74			
Exxon AC-20	**	1.70	2180	3.22	18	58	-	-	-	-	-	4020	32	0.05
	Dickens	-	-	-	-	-	2.75	2580	3.55	7	43			
	Lufkin	-	-	-	-	-	1.55	1810	3.19	6	64			
Dorchester AC-10	**	0.50	930	3.18	35	113	-	-	-	-	-	2380	68	0.13
	Dumas	-	-	-	-	-	0.53	1030	3.21	30	105			
	Lufkin	-	-	-	-	-	0.42	1040	2.88	33	111			
Dorchester AC-20	**	1.11	1810	4.09	26	81	-	-	-	-	-	3240	56	0.05
	Dickens	-	-	-	-	-	2.50	2150	4.53	22	69			
	Lufkin	-	-	-	-	-	0.96	1910	3.96	23	79			
Cosden AC-10	**	0.88	955	2.34	17	80	-	-	-	-	-	2440	42	0.37
	Dickens	-	-	-	-	-	1.15	1260	2.55	15	72			
	Dumas	-	-	-	-	-	0.97	1038	2.48	16	71			
Cosden AC-20	**	2.25	1910	3.10	13	45	-	-	-	-	-	4280	32	0.15
	Dickens	-	-	-	-	-	1.90	1520	2.87	9	53			
	Dumas	-	-	-	-	-	1.60	2350	3.17	10	54			

* Viscosity at 77° F given in poises (X 10^6)
Viscosity at 140 and 275° F given in poises

** These data are representative of asphalts obtained directly from refineries, not from a specific construction site

Table 2-11. Continued

Asphalt Refinery & Grade	Location of Test Pavement	Recovered from Lab Mixes					Recovered from Cores				
		Viscosity*			Penetration		Viscosity*			Penetration	
		77	140	275	39.2	77	77	140	275	39.2	77
Dia. Sham. AC-10	Dickens	12.0	2000	5.93	21	62	17.0	12,400	7.29	15	37
	Dumas	1.6	1723	5.24	20	75	2.0	2600	4.81	15	57
Dia. Sham. AC-20	Dickens	18.4	9560	11.0	14	20	12.0	12,300	11.8	5	25
	Dumas	3.4	2980	7.13	12	51	5.8	4470	8.41	10	41
	Lufkin	4.5	3780	7.45	15	52	3.55	3470	6.92	10	48
MacMillan AC-10	Dumas	0.56	1360	3.49	57	107	0.7	1450	3.59	30	90
	Lufkin	3.45	3600	5.46	22	57	3.70	3890	6.26	7	56
MacMillan AC-20	Dickens	7.0	11,250	8.30	20	38	21.0	3790	5.67	3	17
Exxon AC-10	Dumas	2.9	3000	3.86	7	45	2.06	2480	4.41	15	62
Exxon AC-20	Dickens	16.0	8670	6.06	8	21	8.00	5520	8.08	8	32
	Lufkin	3.3	2939	4.40	9	48	3.80	2750	3.87	10	46
Dorchester AC-10	Dumas	1.5	1990	3.98	26	66	1.28	1930	4.04	26	71
	Lufkin	1.28	1870	3.90	19	73	1.20	2420	4.44	16	63
Dorchester AC-20	Dickens	1.40	11,400	8.74	21	32	21.0	8670	5.79	2	20
	Lufkin	4.10	5940	5.77	5	45	3.80	2975	4.98	12	52
Cosden AC-10	Dickens	1.30	4322	4.16	8	28	18.5	23,100	9.70	10	21
	Dumas	2.00	1940	3.08	12	47	-	-	-	-	-
Cosden AC-20	Dickens	14.0	4750	4.49	9	29	30.0	7.45	7.45	0	18
	Dumas	5.0	2374	3.42	12	41	14.5	5.06	5.06	4	23

* Viscosity at 77° F given in poises (X 10^6)
Viscosity at 140 and 275° F given in poises

** These data are representative of asphalts obtained directly from refineries, not from a specific construction site

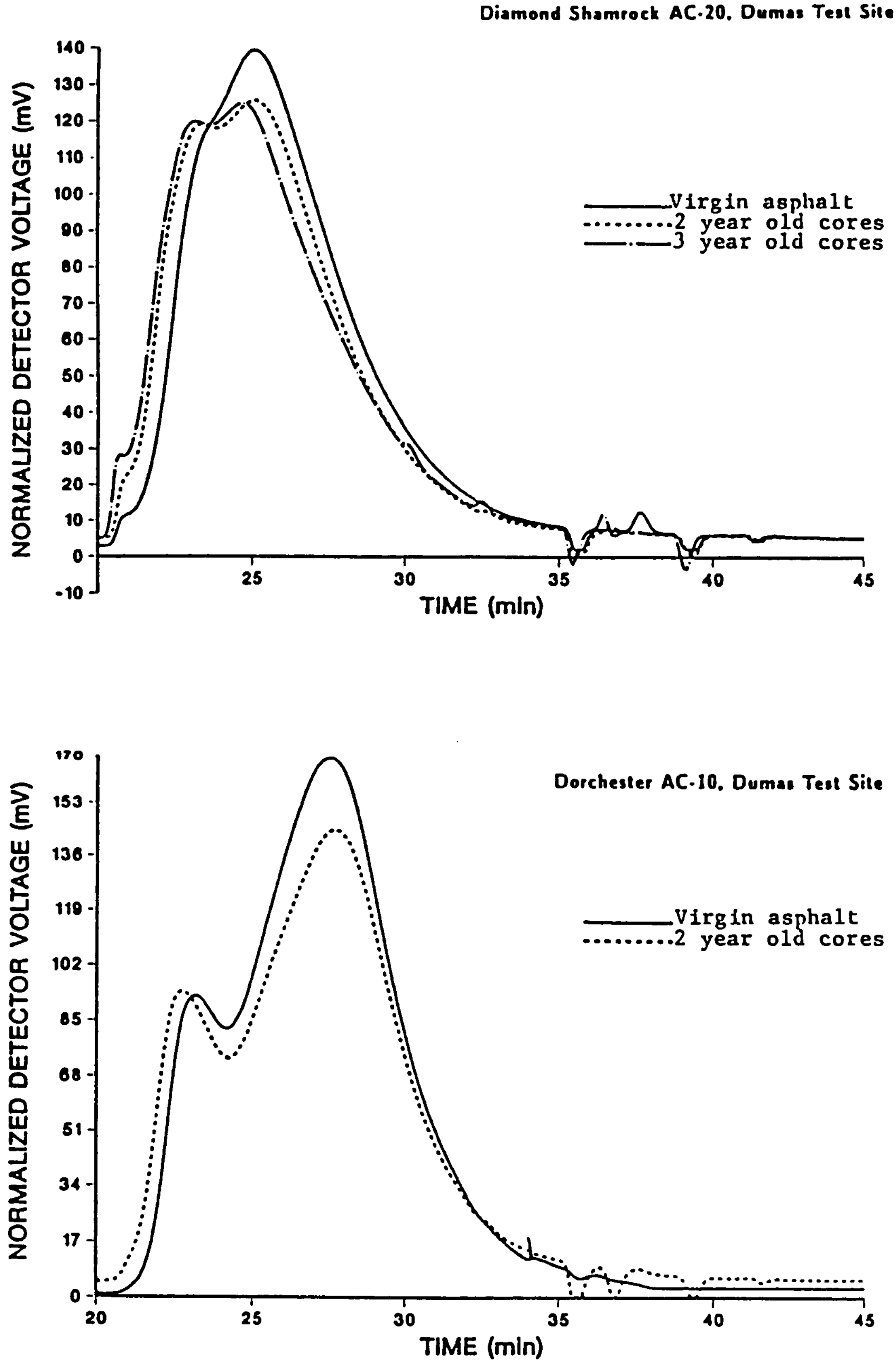


Figure 2-3. Comparison of core samples to the original asphalt using THF (Glover et al., 1987).

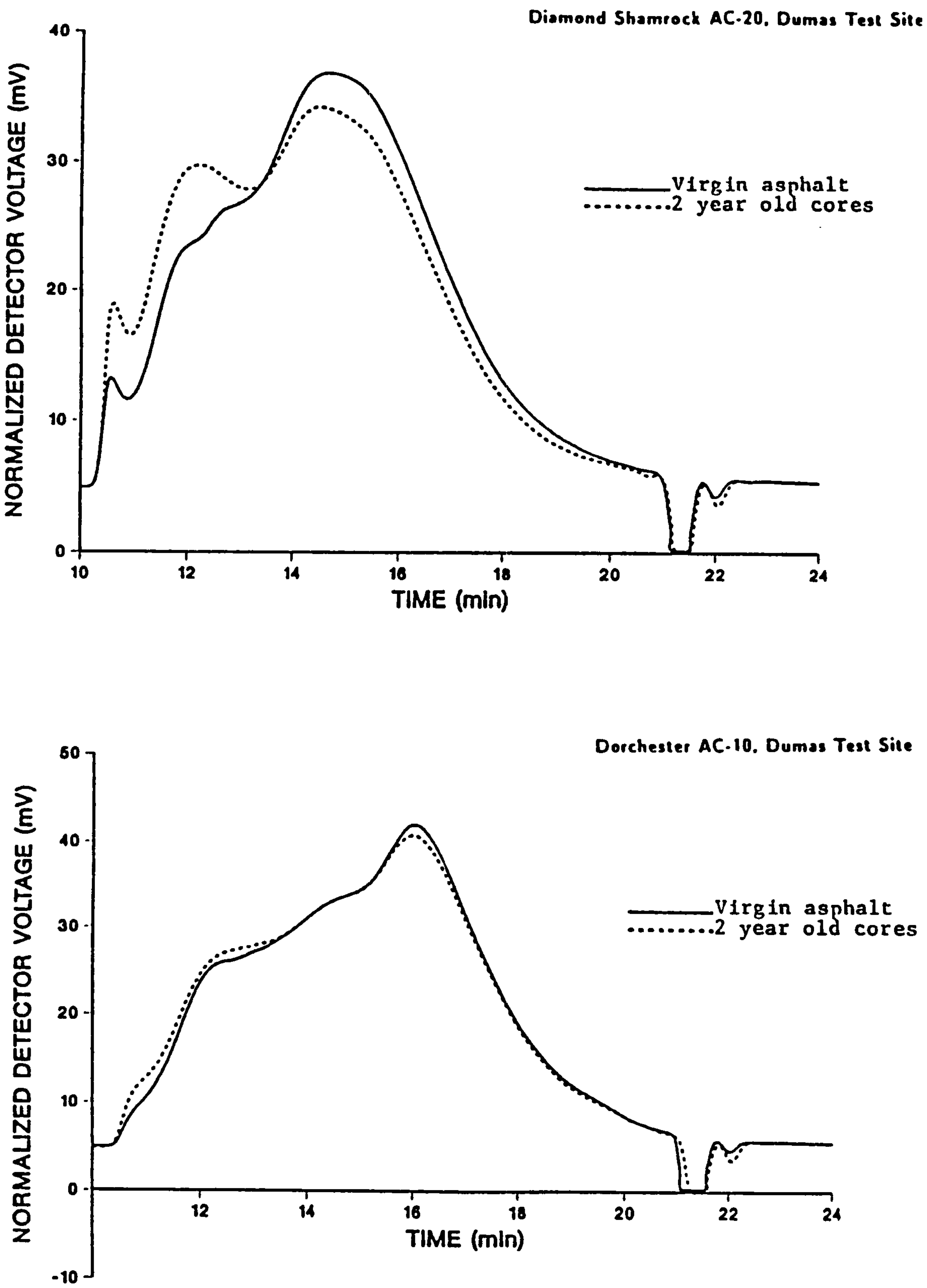


Figure 2-4. Comparison of core samples to the original asphalt using Toluene (Glover et al., 1987).

chromatograms for each asphalt are easier to differentiate using toluene as a solvent rather than THF. Hence, toluene is a much more "visible" solvent and the asphalt shows greater "resolution". Also, the GPC analysis done with toluene only used one column; hence, the solution probably did not have a long path for the absorption of certain polar molecules on the way, thus giving a clearer image of the asphalt.

3. GPC Analysis of the Corbett Fractions Figure 2-5 shows a GPC chromatogram for a whole asphalt as well as the chromatograms for the individual Corbett fractions for a 1984 core sample. The asphaltene fraction had, on average, a higher molecular weight than the other fractions and thus eluted sooner; but there was a wide range indicated for the molecular size of this fraction. Glover et al. (1987) indicate that this was not surprising as asphaltenes result as much from polarity as molecular weight, and even the higher molecular weight species probably result from association of smaller molecules. Some of the apparently smaller molecular size material may actually be of larger size but because of its polarity, is weakly adsorbed on the column resulting in an increased retention time. Glover et al. hypothesize that a part of the molecules that elute at later times (i.e., in the SMS region; hence the word "apparently" smaller molecular size material) are actually larger polar molecules that get weakly adsorbed on the column. Therefore, we see a smaller LMS area on the chromatogram than had there been no such adsorption. The other three groups did not differ greatly in maximum peak location, but there was a trend of decreasing size from polar aromatics to saturates.

4. GPC and Tenderness - Pavement tenderness is a subjective rating and is based on user comments pertaining to the asphalts general performance history with particular emphasis on construction and early pavement performance. The tenderness rating is based on a scale from 0 to 5; zero indicates that tenderness or slow setting problems are never associated with the asphalt and five indicates these problems are always associated with asphalt. Tenderness ratings for asphalts used in this study were correlated with the LMS. The relationship between LMS and tenderness rating is shown in Figure 2-6. This correlation has a coefficient of determination (R^2) of 0.6. However, note that the data could be separated into two populations: one at a LMS of 17-25% and the other at 0-10%; hence, leaving a gap in the data from 10-17%.

Basically, asphalts may be broken into two families (Figure 2-7) with regard to tenderness. The tender asphalts consist of those with tenderness ratings above two. These asphalts have low flocculation ratios, low LMS (with some exceptions) and low asphaltene content. The non-tender asphalts have tenderness ratings at 2 or below. Accordingly, they

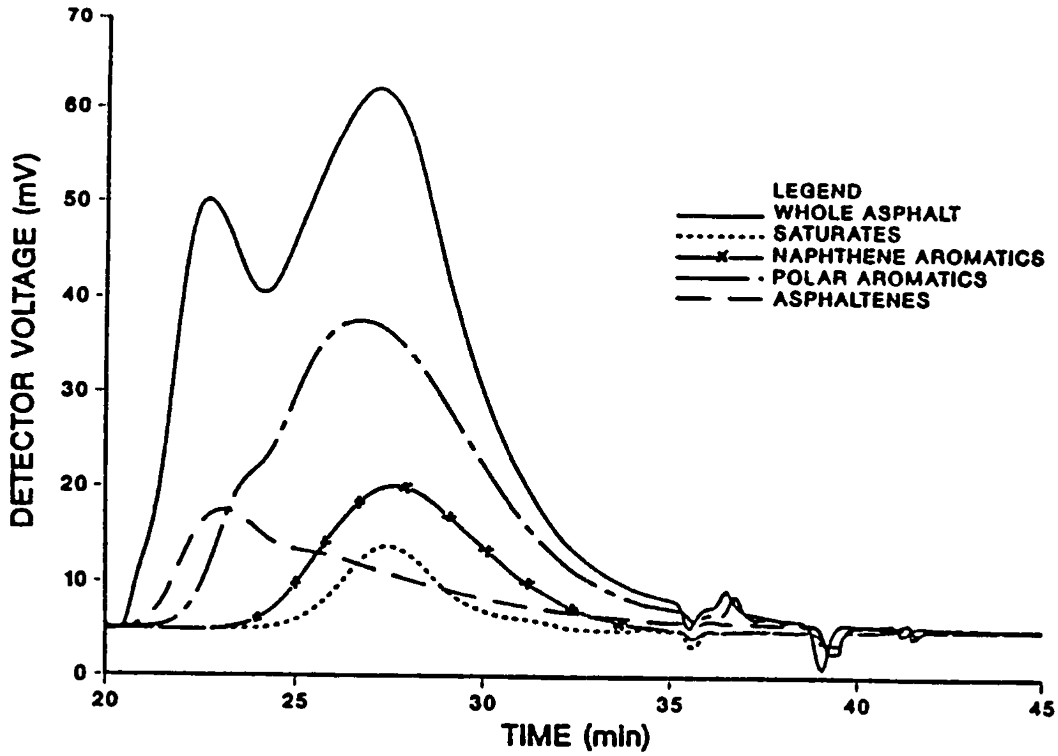


Figure 2-5. GPC profiles of individual Corbett fractions and the whole asphalt (Glover et al., 1987).

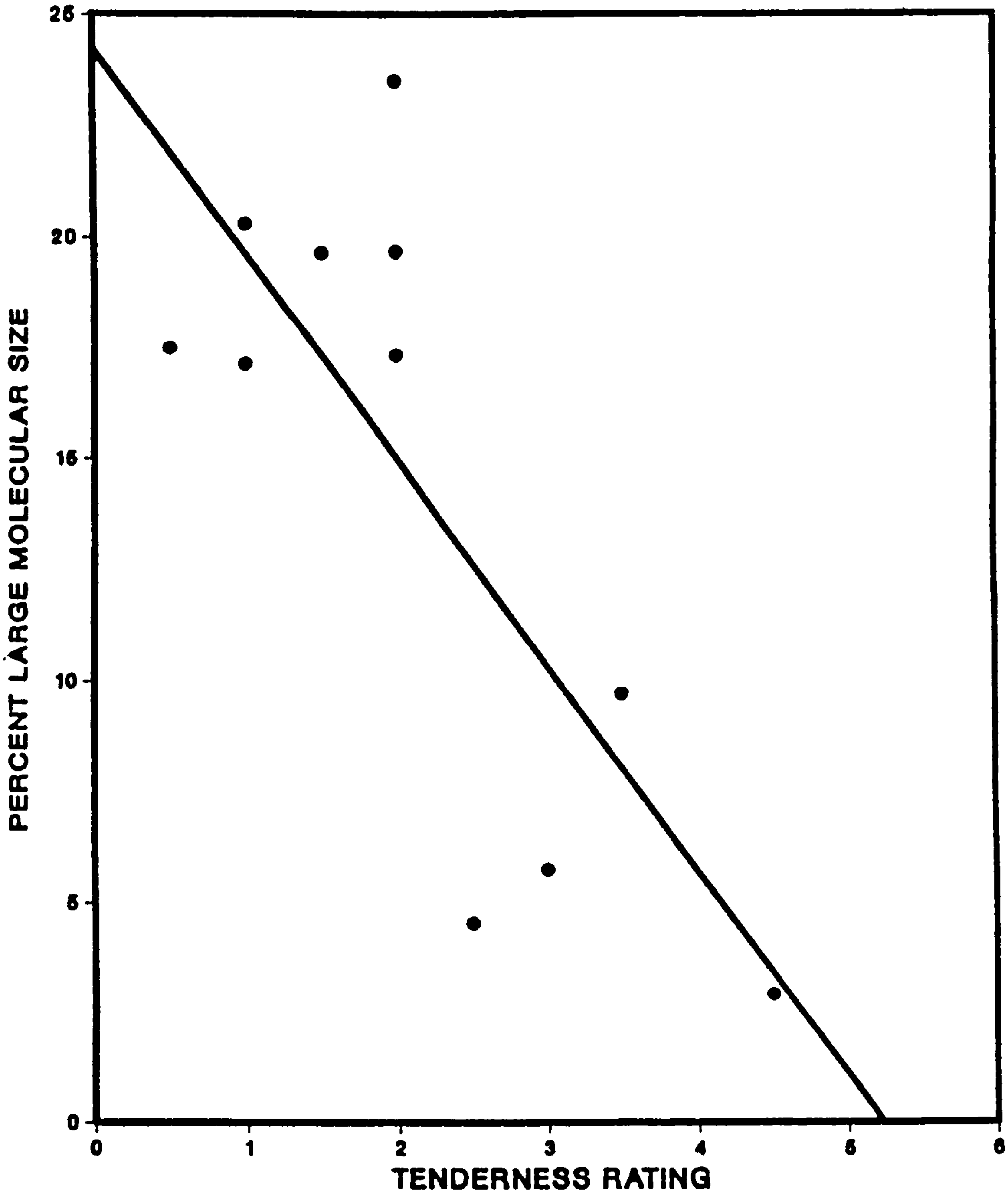


Figure 2-6. Large molecular size fraction vs. tenderness rating (Glover et al., 1987).

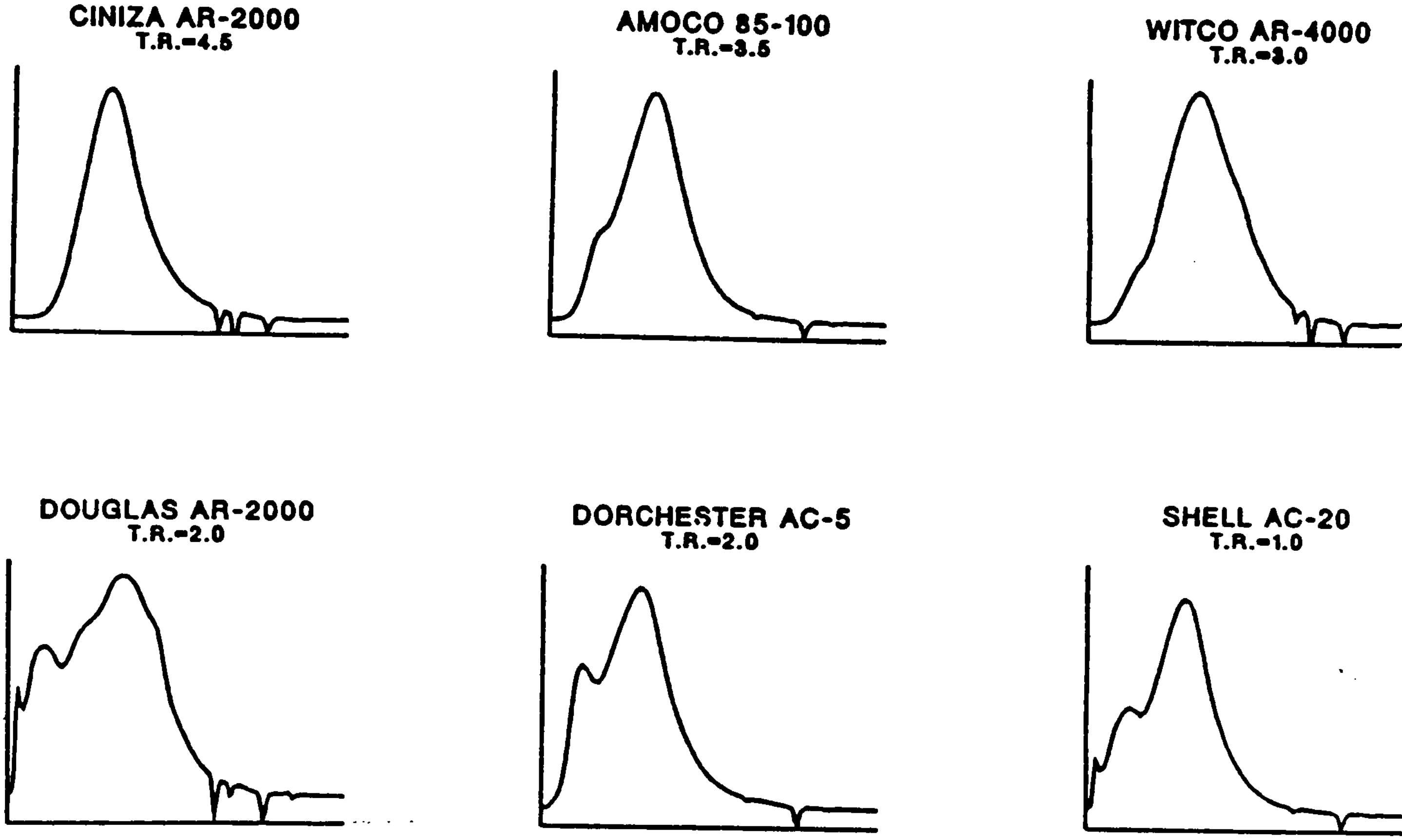


Figure 2-7. Comparison of GPC profiles to tenderness rating (Glover et al., 1987).

have high flocculation ratios, high LMS, and high asphaltene contents. A comparison of GPC chromatograms for asphalts with high and low tenderness ratings is given in Figure 2-7. The Ciniza AR-2000, Amoco 85-100, and WITCO AR-4000 are the relatively tender asphalts (tenderness rating >2.0), and when compared with the Douglas AR-2000, Dorchester AC-5 and Shell AC-20 asphalts (non-tender asphalts), there is a marked absence of the LMS component peaks that is present in the latter three asphalts. While there is not a perfect correlation between LMS and the tenderness rating, the difference between the two groups is obvious. Thus, considering the speed of performing a GPC analysis as compared with the other procedures, the GPC appears to be a useful tool for identifying asphalts with tenderness problems.

5. <u>Relationship Between GPC and Pavement Performance</u> There is, to date, relatively little distress and almost no difference in pavement performance of the field trials in Dickens, Dumas and Lufkin with which to relate to GPC results. The limited quantity of data makes it difficult to derive and support conclusions regarding asphalt quality. However, an important point on relating GPC data to the performance of asphalt pavements should be made. Even though poor performance may be the result of poor asphalts, it also is possible that other factors are involved. For example, while pavement disintegration may be the result of poor adhesive characteristics of the asphalt, it may also result from aggregate surface characteristics or inadequate compaction. Similarly, while laboratory tests show that fatigue-type cracking is related to the characteristics of the asphalt in the mix, studies also show that fatigue-type cracking may be related to the volume fraction of asphalt cement in the mix. That is, low binder content or poor compaction can lead to cracking in a mix with a perfectly satisfactory binder. Even if the mix is well compacted and contains adequate asphalt cement, a weak substrate will subject the pavement to large tensile strains and it will crack.

This discussion could be extended to other forms of cracking as well as other distress modes. Glover et al. stress that careful monitoring and investigation of pavement performance is necessary in order to obtain meaningful correlations with GPC and other test results.

<u>Conclusions</u>: Some of the conclusions presented in this report (Glover et al., 1987), pertaining to GPC analysis as an analytical tool and as a predictor of asphalt pavement performance, are presented below:

1. Gel Permeation Chromatography (GPC) is a very rapid procedure for asphalt characterization. There is a considerable body of literature indicating that it is also a useful tool for identifying asphalt changes and for correlating cracking and

tenderness in asphalts.

2. Changes in asphalt composition caused by changes in processing and feedstock can be detected by GPC. In most instances the differences between asphalts from various sources are distinguishable.
3. For all the cores taken from the test sections, the GPC large molecular size (LMS) region increased relative to the virgin asphalt. This implies that the LMS content of asphalt increased with age.
4. Using toluene instead of tetrahydrofuran as a solvent for GPC results in a more distinctive chromatogram for the asphalt. This should be noted when GPC analysis is used for identification of asphalts from different crude sources.
5. There was insufficient field performance information to draw any conclusions between performance and asphalt properties.

2.4 GARRICK & WOOD (1986, 1988)

Description: Two studies were made by Garrick & Wood (1986, 1988) to predict physical properties of asphalt cements and asphalt concrete mixes from HP-GPC parameters. This section summarizes the results of both these studies, first concentrating on the 1986 study and then on the 1988 study. In 1986, Garrick & Wood published the results of a study that investigated the possible relationship between High Pressure Gel Permeation Chromatography (HP-GPC) data and three rheological properties of an asphalt:

- penetration at 25°C
- absolute viscosity at 60°C
- kinematic viscosity at 135°C

The asphalt samples (from the same crude source) used were blended from products of a residuum oil supercritical extraction (ROSE) refinery unit. This ensured that the asphalts were all from the same refinery process as well as crude source. Any variation in their rheology may therefore be directly attributed to changes in their chemical composition. A Strieter chemical analysis (see Appendix C) of the ROSE products showed three basic fractions, as shown in Table 2-12.

The three products (asphaltene, resin and DAO) from the ROSE unit were combined in various proportions selected to ensure a large range of viscosity values for these asphalts. These products were blended on a hot plate in the following manner:

1. The required amounts of deasphalted oil (DAO) and resin fractions were heated to

Table 2-12. Strieter chemical analysis results (Garrick & Wood, 1986).

FRACTION	ASPHALTENE (WtX)	RESIN (WtX)	OIL (WtX)
Asphaltene-rich	40.8	26.8	32.4
Resin Rich	6.5	54.6	38.9
Deasphalted Oil (DAO)	1.1	19.4	79.5

approximately 65°C, at which point both fractions were fluid and miscible.

2. A small proportion of the required amount of asphaltene fraction was then added and the mixture stirred with a spatula. Stirring was continued until all traces of the solid asphaltene dissolved.
3. The second step was repeated until all the asphaltene had been added. The maximum temperature attained was 120°C.

A total of nineteen different asphalts were blended. Absolute viscosity at 60°C, kinematic viscosity at 135°C, and penetration at 25°C were measured for each of these asphalts. Table 2-13 lists the proportions of asphaltene, resin, and DAO used for blending and the corresponding PVN (pen-vis number) for these blended asphalts.

HP-GPC profiles were obtained for fourteen of the nineteen blends and for each of the three ROSE products. The HP-GPC profiles for the three ROSE products were obtained for use as a baseline for comparing the other profiles. The HP-GPC system for this study utilized:

Column Type: 6 μ-styragel columns connected in order: 10^3 Å, 500 Å, 500 Å, 500 Å, 10^5 Å, 10^6 Å
Detector Type: Differential refractometer
Solvent: Tetrahydrofuran (THF)
Sample Concentration: 1.0%
Injection Volume: 0.5 ml
Flow Rate: 2.0 ml/min

The HP-GPC profiles obtained were broken down into eight sections (Figure 2-8) or areas under the curve. This number was selected by Garrick & Wood as the optimum needed to provide an accurate model of HP-GPC profiles. It was also determined that the typical division into three sections (SMS, MMS, LMS) were not sufficiently sensitive enough to model the asphalts in this study. The cutoff points were selected to ensure that each section contains approximately the same proportion of the total area. Various numerical descriptors have been used by researchers to distinguish HP-GPC profiles (e.g., Jennings et al., 1985; Plummer et al., 1984). Most frequently, the area under the curve is divided into three sections (LMS, MMS and SMS), and the proportion of total area in each section determined. These proportions are an approximate measure of the amount of material emerging from the system in a given time period.

Results: The results of regression analyses relating absolute viscosity to kinematic viscosity and absolute viscosity to penetration are shown in Figures 2-9 and 2-10, respectively. A direct relationship was observed between each pair of rheological variables which, according to Garrick &

Table 2-13. Proportions of blended asphalts (Garrick & Wood, 1986).

ASPHALT NO.	PROPORTIONS			PEN-VIS NUMBER (PVN)
	ASPHALTENE	RESIN	DAO	
1	0.329	0.255	0.416	-1.10
2	0.201	0.611	0.188	-1.12
3	0.201	0.611	0.188	-1.19
4	0.200	0.400	0.400	-0.88
5	0.223	0.679	0.098	-1.15
6	0.290	0.410	0.300	-1.10
7	0.200	0.450	0.350	-1.05
8	0.360	0.140	0.500	-1.21
9	0.201	0.611	0.188	-1.12
10	0.200	0.530	0.270	-1.06
11	0.300	0.450	0.250	-1.15
12	0.100	0.900	0.000	-1.24
13	0.380	0.000	0.620	-1.30
14	0.060	0.905	0.035	-1.25
15	0.240	0.460	0.300	-1.23
16	0.200	0.555	0.245	-1.13
17	0.425	0.000	0.575	-1.12
18	0.100	0.810	0.090	-1.18
19	0.198	0.550	0.252	-1.22

Penetration-Viscosity Number = -1.5 (A - $\log_{10}$ N275) / (A - B)

where: A = 4.258 - 0.79674 $\log_{10}$ (pen 25°C)
B = 3.46289 - 0.61094 $\log_{10}$ (pen 25°C)
N275 is the Kinematic Viscosity at 135°C (275°F), cst

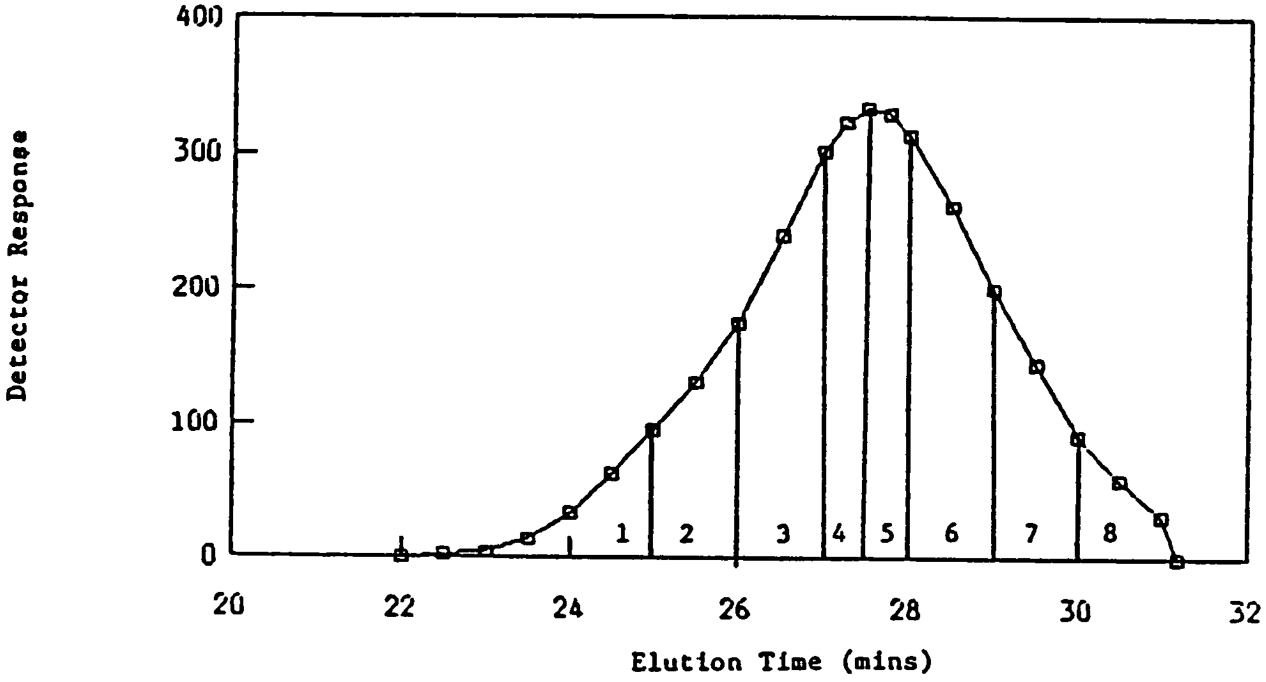
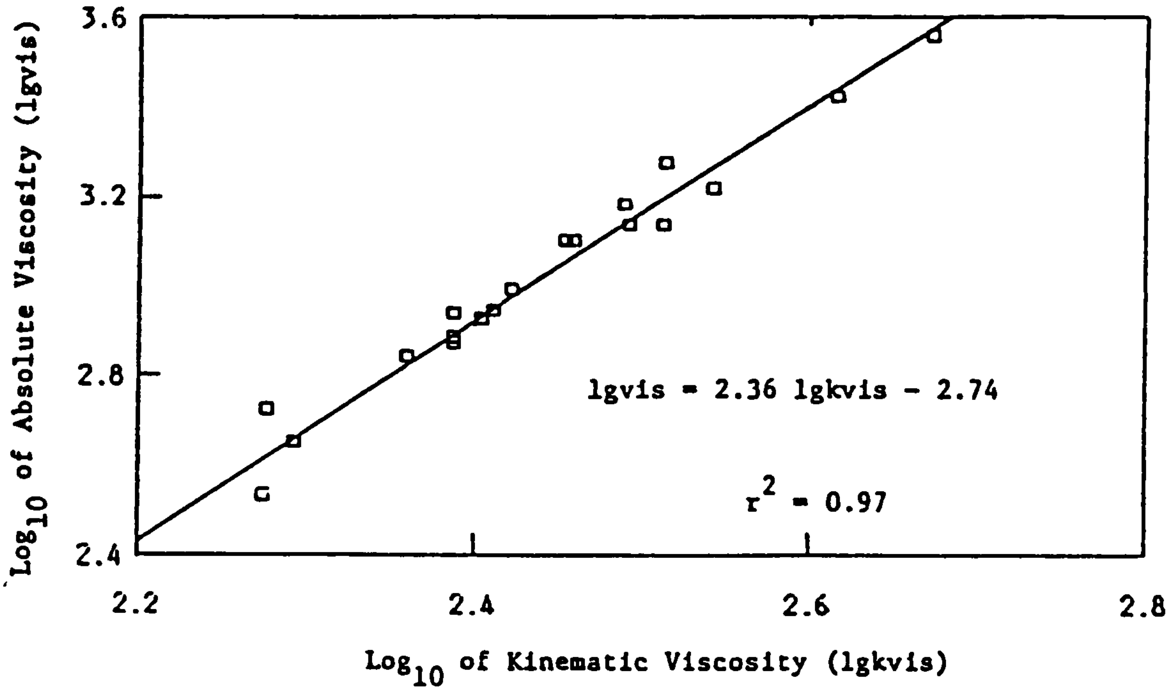
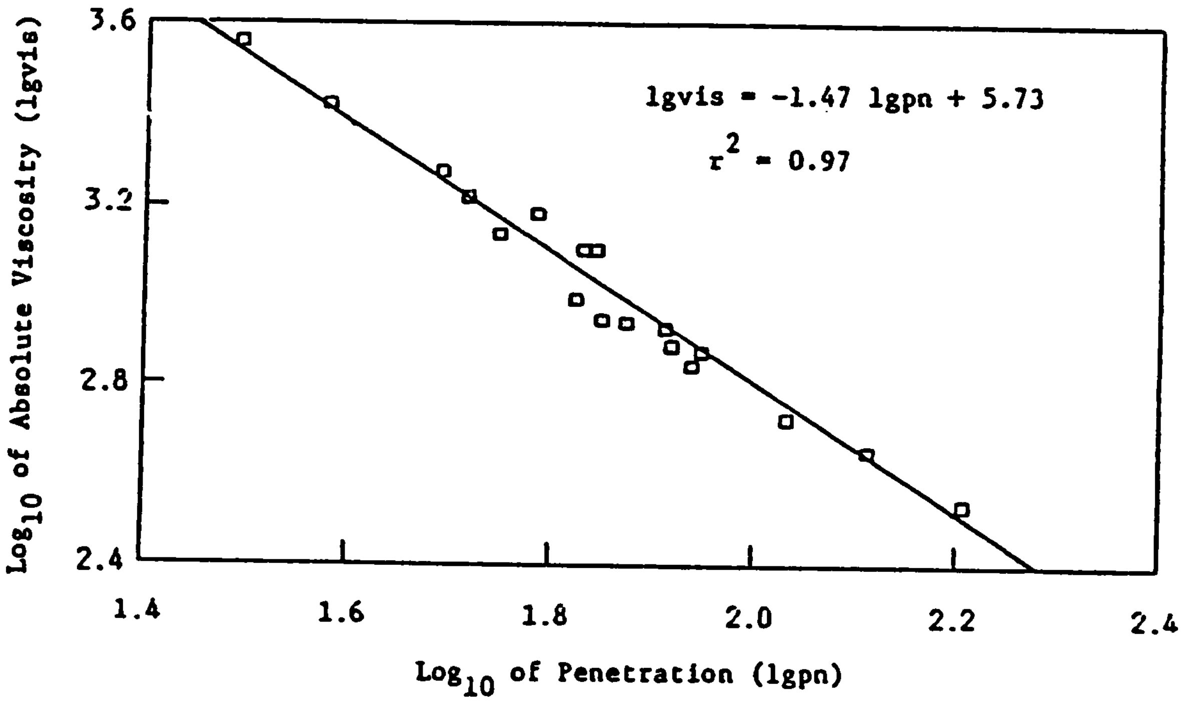


Figure 2-8. Typical HP-GPC profile showing cut-off points (8 nearly equal areas under the curve) (Garrick & Wood, 1986).



Note: Absolute viscosity @ 60•C, Kinematic Viscosity @ 135•C.

Figure 2-9. Absolute viscosity vs. kinematic viscosity (Garrick & Wood, 1986).



Note: Absolute viscosity @ 60°C, penetration @ 25°C.

Figure 2-10. Absolute viscosity vs. penetration (Garrick & Wood, 1986).

Wood, implies little variation in temperature susceptibility between these asphalts. The values of the Pen-Vis (PVN) number for these blended asphalts vary over a very narrow range (-1.30 to -1.05). This shows that temperature susceptibility for these asphalts, in the temperature range of 25°C to 135°C, is relatively insensitive to variation in chemical composition.

The HP-GPC profiles for the three ROSE products are shown in Figure 2-11. The asphaltene fraction contained the greatest amount of large molecules (lowest retention time). Hypothetical HP-GPC parameters were calculated for each asphalt using the following simple equation:

$$X_i = aX_{ia} + bX_{ir} + cX_{id}$$

where: X_i = proportion of area in section 'i' for the asphalt
X_{ia}, X_{ir}, X_{id} = proportions in section 'i' for the asphaltene, resin and DAO fractions respectively
a, b, c = proportions of asphaltene, resin and DAO respectively, in the asphalt according to the Strieter chemical analysis.

A comparison of the actual and hypothetical parameters for the HP-GPC data showed a systematic pattern of variation, as shown in Table 2-14. In most cases, the proportion of area in sections two and three were greater for the actual data than for the hypothetical data. Garrick & Wood hypothesized that this systematic difference resulted from heating the ROSE products during blending. Heating appears to cause an increase in the percentage of large molecules. This phenomenon can be applied to monitoring of a specific asphalt (using HP-GPC) as it undergoes processing.

A regression function was also developed relating absolute viscosity and HP-GPC parameters. This is shown below (coefficient of determination is 0.95):

$$\text{Log } V_{ABS} = -91.23 + 1.01X_1 + 1.06X_2 + 1.31X_3 + 0.21X_4 + 0.29X_5 + 1.67X_6 + 0.53X_7 + 0.82X_8$$

where: V_{ABS} = absolute viscosity @ 140°F, Poises
X = proportion of areas in Sections 1 to 8

Apparently viscosity is not determined by the preponderance of one molecular size in the asphalt, but is dependent on the overall interaction of the molecules of different functional types. Similar results were obtained for regression analyses relating HP-GPC data to penetration and kinematic viscosity.

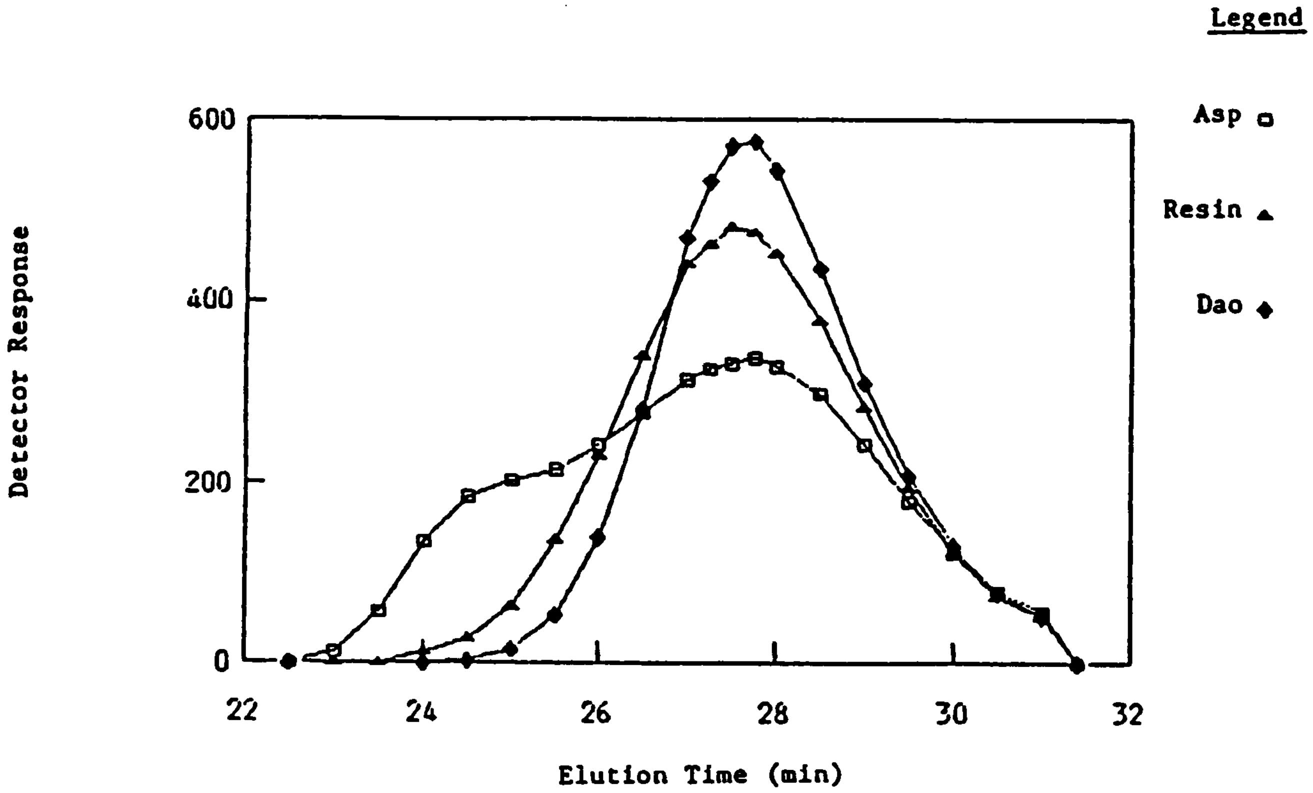


Figure 2-11. HP-GPC profiles of ROSE products (Garrick & Wood, 1986).

Table 2-14. Actual vs. hypothetical HP-GPC data (Garrick & Wood, 1986).

ASPHALT NO.	DIFFERENCE BETWEEN ACTUAL AND HYPOTHETICAL RESULTS BY SECTION*							
	1	2	3	4	5	6	7	8
1	-0.5	+1.7	+1.0	-0.3	-0.5	-0.8	-0.5	-0.3
3	+0.0	+1.6	+0.9	-0.1	-0.4	-1.0	-0.7	-0.4
4	-0.1	+1.6	+1.2	-0.1	-0.5	-1.3	-0.8	-0.2
6	-0.7	+1.4	+0.9	-0.2	-0.4	-0.7	-0.4	+0.0
7	-0.8	+1.1	+1.0	+0.1	-0.2	-0.6	-0.3	-0.3
8	-1.6	+1.1	+0.6	-0.5	-0.3	+0.0	+0.2	+0.7
9	-0.5	+1.0	+0.8	0.0	-0.1	-0.6	-0.7	+0.1
11	+0.1	+1.5	+0.8	-0.3	-0.6	-1.1	-0.7	+0.1
12	+0.0	+1.0	+0.9	0.0	-0.2	-0.7	-0.7	-0.5
13	+0.0	+1.6	+0.3	-0.5	-0.5	-0.8	-0.1	+0.0
14	-0.5	+0.4	+0.4	0.0	0.0	-0.1	-0.3	-0.1
15	+0.0	+1.7	+0.9	-0.4	-0.7	-1.4	-0.7	+0.4
17	+0.0	+2.2	+1.6	-0.2	-0.7	-1.5	-0.8	-0.6
19	-1.3	+0.4	+0.5	+0.1	+0.2	+0.1	-0.1	
AVG	-0.4	+1.3	+0.8	-0.2	-0.4	-0.7	-0.4	-0.1

*A positive difference means that the actual HP-GPC parameter is greater than the hypothetical value (these values are percentages).

Conclusions: Keeping in mind that the asphalts used in this study were produced by blending the products of a residuum oil supercritical extraction (ROSE) plant, the authors concluded that:

1. In the temperature range of 25°C to 135°C there is very little variation in temperature susceptibility for the asphalts tested.
2. Heating appears to cause an increase in the amount of large molecule sizes (LMS) in the asphalt. HP-GPC can be used for monitoring a specific asphalt as it undergoes processing.
3. Viscosity (@ 60°C and 135°C) and penetration (@ 25°C) were found to be directly related to HP-GPC parameters of these asphalts.

Description: In 1988, another study was completed that examined the relationship between HP-GPC profiles and the properties of asphalts and asphalt concrete mixes. The asphalts used came from six separate sources: two groups were ROSE blends using Pester (Plant A) in Kansas and Kerr-McGee (Plant B) in Oklahoma; the third group was an AC-10 from Amoco refinery (Plant C) in Indiana; the last three groups were from three other facilities (D, E, F) in Indiana. The original asphalt as well as TFOT residue and pavement residue was available for Source D; Source E had both original asphalt and TFOT residues and Source F had only the pavement residue. The different types of samples were useful for examining the changes in GPC profiles caused by heat and aging.

Tables 2-15 and 2-16 summarize the physical properties of the asphalt cements treated. In addition, asphalt concrete sand mixes were made and resilient modulus (50°F and 72°F) and indirect tensile strength (@ 72°F) tests were run (Table 2-17). Finally, Table 2-18 summarizes the HP-GPC results for the test asphalts.

Regression analyses were used to examine the relationship between HP-GPC parameters and individual properties of both the asphalt cements and the asphalt concrete sand mixes. The relationships are as shown below:

Rheological Properties:

1. Log Vis(140) = $0.81 + 0.13x_1 + 0.2x_3 - 0.03x_4$
$-0.74x_5 + 0.38x_6 - 0.03x_7$ $(R^2 = 0.98)$
2. Log Vis(275) = $3.55 + 0.04x_1 - 0.03x_2 + 0.9x_3$
$- 0.41x_5 + 0.14x_6$ $(R^2 = 0.95)$
3. Log Pen(77) = $- 17.55 + 0.12x_1 + 0.26x_2 + 0.19x_4$
$+ 1.04x_5 - 0.21x_6 + 0.25x_7$
$+ 0.19x_8$ $(R^2 = 0.94)$

Table 2-15. Rheological properties of asphalts (Garrick & Wood, 1988).

Number	Viscosity 140 F, P	Viscosity 275 F, cst	Penetration 39.2 F, 0.1mm	Penetration 77 F, 0.1mm
LAC-10-1(0)	950	274	27	78
LAC-10-2(0)	1070	260	17	74
MAC-10-1(0)	1022	273	23	75
MAC-10-2(0)	1185	271	29	72
HAC-10-1(0)	1178	274	24	70
HAC-10-2(0)	1076	256	20	76
LAC-20-1(0)	1929	348	14	44
LAC-20-2(0)	2246	362	14	40
MAC-20-1(0)	2195	360	16	47
MAC-20-2(0)	2326	376	18	46
HAC-20-1(0)	2326	361	21	52
HAC-20-2(0)	2270	350	20	50
LAC-10-1(TR)	1804	349	15	40
LAC-10-2(TR)	1924	347	15	40
MAC-10-1(TR)	2004	395	19	37
HAC-10-1(TR)	4589	405	18	37
HAC-10-2(TR)	4458	405	18	37
LAC-20-1(TR)	4317	459	9	25
LAC-20-2(TR)	4358	459	11	22
MAC-20-1(TR)	5287	493	14	25
HAC-20-1(TR)	9273	565	13	26
700-10-1(0)	1150	341	34	94
700-10-2(0)	1150	345	32	96
900-20-1(0)	1910	433	29	70
001-20-1(0)	1993	391	-	-
001-20-1(TR)	4646	576	-	-
001-20-1(RR)	11832	1038	-	-
002-20-1(0)	2373	402	44	59
003-NA-1(RR)	34397	1446	-	-

Note: O - original asphalt
TR - thin film oven test residue
RR - roadway residue

Table 2-16. Thin Film Oven Test results (Garrick & Wood, 1988).

Asphalt No.	Viscosity Ratio at 140'F	Viscosity Ratio at 275'F	Penetration Retained at 39.2'F	Penetration Retained at 77'F
LAC-10	1.84	1.30	72	54
MAC-10	2.35	1.39	75	52
HAC-10	4.05	1.55	82	52
LAC-20	2.17	1.30	52	60
MAC-20	2.37	1.39	82	56
HAC-20	4.32	1.59	72	51
700-10	2.32	1.25	91	66
900-20	2.76	1.45	96	67
001-20	2.33	1.47	—	—
002-20	3.06	1.70	—	80

Table 2-17. Asphalt concrete test results (Garrick & Wood, 1988).

Asphalt No.	Resilient Modulus at 50'F($x10^6$psi)	Resilient Modulus at 72'F($x10^6$psi)	Indirect Tensile Strength (psi)
LAC-10	1.49	0.41	91
HAC-10	1.24	0.34	85
LAC-20	1.92	0.63	138
HAC-20	1.23	0.39	107
700-10	0.58	0.12	66

Table 2-18. HP-GPC test results for test asphalts (Garrick & Wood, 1988).

	HP-GPC Parameters							
Asphalt No.	x1	x2	x3	x4	x5	x6	x7	x8
LAC-10(O)	2.7	9.2	20.8	14.2	14.2	22.1	11.6	5.3
MAC-10(O)	3.6	9.2	19.9	13.8	14.1	21.9	11.5	5.9
HAC-10(O)	4.4	8.2	17.6	13.1	14.0	22.7	13.0	6.9
LAC-20(O)	2.9	9.3	20.2	13.8	13.9	22.2	12.0	5.8
MAC-20(O)	4.6	9.8	19.3	13.3	13.8	22.2	12.1	4.7
HAC-20(O)	5.6	9.3	17.7	13.0	13.6	22.1	12.4	6.3
LAC-10(TR)	4.0	10.2	20.5	13.6	13.6	21.4	11.2	5.5
MAC-10(TR)	5.2	10.0	19.6	13.5	13.8	22.2	12.2	3.5
HAC-10(TR)	8.8	10.6	18.1	12.6	12.9	20.3	11.2	5.5
LAC-20(TR)	5.5	10.9	20.4	13.3	13.1	20.6	11.0	5.2
MAC-20(TR)	6.3	10.8	19.5	13.1	13.1	20.8	11.2	5.2
HAC-20(TR)	9.3	9.3	17.1	12.1	12.8	20.8	11.4	6.1
700-10(O)	8.3	13.3	23.5	14.3	12.9	16.8	7.4	3.1
900-20(O)	9.3	13.5	23.2	14.1	12.7	16.6	7.4	3.1
001-20(O)	6.2	10.4	20.0	13.3	13.2	20.5	10.7	5.7
001-20(TR)	9.5	11.5	19.6	12.8	12.7	19.3	9.7	4.8
001-20(RR)	13.3	12.9	18.8	12.1	11.7	17.4	8.9	4.8
002-20(O)	12.4	11.0	19.0	12.7	12.7	17.7	8.3	6.2
003-NA(RR)	14.4	11.4	16.0	10.4	11.4	18.8	11.1	6.4

Note: O - original asphalt
TR - thin film oven test residue
RR - roadway residue

4. Log Pen(39.2) = $-0.46 + 0.03x_2 - 0.12x_3 + 0.64x_5 - 0.21x_6 - 0.11x_7$ ($R^2 = 0.85$)

5. Log Log TS = $-4.658 + 0.009x_1 + 0.020x_2 + 0.89x_3 - 0.183x_4$ ($R^2 = 0.69$)

6. Log Log PVN = $-2.83 + 0.08x_2 - 0.11x_3 + 0.68x_5 - 0.32x_6 + 0.07x_7$ ($R^2 = 0.84$)

7. Log Log PR = $48 + 6x_1 - 6x_2 + 9x_3 - 22x_4 + 11x_6 - 7x_7 - 3x_8$ ($R^2 = 0.63$)

where: Vis(140) = Absolute viscosity @ 140°F, Poises
Vis(275) = Kinematic viscosity @ 275°F, cst
Pen(77) = Penetration @ 77°F, dmm
Pen(39.2) = Penetration @ 39.2°F, dmm
TS = Temperature susceptibility
PVN = Pen-Vis Number
PR = Penetration ratio
x_i = HP-GPC parameters (properties of area in Section i, where i = 1 to 8)

Thin Film Oven Test (TFOT) Results:

1. VR(140) = $-261.35 + 2.72x_1 + 2.92x_2 + 1.99x_3 + 4.16x_4 + 2.97x_5 + 0.76x_6 + 4.76x_7 + 2.81x_8$ ($R^2 = 0.89$)

2. VR(275) = $3.80 + 0.03x_1 - 0.05x_2 - 0.14x_3 + 0.31x_4 - 0.25x_5$ ($R^2 = 0.87$)

3. Pen Retained(77) = $583 - 13x_2 - 30x_5 + 14x_6 - 20x_7 - 7x_8$ ($R^2 = 0.89$)

where: VR(140), VR(275) = Viscosity ratio @ 140°F and 275°F
Pen Retained(77) = Penetration retained @ 77°F

Sand Mix Properties:

1. MR(50) = $18564 - 321x_1 + 445x_3 - 1800x_4$ ($R^2 = 0.99$)

2. MR(72) = $5260 - 179x_1 + 209x_2 - 439x_4$ ($R^2 = 0.97$)

3. MRR = $5.23 - 0.39x_2 + 1.09x_4 - 0.93x_6 + 1.27x_8$ ($R^2 = 0.94$)

4. ITS = $-453 + 33x_2 + 49x_3 - 190x_4 + 53x_5 + 81x_6 - 55x_7$ ($R^2 = 0.97$)

where: MR = Resilient modulus @ 50°F and 72°F, psi
MRR = Resilient modulus ratio
ITS = Indirect tensile strength, psi

The above results suggest that compositional data for HP-GPC analysis may be used to predict asphalt and mix properties.

3.0 OTHER HP-GPC STUDIES

In this chapter, six HP-GPC studies which are considered significant in terms of asphalt characterization (using HP-GPC) and the relationship between these characteristics and the performance of the asphalts have been reviewed. All six studies, in one way or another, were part of a larger research effort. Therefore, only those portions where HP-GPC analysis was used to characterize the asphalts, to predict the rheology of the asphalts, or to predict the actual field performance (if any) of the asphalts have been summarized. These summaries are presented in chronological order and supplement the reviews in Chapter 2.0. Information not related to HP-GPC in these studies have been omitted, e.g., Brûlé et al. (1986) used differential scanning calorimetry (DSC) in addition to HP-GPC to determine the composition of the asphalts; however, this information is not included in this review. Information such as the type of apparatus, detector and solvent used in the HP-GPC analysis have been documented.

3.1 BYNUM AND TRAXLER (1970)

Gel Permeation Chromatography (GPC) techniques were applied by Bynum & Traxler (1970) during a cooperative research study conducted by the Texas Transportation Institute and the Texas Highway Department. The pavements, laid at 13 sites (only nine were studied in this report) in 1963, were hot-mix surfaces at least 1.5 inches thick. The asphalts were of 85-100 penetration grade, obtained from nine sources. Nine asphalts (virgin and those recovered after four and 24 months of service) were used to determine the feasibility of the GPC method for determining differences in the molecular weight distribution for each original asphalt and changes in molecular composition caused by environmental factors encountered during service. Table 3-1 shows the properties of asphalts that were subjected to GPC analyses. The following GPC set-up was used:

Apparatus:	Waters Model 200 GPC
No. and Size of Columns:	4 styragel columns designated 50, 500, 1000, and 10,000 Å
Type of Detector:	Refractive Index
Solvent Type:	Tetrahydrofuran

Extracted and recovered asphalts were tested for viscosity in the same way as the original material to establish the extent of hardening developed in each asphalt during the preparation and construction of the hot bituminous pavement and at intervals of service in the pavement. Each source (no information is available on asphalt sources) of supply for the original asphalts yielded

Table 3-1. Properties of asphalt subjected to GPC analyses (Bynum & Traxler, 1970).

Asphalt No.	8-3	3-1	3-9	6-14	11-4	11-10	6-11	7-8	7-6
Pavement Location in Texas	North Panhandle	Central	North East	Central	East Central	East Central	South Central	South Panhandle	Central Panhandle
Temperature of Plant Mix °F	300	320	325	325	270	270	265	325	250
Pavement Condition after 2 years service	Excellent	Good	Very Good	Excellent	Fair	Fair	Inadequate	Inadequate	Inadequate
Penetration, 77°F/100grms/5sec.	77	84	81.5	99.5	85	88.5	99.5	80	79
(a) Viscosity of original asphalt									
Megapoises at 77°F (1)	0.98	1.15	1.18	0.58	1.17	1.12	0.56	0.86	1.00
Stokes at 140°F (2)	2650	1830	1870	1280	1620	1660	1110	1160	1150
(b) Viscosity, megapoises at 77°F (1) after 4 months service	5.9	10.3	8.7	2.9	11.3	9.3	8.5	12.3	21.5
Relative Hardening b/a	6.0	8.95	7.4	5.0	9.7	8.3	15.2	14.3	21.5
(c) Viscosity, megapoises at 77°F (1) after 24 months service	7.30	10.6	13.3	7.4	15.0	23.0	16.1	28.4	40.0
Relative Hardening c/a	7.45	9.25	11.3	12.7	12.8	20.5	27.0	33.0	40.0
Vanadium ppm (3)	18.5	24.2	23.3	25.2	11.3	10.4	60.5	106	107
Oxygen % (4)	0.50	0.30	0.30	0.60	1.05	1.05	0.55	0.75	0.80

(1) Measured in thin film, sliding plate viscometer. Viscosity calculated at 5×10^{-2} seconds^{-1} rate of shear.
(2) Determined in Cannon vacuum capillary tube viscometer.
(3) Determined by thermal neutron activation analysis.
(4) Determined by fast neutron activation analysis.

different GPC distribution curves. The pavements which showed good resistance to hardening showed very little (but discernible) change in their molecular weight distributions. On the other hand, pavements showing poor resistance to hardening by environmental factors had pronounced differences in their molecular weight distributions over time.

Figures 3-1 through 3-9 show the molecular weight distribution curves for the original asphalt and after four and 24 months of service in the pavement. Figures 3-1 through 3-3 show the molecular size distribution (MSD) curves for the original asphalt and after four and 24 months in service in the pavement for asphalts 6-11, 7-6 and 7-8. These three asphalts showed rapid aging (in terms of hardening) in the field resulting in "inadequate" performance. Figures 3-4 through 3-7 show similar the MSD curves for asphalts 3-1, 3-9, 6-14 and 8-3, which performed in the "very good" to "excellent" range with respect to aging (in terms of hardening). Figures 3-8 and 3-9 show the profiles for asphalts 11-4 and 11-10, which performed in the "fair" range. The last six asphalts showing acceptable performance in pavements appear to have a greater amount of molecules in the 10^4 (equivalent molecular weight) range as compared to (the MSD curves of) those asphalts performing inadequately. Note also that asphalts 8-3 and 6-11 show little difference between the recovered samples after four and 24 months of service. Asphalts 3-1, 7-8, 11-4 and 11-10 show the greatest change in MSD after 24 months of service. Unexpectedly, asphalts 3-9, 7-6 and 6-14 show a greater difference in MSD after four months than after 24 months. No satisfactory explanation for the above results was provided, although it was noted that the asphalt was extracted from the 1.5 inch sample as a whole, with no efforts made to differentiate between the asphalts in the top half-inch versus the bottom half-inch.

Bynum & Traxler (1970) concluded that GPC is a useful method for determining differences in molecular size distribution (MSD) of various road building asphalts. GPC curves for asphalts prepared from different crude oils and by various methods of processing have different shapes, indicating differences in molecular size distribution. Asphalt cements which contain considerable amounts of high molecular size compounds appear to have a greater resistance to hardening in the surface course of a pavement.

3.2 HATTINGH (1984)

This study was done in South Africa where problems were encountered in that asphalts have failed to set or cure, and Hattingh (1984) speculated that this failure could possibly be attributed to the low asphaltene content of the asphalts in question. In addition, Jennings et al. (1980) had also determined that the size and amount of the LMS material present in the asphaltenes was also an influencing factor in the performance of a binder.

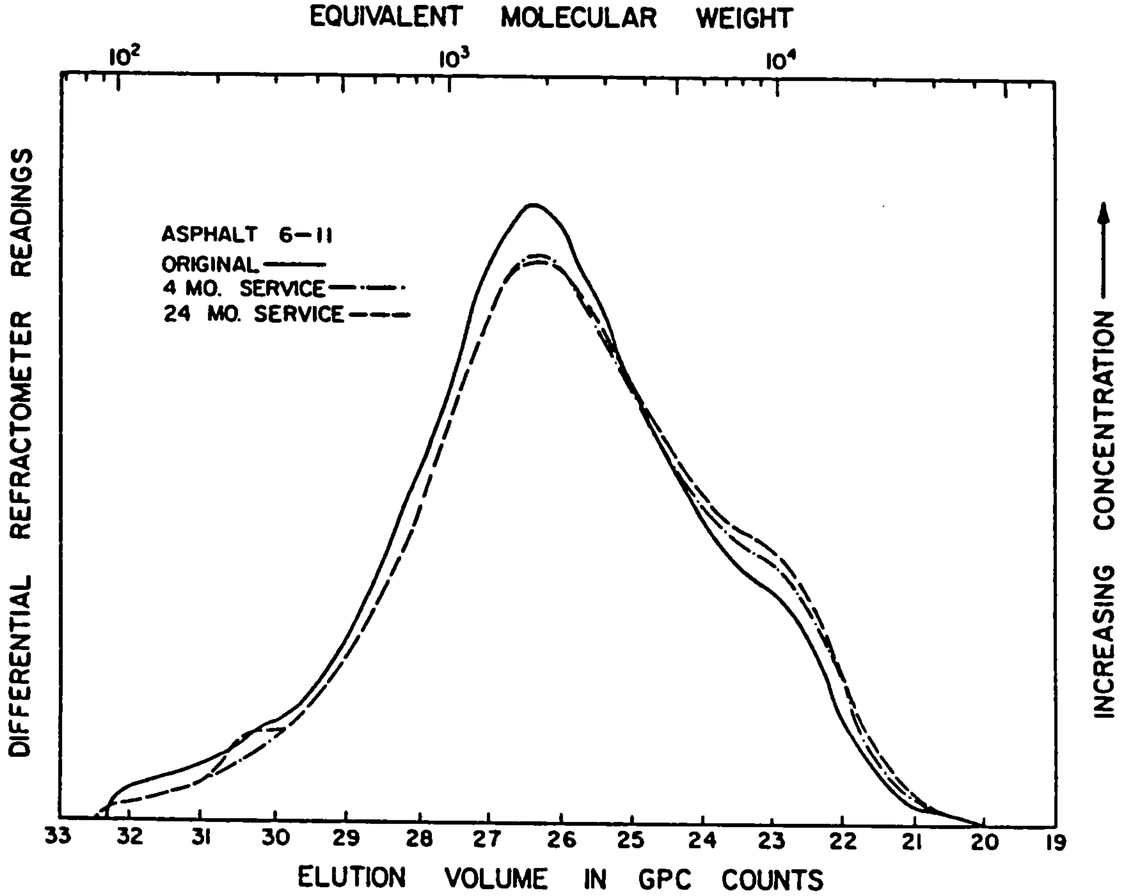


Figure 3-1. Molecular weight distribution curves for original asphalt 6-11 and after 4 and 24 months in service (Bynum & Traxler, 1970).

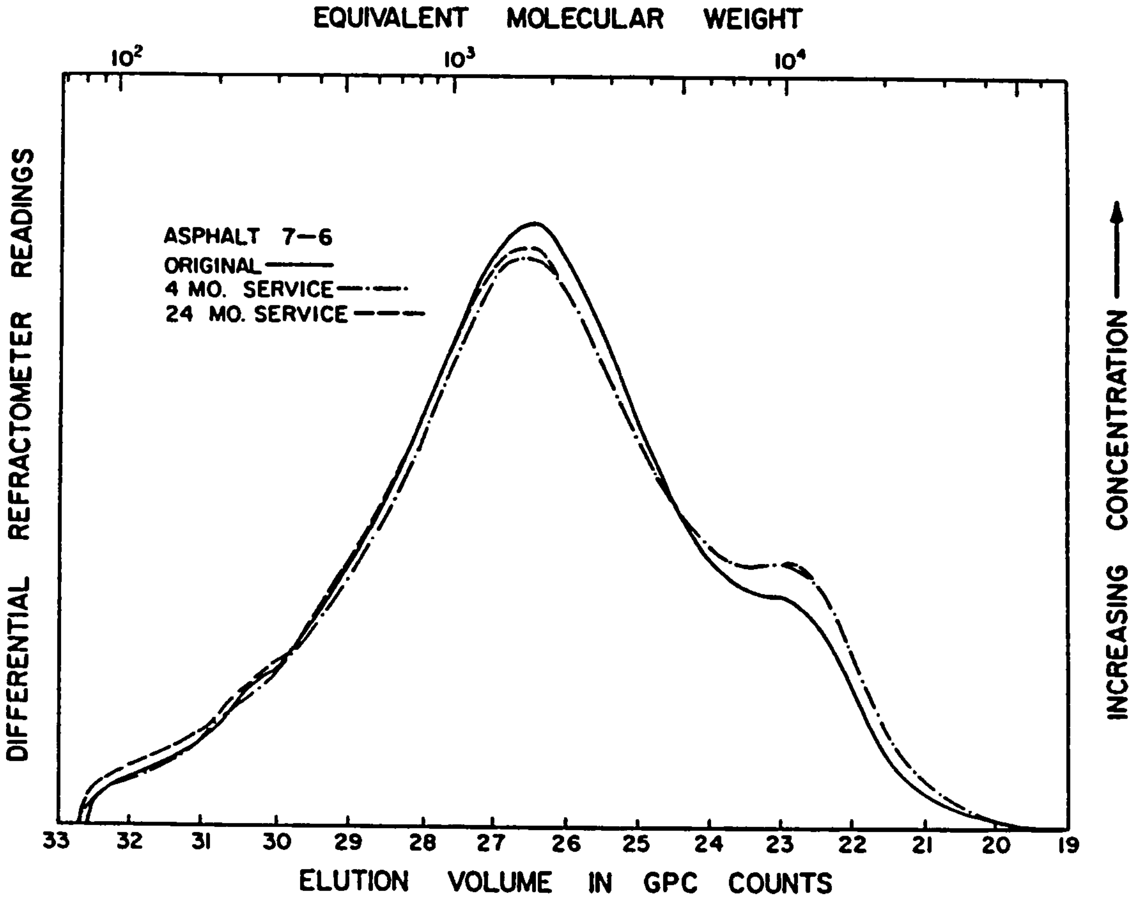


Figure 3-2. Molecular weight distribution curves for original asphalt 7-6 and after 4 and 24 months in service (Bynum & Traxler, 1970).

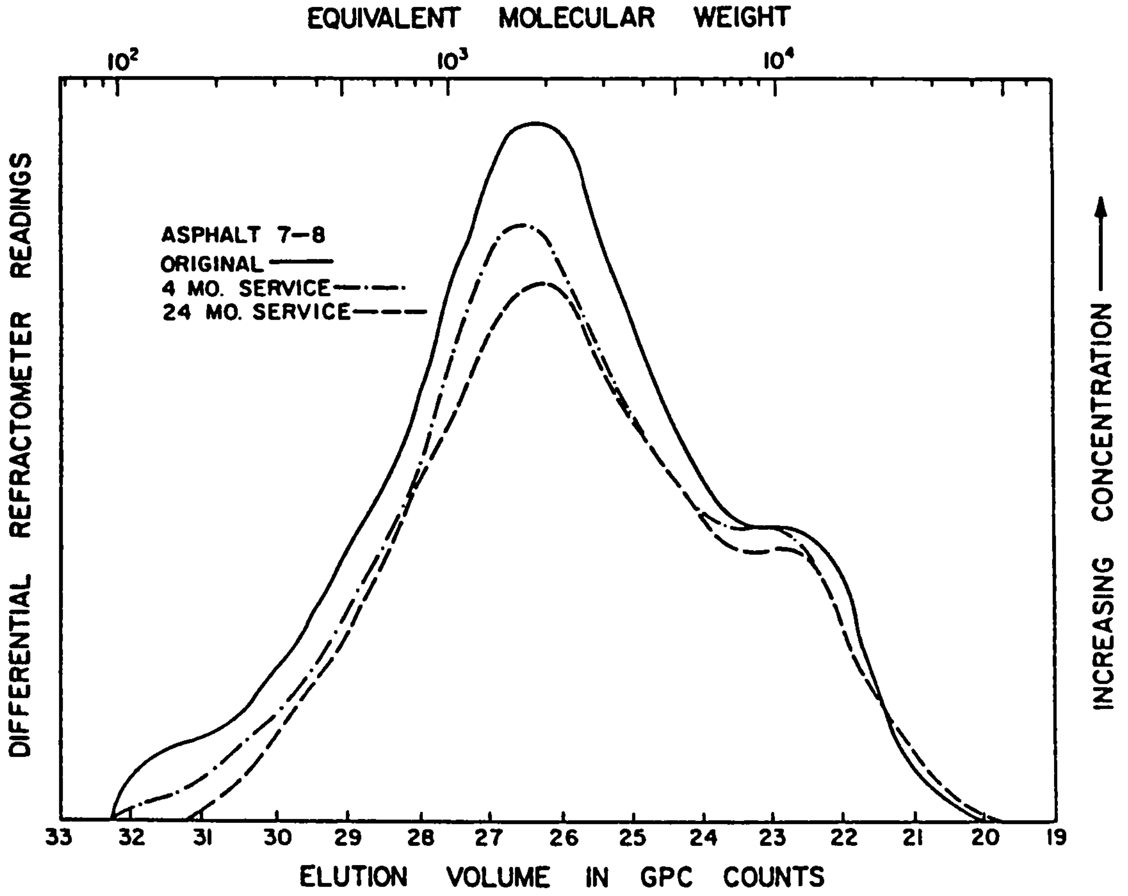


Figure 3-3. Molecular weight distribution curves for original asphalt 7-8 and after 4 and 24 months in service (Bynum & Traxler, 1970).

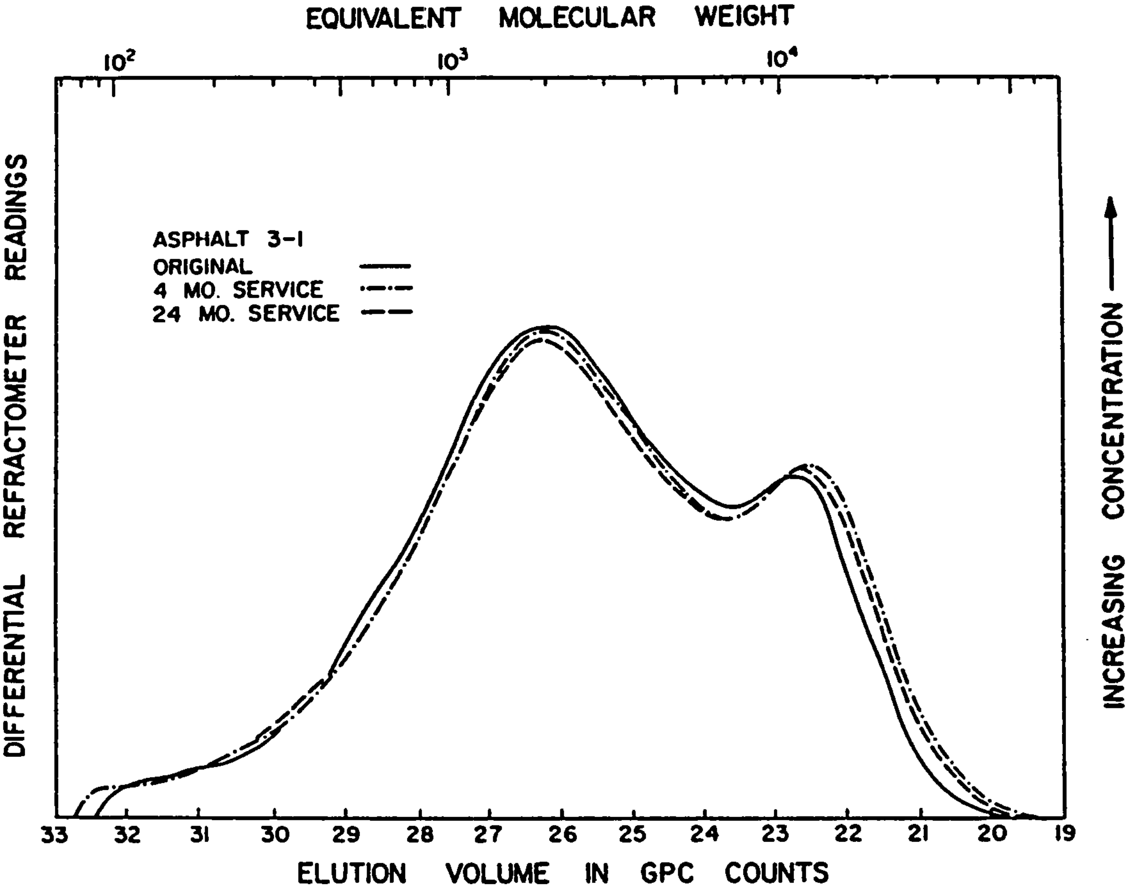


Figure 3-4. Molecular weight distribution curves for original asphalt 3-1 and after 4 and 24 months in service (Bynum & Traxler, 1970).

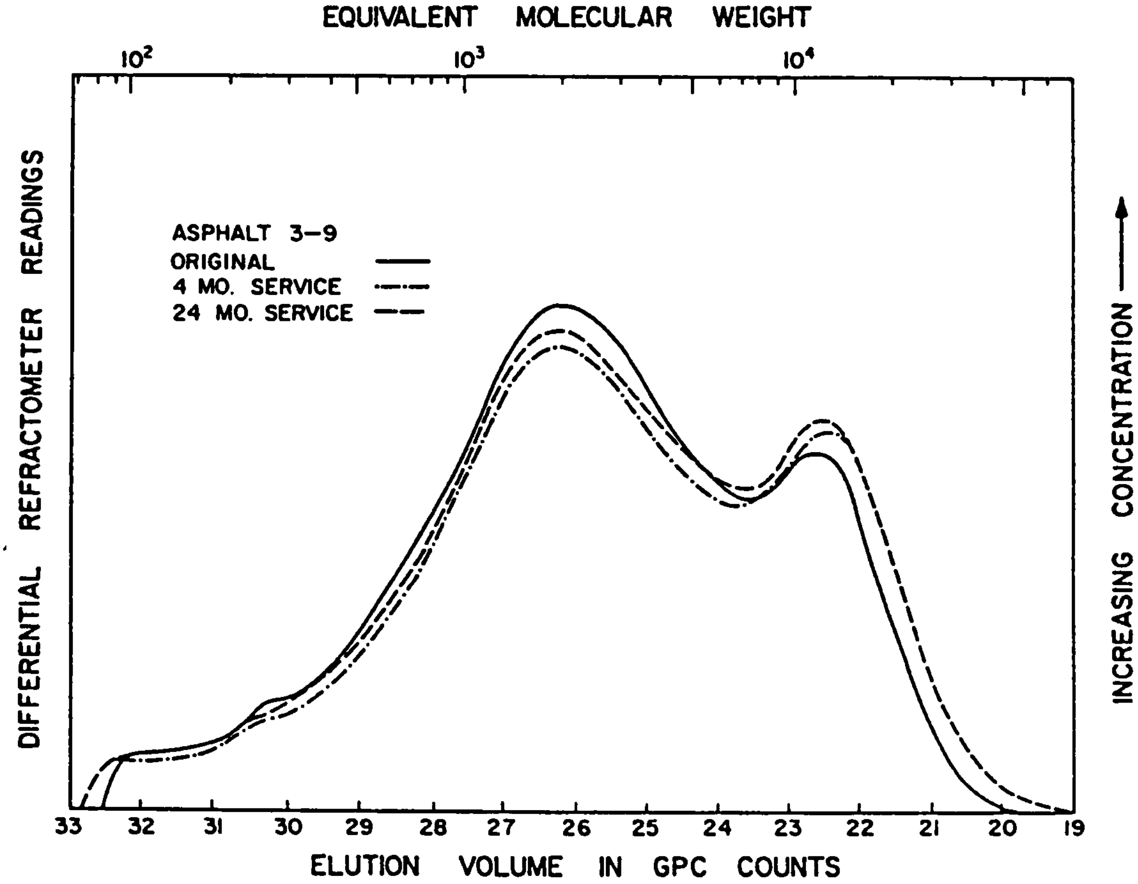


Figure 3-5. Molecular weight distribution curves for original asphalt 3-9 and after 4 and 24 months in service (Bynum & Traxler, 1970).

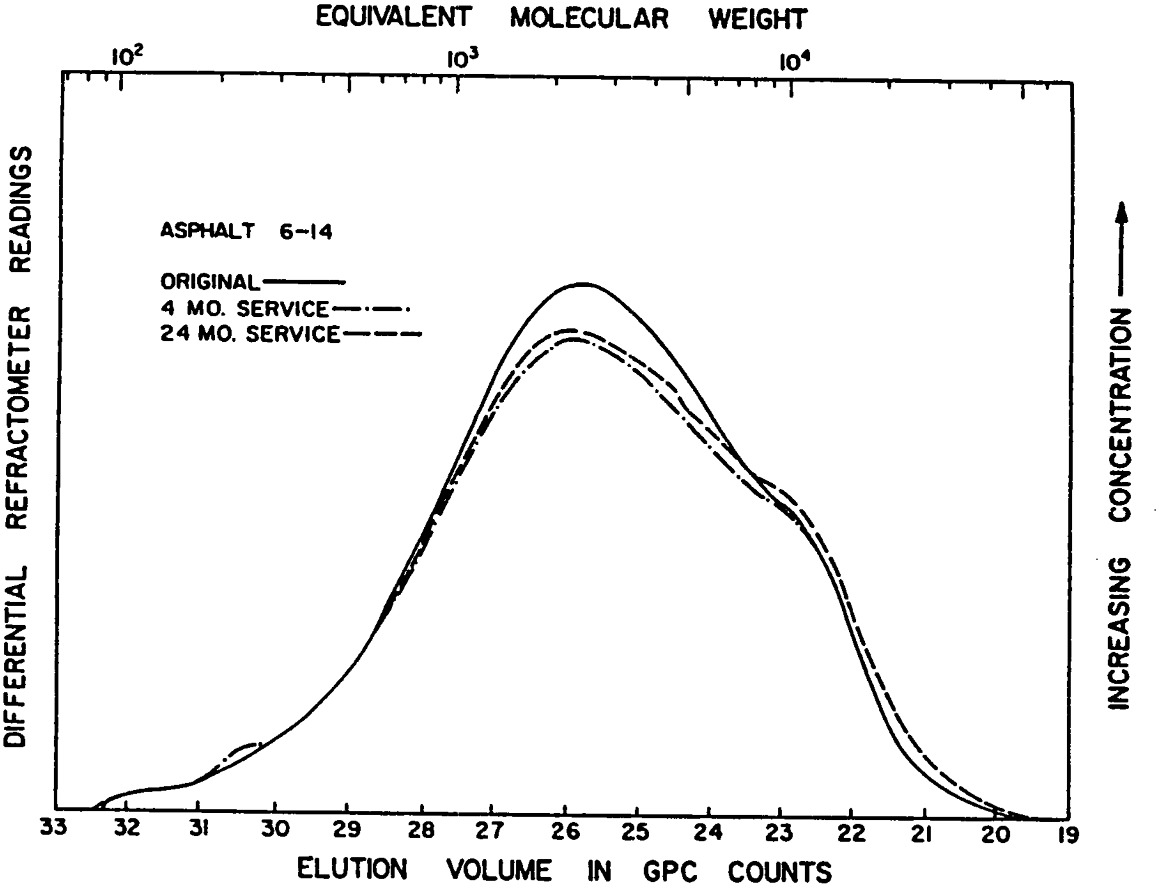


Figure 3-6. Molecular weight distribution curves for original asphalt 6-14 and after 4 and 24 months in service (Bynum & Traxler, 1970).

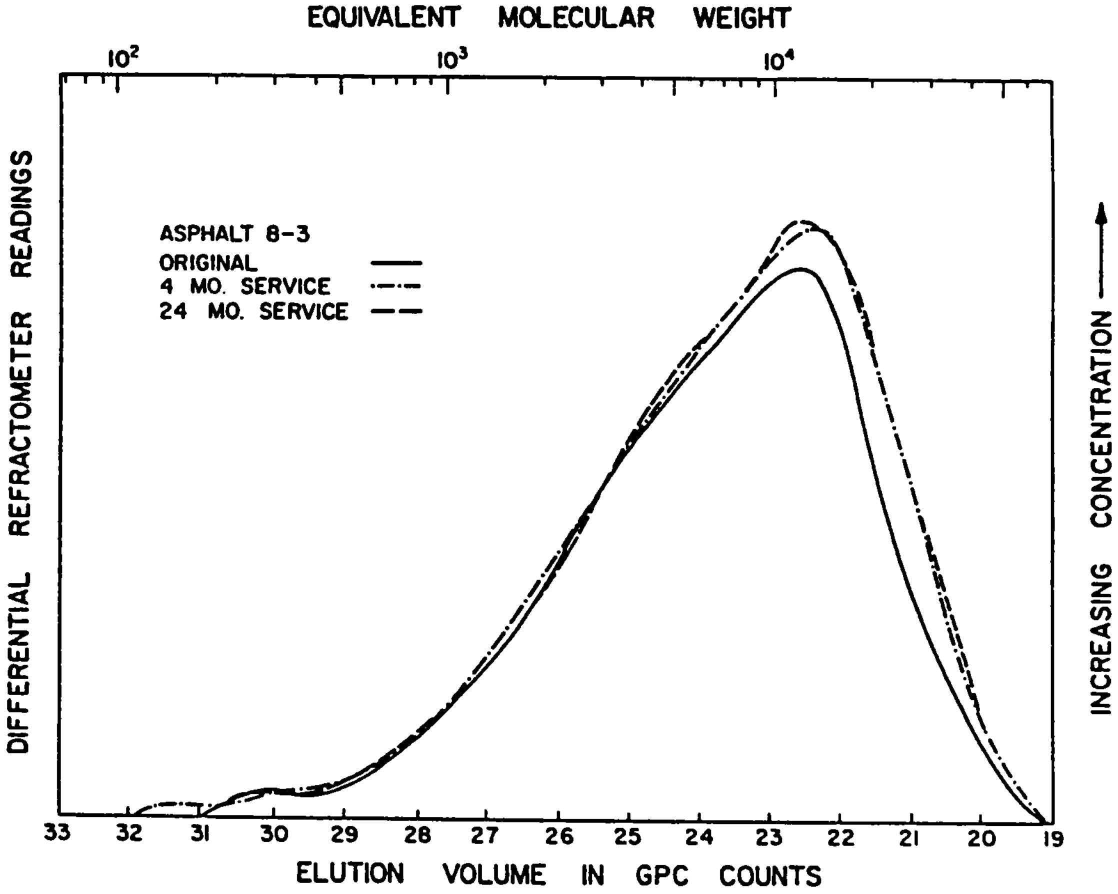


Figure 3-7. Molecular weight distribution curves for original asphalt 8-3 and after 4 and 24 months in service (Bynum & Traxler, 1970).

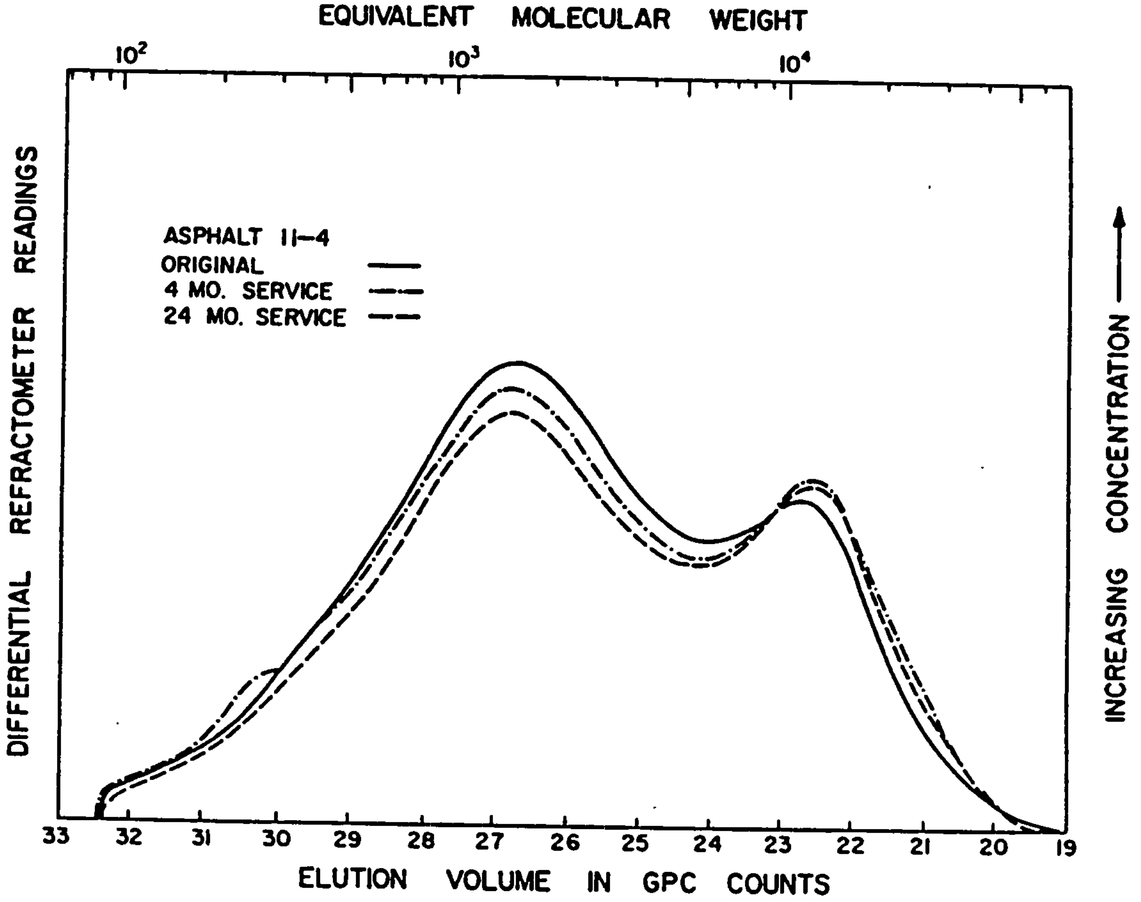


Figure 3-8. Molecular weight distribution curves for original asphalt 11-4 and after 4 and 24 months in service (Bynum & Traxler, 1970).

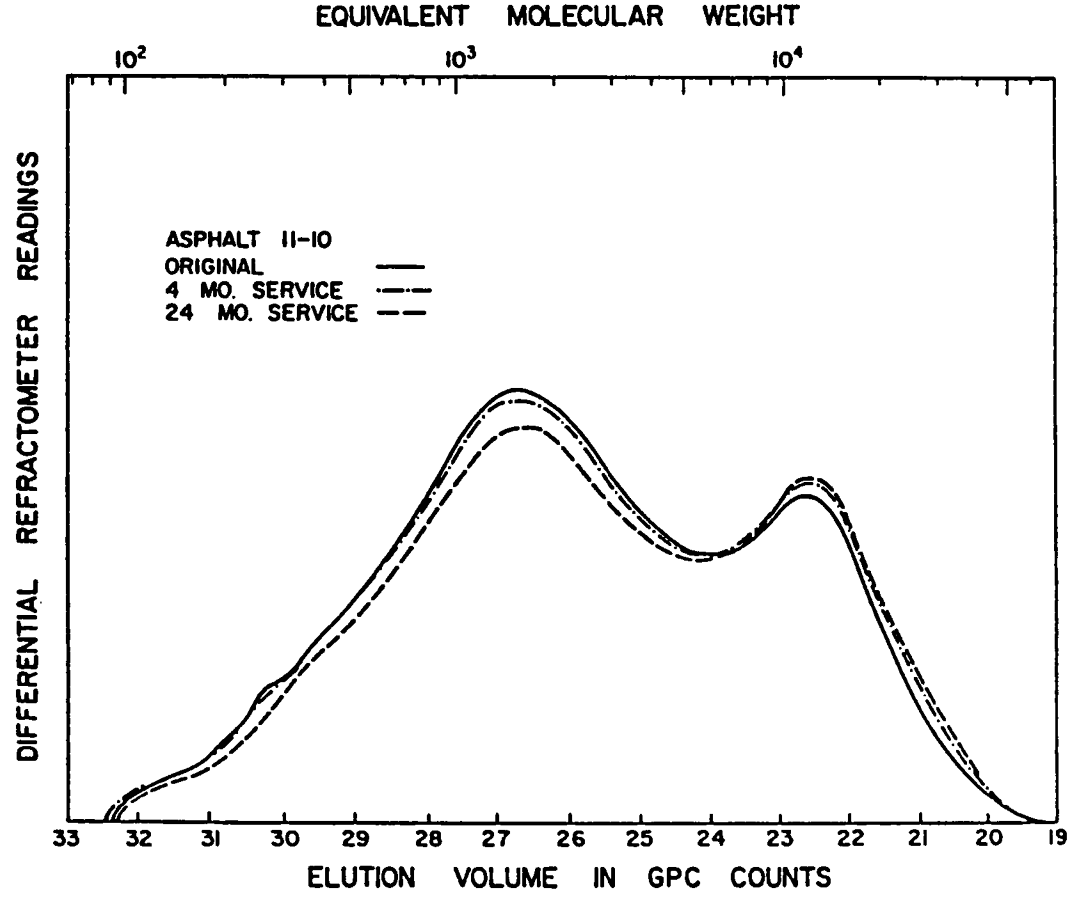


Figure 3-9. Molecular weight distribution curves for original asphalt 11-10 and after 4 and 24 months in service (Bynum & Traxler, 1970).

Hattingh's (1984) main objectives in this study were:

1. To characterize asphalts in terms of their chemical composition after separating them into a number of fractions of similar, or closely-related, molecular structures.
2. To determine any changes taking place in chemical composition and asphaltene content during weathering.
3. To endeavor to relate the chemical composition and/or the asphaltene content of asphalts to road performance.

GPC determinations were carried out as part of the investigation. An analytical scale high performance liquid chromatography (HPLC) with styragel columns and tetrahydrofuran as the solvent was used to determine the molecular masses of the fractions relative to each other. Four 150/200 pen asphalts with different road performance records were analyzed. Road performance was measured in terms of setting (curing) of asphalt and bleeding. All four asphalts were 150/200 pen asphalts and the mixes complied with the South African Bureau of Standards (SABS) specification; yet, two asphalts bled profusely. Tables 3-2 and 3-3 summarize the properties and retention times of the asphaltene fractions and corresponding whole asphalts. Figure 3-10 shows the chromatograms for these asphalts. Asphalts A and B, labelled as "bad", bled profusely immediately after construction, while Asphalts C and D were still in "good" condition after 9 and 3 years performance, respectively.

The two asphalts giving satisfactory performances have a pronounced peak (Asphalt C) or a shoulder (Asphalt D) at a retention time of approximately 18 minutes, whereas the unsatisfactory asphalts show either a complete lack of the presence of high molecular mass constituents (Asphalt A) or only a slight shoulder (Asphalt B). Shown in Figure 3-11 are the chromatograms for the asphaltene fractions of three of these 150/200 pen asphalts (Asphalt B was not included in this comparison as it was tested at a later stage[1]). Hattingh concluded that the poor performance exhibited by Asphalts A and B were partly due to (a) their low asphaltene contents, and (b) insufficient high molecular mass components in the asphaltenes.

Finally, Hattingh concluded that more data was required before any relationship between in-service performance and chemical fractionation could be established. However, a certain percentage of asphaltenes appears necessary to ensure that an asphalt performs well. Too high a percentage of asphaltene leads to cracking and too low a percentage causes setting problems.

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[1] The result was not included in this paper.

Table 3-2. Asphalt contents and ductility measurements of four 150/200 pen original asphalts and their extended TFOT residues and performance assessments in S. Africa (Hattingh, 1984).

	Asphalt A		Asphalt B		Asphalt C		Asphalt D	
	Orig.	ETFOT 32½ h	Orig.	ETFOT 32½ h	Orig.	ETFOT 32½ h	Orig.	ETFOT 32½ h
Ductility (mm)	+1400	+1400	+1400	+1400	+1400	65	+1400	870
Performance	Bad	-	Bad		Good	-	Good	-
Asphaltenes (%)	13.7	24.0	15.3	26.3	20.7	32.0	17.9	26.9
Increase in Asphaltenes after ETFOT	-	10.3	-	11.0	-	11.3	-	9.0

Table 3-3. GPC retention times of four 150/200 pen whole asphalts and the asphalt fractions, whole asphaltene fractions and maltene sub-fractions in S. Africa (Hattingh, 1984).

Samples Tested	Retention Time (mins)							
	150/200 Pen Asphalts							
	Asphalt A		Asphalt B		Asphalt C		Asphalt D	
	Whole Asphalt	Maltene Sub-fraction	Whole Asphalt	Maltene Sub-fraction	Whole Asphalt	Maltene Sub-fraction	Whole Asphalt	Maltene Sub-fraction
Whole Asphalt Fractions/ Maltene Sub-fractions								
1	21.9	21.8	Not tested	Not tested	21.8	21.8	22.0	21.9
2	22.2	22.2			21.4	22.0	22.4	22.8
3	19.4	21.0			18.8	19.0	19.6	21.2
4	19.2	21.2			18.2	22.2	18.2	21.4
5	19.0	23.6			18.8	23.6	18.2	24.0
6	no trace available	24.4			18.4	23.8	18.2	25.2
7	18.8	19.4			16.6	23.6	17.4	19.2
8	18.4	25.4			16.8	25.6	17.2	25.8
9	19.0	23.4			17.2	22.8	17.0	23.4
Whole Asphalts	21.4	-	21.7	-	21.6	-	21.4	-
Asphaltenes	-	19.0	-	17.7	-	17.6	-	18.3

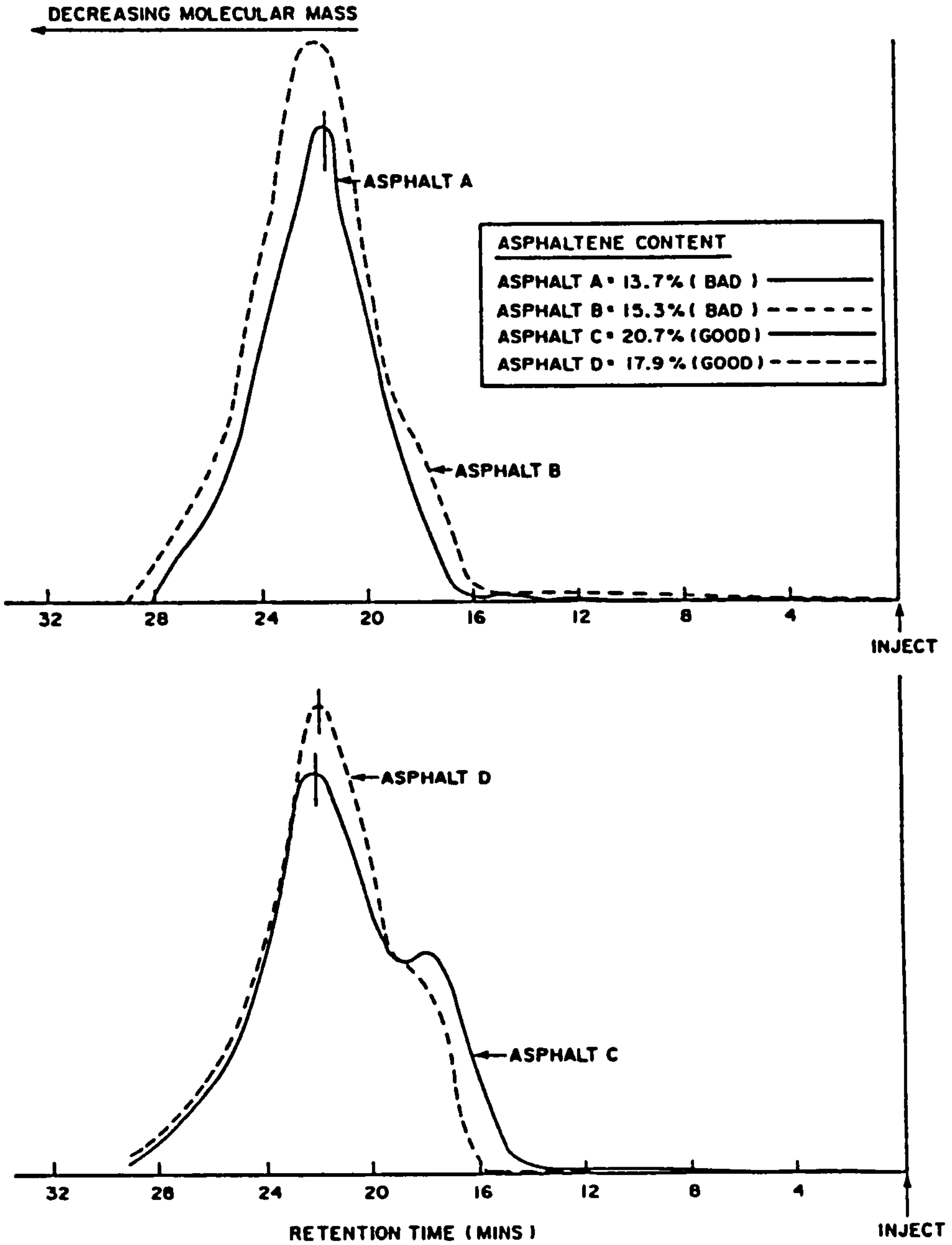


Figure 3-10. Molecular mass profiles of four 150/200 pen whole asphalts (Hattingh, 1984).

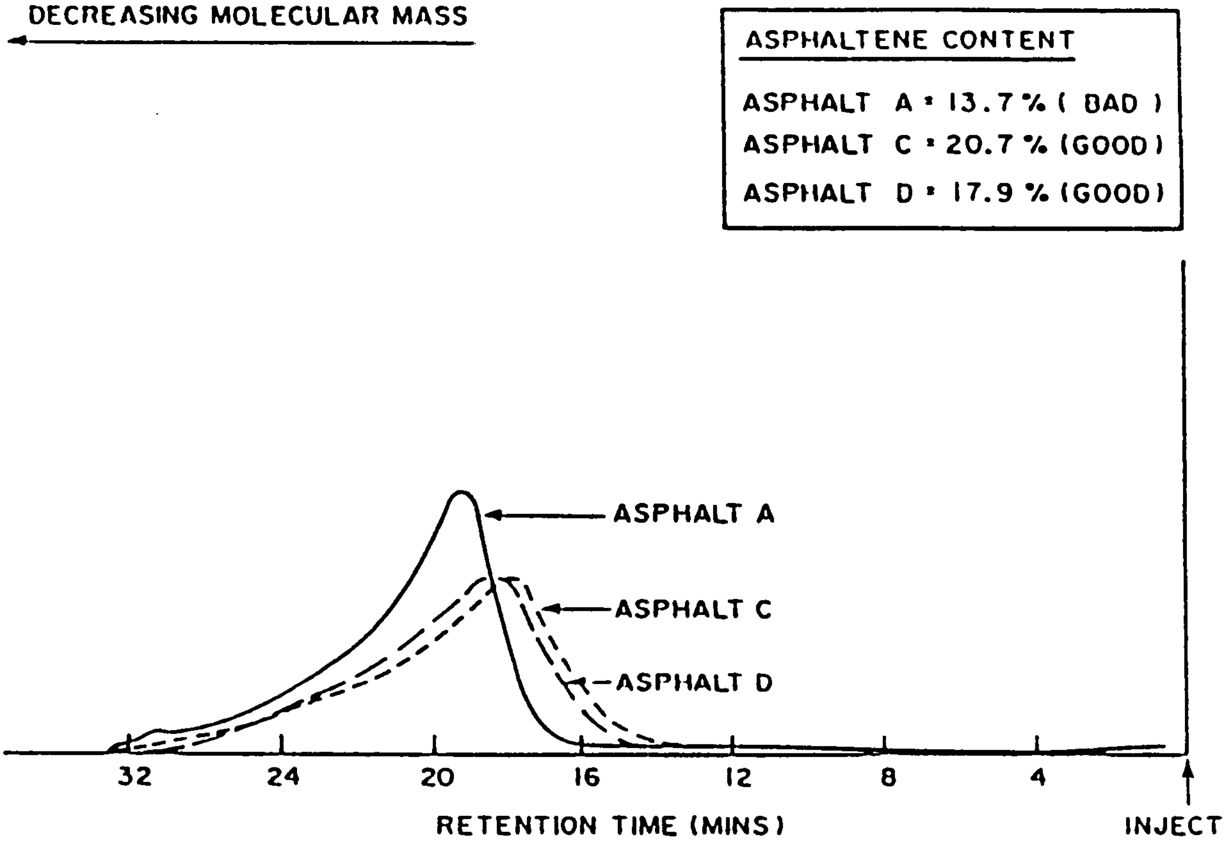


Figure 3-11. Molecular mass profiles of the asphaltene fractions of three 150/200 pen asphalts (Hattingh, 1984).

In addition, asphaltene content alone does not provide sufficient data; the molecular size distribution is also needed to give an indication of the performance of a particular asphalt.

3.3 BRÛLÉ ET AL. (1986)

This paper (Brûlé et al., 1986) describes the ongoing research at France's Laboratoire Central des Ponts et Chaussés (LCPC) in developing methods for characterizing the physicochemical and rheological properties of asphalt cements and the establishment of relationships between these properties and their composition and colloidal structure. For physicochemical characterization, techniques such as high pressure liquid chromatography (HPLC), gel permeation chromatography (GPC), and differential scanning calorimetry (DSC) were used. The rheological behavior of asphalt was studied by the peeling technique, viscoelasticimetry, and viscosimetry on thin films. In addition, conventional asphalt characteristics such as penetration were also measured.

To understand the relationship between the (chemical) composition and its rheological properties, a description of the colloidal structure of asphalt is necessary. Conventionally, it is assumed that asphalt cements are colloidal systems consisting of a suspension of asphaltene micelles peptized by resins in an oily medium. Research by Yen (1981) has led to a proposed model for the macrostructure of asphaltene micelles as shown in Figure 3-12 (note that molecular micelles and aggregates are groups that are defined by their molecular weight). In this model, the overall cohesion of the micelle is provided by interactions between the π electrons of the polynuclear aromatic sheets. According to Brûlé et al., the Yen model is not limited to the formation of micelles. It also offers the possibility of creating complex edifices formed by the association of several micelles into real aggregates, as shown in Figure 3-13. The formation of these aggregates is thought to be related to intermolecular interactions, the nature of which is not indicated. One key parameter governing the equilibrium of such a colloidal structure is the chemical composition of its constituents. And any modification in this equilibrium (e.g., under the action of a temperature variation) leads to a modification in the rheological behavior.

From Brûlé et al.s' work on HPLC, it was possible to characterize asphalt cements and their fractions through the use of a chloroform-methanol-water solution. The maltenes and asphaltenes are clearly differentiated, as shown in Figure 3-14. However, these results are only for specific test conditions. The researchers noted that it was difficult to control the reproducibility over a long time period.

The research activity at LCPC was much more extensive in the GPC area. According to Brûlé et al., GPC was particularly important when comparing the colloidal structure of the binder

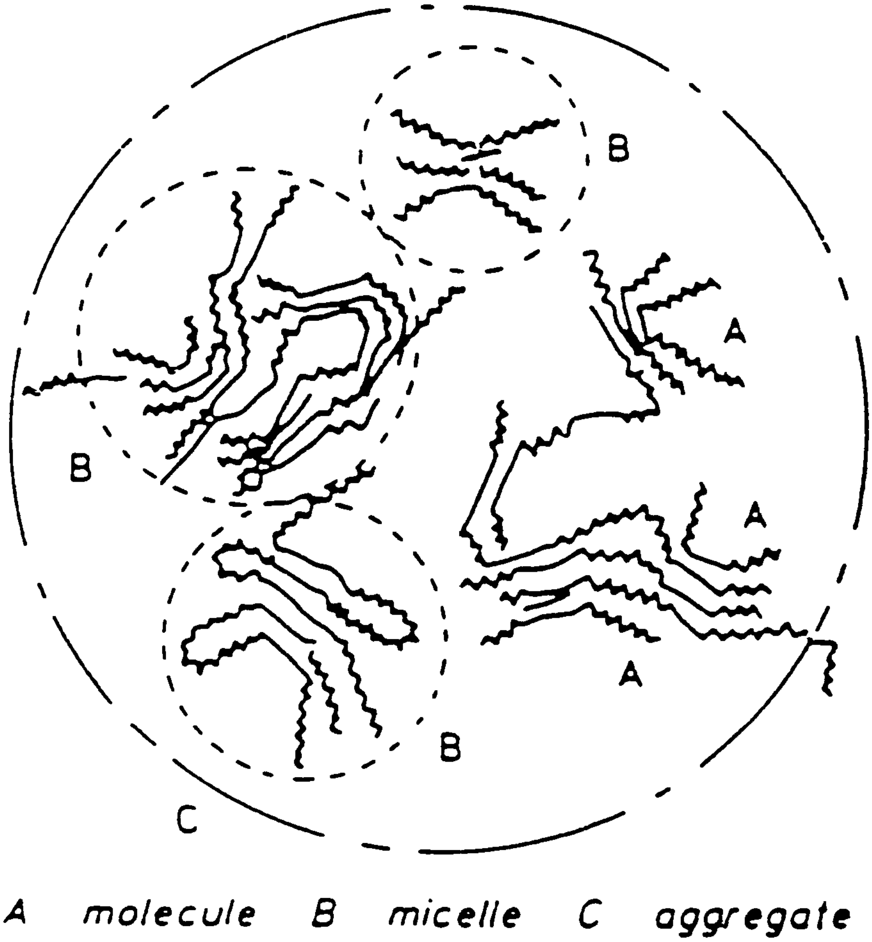


Figure 3-12. Macrostructure of asphaltenes according to Yen (1981) (Brûlé et al., 1986)

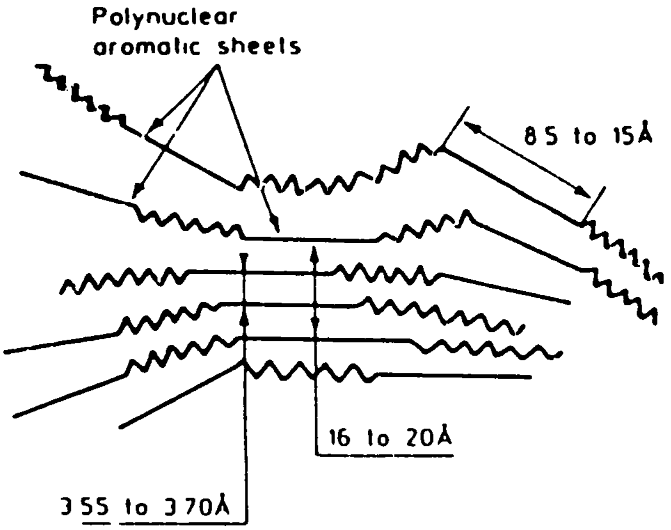


Figure 3-13. Section of an asphaltene micelle model according to Yen (1981) (Brûlé et al., 1986)

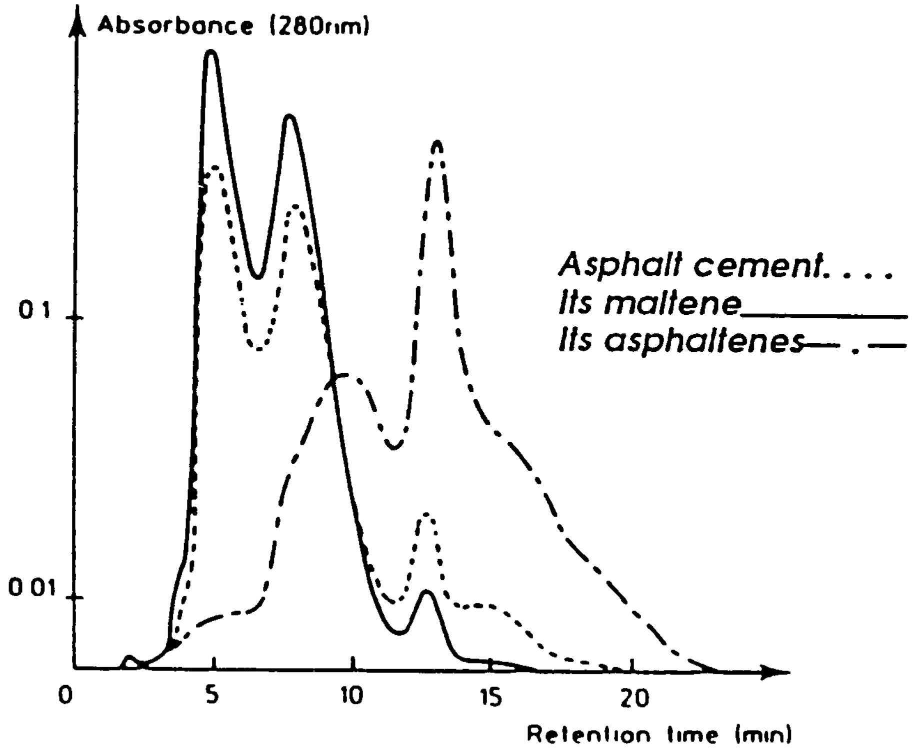


Figure 3-14. HPLC chromatograms of air-blown and acidified Safaniya crude residue (Brûlé et al., 1986).

versus the colloidal behavior of the solution. It was also possible to obtain an image of the composition of the medium, in the colloidal sense of the term (intermicellar phase and dispersed phase distribution), and to assess the interaction properties of micelles within the colloidal system. However, conventional GPC (using a set of several columns with typical particle sizes from 37 to 75 μm on very diluted solutions) do not differentiate between molecular weight distribution greatly. In other words, it was difficult to distinguish between chromatograms of the original asphalt and of the same asphalt after aging (natural or artificial). This is because such a GPC operates slowly enough so that dissociations have time to develop, i.e., the aggregations developed during the aging process dissociate. Therefore, a "fast" method designed to prevent this dissociation was proposed as follows:

Columns:	Dual columns of μ-Styragel of 10^3 and 10^4 Å, 30 cm long;
Solvent:	Freshly distilled tetrahydrofuran;
Injected Quantity:	1 mg (10 μL of 10 percent solution);
Flow Rate:	3.5 mL/min; and
Detection:	Ultraviolet at 350 nm.

Using this "fast" GPC method, Brûlé et al. were able to show that there was a bimodal distribution in the chromatogram for both the asphalt cements as well as the asphaltenes, for both the straight-run and blown asphalt cements (Figure 3-15). In addition, blowing tended to result in a third population located towards the large molecular sizes (1000 Å in Figure 3-15).

By observing the chromatograms (Figure 3-16) of five 40-50 asphalt cements (A through E) before and after the Rolling Thin Film Oven Test (RTFOT), it was concluded that the entities eluted at the level of a molecular weight of about 10^5, which corresponds to aggregates in the process of dissociation. To further highlight intermicellar interaction property, Brûlé et al. eliminated one of the GPC columns (10^4 Å porosity) to reduce the elution time by half to a few minutes. This thereby limited the dissociation that was occurring in aggregates with a molecular weight of 10^5. Also, by deliberately reducing the efficiency of the system in the range of large masses, these masses grouped within a narrow range of elution volumes. Figure 3-17 shows the chromatograms for the same five 40-50 asphalt cements before and after RTFOT under these "ultra-fast" GPC conditions. As can be seen, there is an obvious peak in the chromatogram at the right. The authors defined a term called the interaction index (for comparison purposes) as the height of the signal at the exclusion volume for the ultraviolet detector. In Figure 3-17, the interaction indices are indicated by the vertical bars A through E (one for each asphalt cement).

In addition, the authors were able to conclude that the molecules (first population) are representative of the intermicellar phase (Figure 3-18); the micelles (second population) with a molecular weight of about 10,000 are representative of the "sol" type dispersed phase; and the

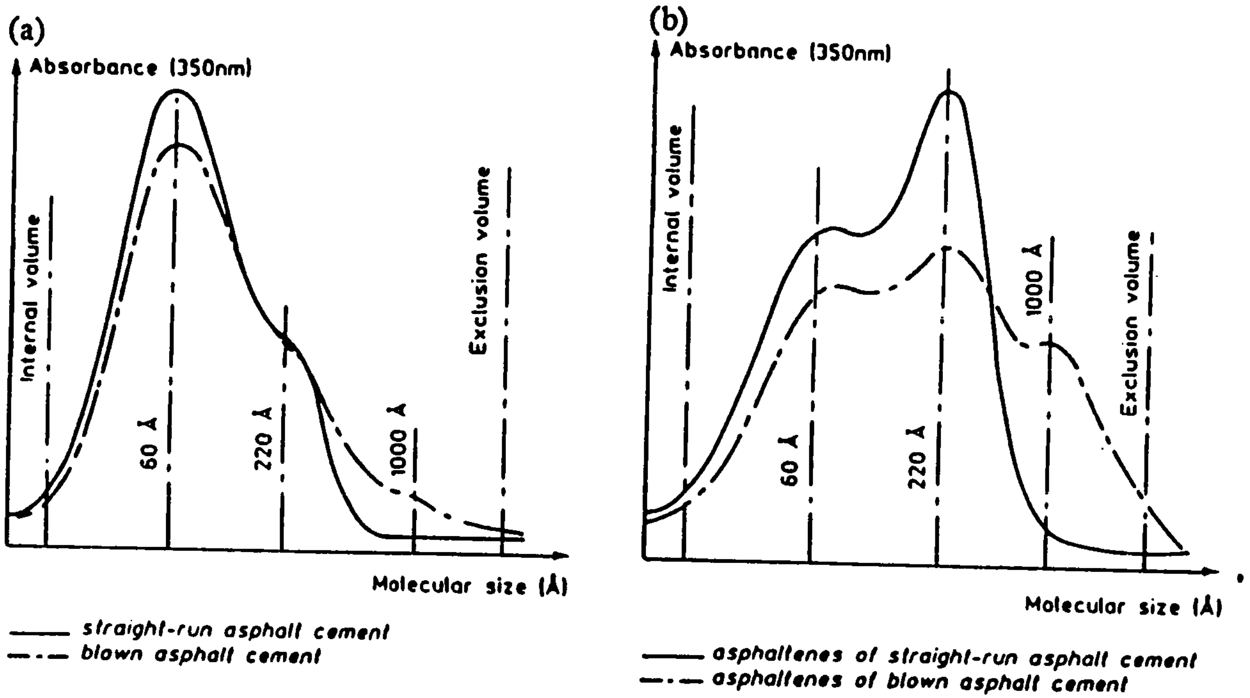


Figure 3-15. Chromatograms of asphalt cements and asphaltenes (Brûlé et al., 1986).

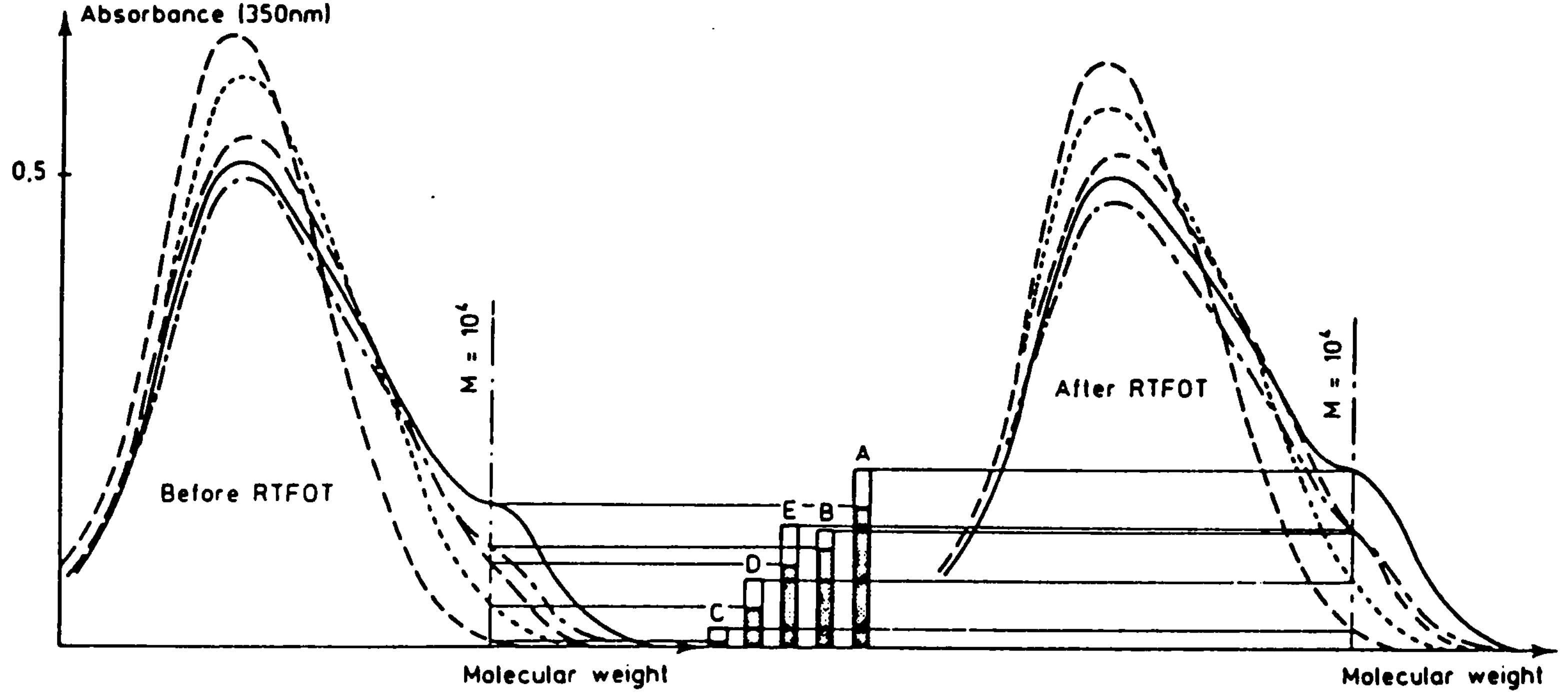


Figure 3-16. GPC Chromatograms of 40-50 asphalt cements before and after RTFOT (Brûlé et al., 1986).

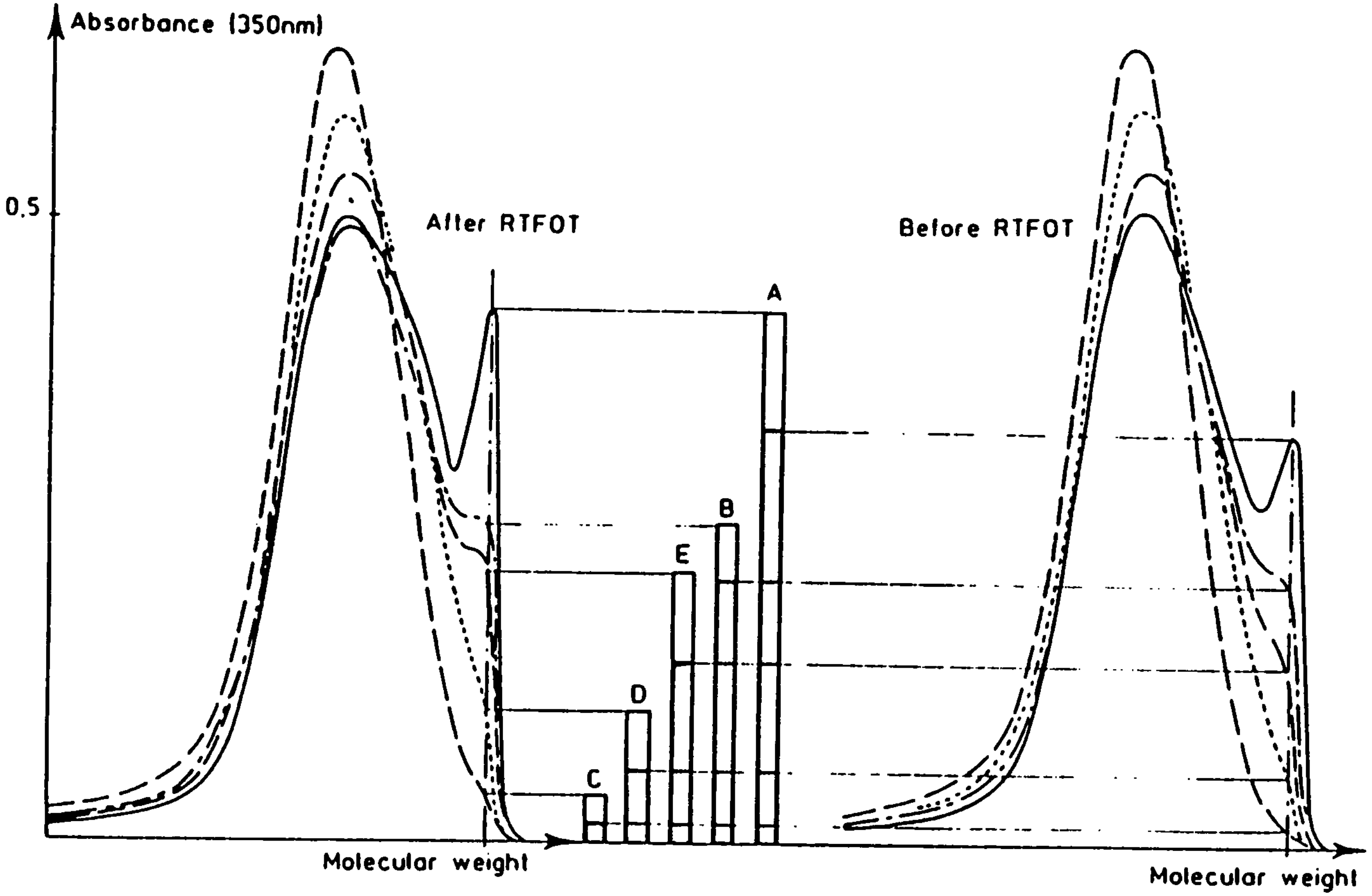


Figure 3-17. Chromatograms of 40-50 asphalt cements before and after RTFOT under 'ultra-fast' GPC conditions (Brûlé et al., 1986)

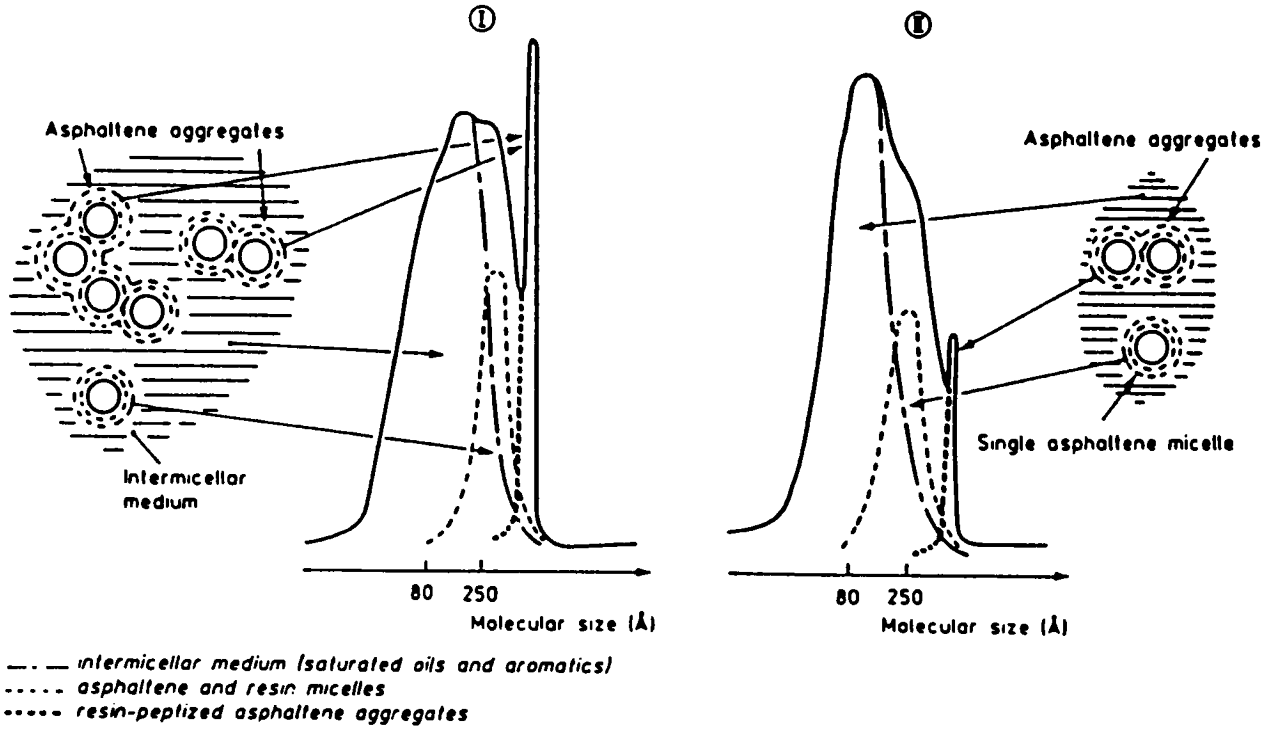


Figure 3-18. GPC chromatograms (broken down into three populations) and colloidal structure of asphalt cements (I = blown asphalt cement and II = straight-run asphalt cement) (Brûlé et al., 1986).

interaction peaks (molecular weights exceeding 100,000) is an image of the fraction of the dispersed phase giving the binder its gel-character. Hence, GPC can be used for the qualitative characterization of the complex equilibrium existing within the asphalt cement between:

$$\text{Molecules} \rightleftarrows \text{Micelles} \rightleftarrows \text{Aggregates}$$

However, Brûlé et al. (1986) also emphasized that there was no relationship between the interaction index and the consistency of the asphalt cement as evaluated by, for example, penetration. Similarly, there is no relationship between the interaction index and the asphaltene content. Figure 3-18 shows the colloidal structure of the binder and the GPC chromatogram obtained in a few minutes under the previously proposed "ultra-fast" conditions. The hypothesis set forth by Brûlé et al. to explain the formation of aggregates after blowing (on weathering) is that the latter creates a number of active centers (polar functions) that are responsible for the intermicellar interactions (hydrogen bonding). The more severe the blowing, the more numerous these interactions would be. A straight-run asphalt cement is a colloidal system made up of individual micelles (i.e., the sol type) as shown to the right of Figure 3-18 (I). During blowing, the asphaltene content increases together with an increasing amount of micelles interacting to form aggregates that give the material an intermediate sol-gel structure with viscoelastic behavior. In the extreme case, for oxidized asphalt cements, the perfect gel structure is reached (left part of Figure 3-18 (II)) in which the asphaltenes are organized in a three-dimensional network, giving the medium its elasticity.

In addition to the above experiments, the rheological properties of the asphalt cements were measured using the peeling test, as previously mentioned. Peeling is a method used to evaluate the cohesion of asphalt cements and consists of measuring the force required to cause the failure of a film of binder under given speed and temperature conditions. A series of tests was performed on 12 asphalt cements. In Table 3-4, the calculated values of the medians and average width of the loss modulus and peeling curves are summarized for six of the asphalt cements studied (F through K), along with their conventional characteristics. From these tests, Brûlé et al. were able to conclude that 1) peeling fracture energy is related to the complex modulus, and master curves were obtained; 2) a "good" correlation was found between the speed giving the maximum force applied and the Fraass brittleness temperature; and 3) a relationship was found between peeling resistance and the loss modulus.

Therefore, it was concluded that the peeling test appears to allow a good discrimination of the binders from the viewpoint of cohesion and brittleness. Since peeling force depends on the viscoelastic properties, and in particular, the complex modulus, it may directly be able to provide qualitative information on the rheological behavior of the asphalts tested. Under slightly different

Table 3-4. Physical properties, peeling and complex modulus for six asphalt cements (Brûlé et al., 1986).

	Pen_{25} (0.1 mm)	R & B (°C)	P.I (Pen.)	log f_m (Hz)	σ_f	log V_m (mm/min)	σ_v	σ_v/σ_f	λ_m (10^{-9}m)
F	88	54	1.2	≃ 7	≃ 2.5	≃ 2.6	≃ 1.3	0.52	0.01
G	88	46	– 1.1	4.1	1.6	1.3	0.9	0.56	0.26
H	82	48	0.1	5.1	2.1	1.8	1.25	0.60	0.083
I	82	44	– 1.7	3.0	1.5	0.5	0.8	0.53	0.53
J	38	60	1.1	5.5	2.5	1.3	1.3	0.52	0.01
K	54	53	– 0.3	4.0	1.9	0.65	1.2	0.63	0.7

Note:

Pen_{25} = Penetration @ 25°C
R & B = Ring and ball temperature
P.I. = Penetration Index
log f_m = median peak width of loss modulus
σ_f = average peak width of loss modulus
log V_m = median peak width for peeling
σ_v = average peak width for peeling
λ_m = average distance between two consecutive molecules

conditions, it may be possible to utilize this test in determining the overall adhesion on mineral supports with or without the presence of water.

For the thin-film viscometric experiments, the first experiments conducted were aimed at verifying and specifying the performance of the equipment. In the thin-film viscosimetric experiments, a simple shear stress was applied to two sliding parallel planes, with a thin film (approximately 10 microns) of asphalt film between the planes. This was to investigate the creeping of thin film to determine the behavior of the binder located at the interface. Brûlé et al. were able to adapt nonlinear viscoelastic behavior models to the experiment results obtained for asphalt cements. A rheological model known as the Maxwell-Norton model was adopted. In this model, a parameter, n, is a structural coefficient related to the spatial distribution of intermicellar interactions; the higher the value of n, the more gel-like the material becomes. On the other hand, as n approaches 1, the more numerous and dispersed will be the asphaltene micelles without any strong interaction between them. In short, the Maxwell-Norton model defines the degree of medium organization. Therefore, as the interaction index increases, the parameter n also increases.

Using the Maxwell-Norton model, Brûlé et al. were then able to calculate the standard deviations of the relaxation spectrum and predict these standard deviations with regression models using the GPC interaction index and asphaltene content. A systematic study of 22 road asphalt cements of different origins (different crude and production processes), including a number of naturally and artificially weathered samples, indicated that the standard deviation of the relaxation spectrum (estimated by measuring the complex modulus at variable temperatures and frequencies) depends on both the amount of asphaltenes and the intensity of their interactions. The following models were determined:

$$K\sigma = 2.08 + (0.899\ I/200) + 0.0348\ A$$

$$K\sigma = 2.305 + 0.0428\ [1 + (I/200)]\ A$$

where: K = proportionality constant,
σ = standard deviation of relaxation spectrum,
I = GPC interaction index (height in mm of interaction peak under given operating conditions), and
A = asphaltene content.

The first model has a correlation coefficient of 0.952 and a residual variance of 0.0208, and the second model has a correlation coefficient of 0.944 and a residual variance of 0.02277. Figure 3-19 allows a comparison of the values of $K\sigma$ measured and estimated on the basis of the first model.

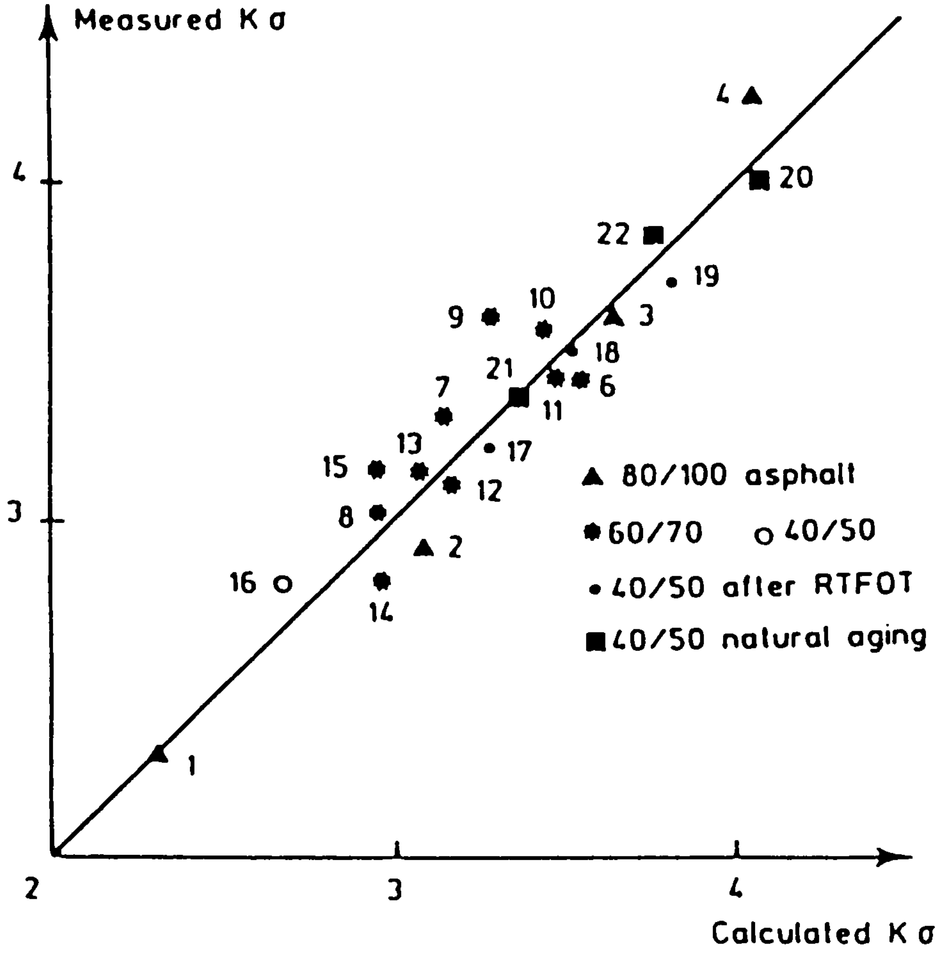


Figure 3-19. Comparison of calculated and measured standard deviations (Brûlé et al., 1986).

The results of this comparison confirm the significance of interactions between asphaltenes (aggregation) and the interaction index (using GPC). They are of significant practical value because they allow: a) an a priori classification of asphalt cements of a given category, and b) follow-up of natural or artificial weathering. In conclusion, GPC can be used to evaluate the degree of evolution of in-situ weathered asphalt cements.

In summary, the paper by Brûlé et al. discussed the results of HPLC, GPC and rheological investigations as a means of characterizing asphalt cements. Although no field performance data were available, much useful information on the asphalt model was presented. It was concluded that:

1. Asphalt cements of the same grade can have substantially different chemical compositions and rheological behavior.
2. GPC enables a characterization of the complex colloidal equilibrium of asphalt cement. Shifting the equilibrium from molecules to micelles to aggregates (as a result of blowing or weathering) is accompanied by changes in the rheological properties from a sol system to a gel system.
3. GPC can be used to evaluate the blowing rate of new asphalt cements as well as the degree of in-situ weathering.
4. The authors also recognized that the use of the RTFOT to simulate in-situ weathering may not be valid because of the temperature used in the test (160°C). Current research is underway to look at other techniques.

3.4 ISHAI ET AL. (1988)

This bi-national study (France and Israel) was conducted to correlate, explain, and predict the long term aging characteristics of the asphalts with its fundamental rheological and physico-chemical properties (Ishai et al., 1988). The long-term asphalt durability was related to some basic rheological and physico-chemical characteristics of the original and standard aged asphalt cements.

Four propane precipitated (PPA) 60/70 asphalt cement blends (A, B, D & E), a control straight-run 60-70 asphalt cement, a vacuum tower bottom (VTB), and PPA residue were tested. The pure PPA component was also tested. The various tests and analyses performed, before and after RTFOT, are shown in Tables 3-5 and 3-6, respectively. GPC was used to characterize all the asphalt samples before and after aging in the rolling thin film oven test (RTFOT). By using "fast" and "ultra-fast" GPC conditions (previously defined by Brûlé et al., 1986, in Section 3.3), information can

Table 3-5. Basic properties of Israeli asphalt samples tested in France (before RTFOT) (Ishai et al., 1988).

ASPHALT IDENTIFICATION		PPA_1	A	B	D	E	Control	VTB 250
ASPHALT GRADE	ASTM D 946		60-70		60-70		60-70	
	ASTM D 3381	-	AC-20	AC-20/10	AC-10	AC-20	AC-20/10	
BLEND PROPORTIONS (PPA/VTB/EXT), %		100/0/0	20/80/0	30/70/0	60/40/0	83/0/17	0/100/0	0/100/0
PENETRATION OF VTB COMPONENT, 0.1 mm		-	100	-	500$^+$	-	60-70	250
Penetration, 0.1 mm, at:	15°C	-	18	20	16	15	21	-
	20°C	-	32	34	35	29	39	-
	25°C	11	63	61	71	54	66	247
	30°C	-	101	100	121	91	101	-
	35°C	32	179	170	206	166	174	-
	45°C	109	-	-	-	-	-	-
Penetration Index (LCPC)		-	-1.4	-1.0	-2.0	-1.6	-0.8	-
Penetration Index (Pfeiffer)		-	-1.2	-0.5	-1.0	-1.3	-0.1	-
Softening Point (R&B), °C		61.0	48.0	51.0	47.5	49.0	51.5	38.0
Temperature of 800 Pen., °C		-	48.0	49.5	45.0	48.0	49.5	-
Frass Breaking Point, °C		0	-15	-15	-13	-11	-18	-
Group Composition (Introscan)	Asphaltenes, %	10.4	11.6	12.7	8.8	8.7	13.9	10.3
	Resines, %	20.1	25.6	20.6	22.9	18.7	20.8	18.7
	Aromatics, %	66.4	56.3	57.9	59.6	68.2	54.4	57.9
	Saturates, %	3.1	6.5	8.8	8.7	4.4	10.9	13.1
Gaestel Index (IC)		0.16	0.22	0.27	0.21	0.15	0.33	0.31
Vandium Content, %		183	-	-	147	144	280	145
Nickel Content, %		66	-	-	51	58	46	64

Table 3-6. Basic properties of Israeli asphalt samples tested in France (after RTFOT) (Ishai et al., 1988).

ASPHALT IDENTIFICATION		PPA_1	A	B	D	E	Control	VTB 250
ASPHALT GRADE	ASTM D 946		60-70		60-70		60-70	
	ASTM D 3381	-	AC-20	AC-20/1	AC-10	AC-20	AC-20/1	
BLEND PROPORTIONS (PPA/VTB/EXT), %		100/0/0	20/80/0	30/70/0	60/40/0	83/0/1	0/100/0	0/100/0
PENETRATION OF VTB COMPONENT, 0.1 mm		-	100	-	500^+	-	60-70	250
Penetration, 0.1 mm, at:	15°C		12	15	15	10	16	-
	20°C		18	19	25	19	22	-
	25°C		34	36	39	35	42	127
	30°C		52	52	71	60	56	-
	35°C		96	91	130	97	93	-
Penetration Index (LCPC)			-0.8	0	-1.0	-1.4	+0.2	-
Penetration Index (Pfeiffer)			-1.0	-0.5	-1.4	-1.2	-0.1	-
Softening Point (R&B), °C			54.5	56.0	51.5	53.0	56.5	44
Temperature of 800 Pen, °C			55.5	59.0	52.5	53.0	59.0	-
Frass Breaking Point, °C			-9	-12	-10	-8	-17	-
Group Composition (Iatroscan)	Asphaltenes, %		14.3	15.4	11.4	11.8	16.7	13.6
	Resines, %		26.4	21.0	23.7	20.3	23.0	20.7
	Aromatics, %		52.9	54.9	56.1	63.5	49.4	53.1
	Saturates, %		6.4	8.7	8.8	4.4	10.9	12.6
Gaestel Index (IC)			0.26	0.32	0.25	0.19	0.38	0.36

be obtained about the complex equilibrium among molecules, micelles, and agglomerates of the colloidal structure of asphalt cement.

In the "fast" condition, two columns (10^3 and 10^4 Å) of μ-styragel are used. Figure 3-20 shows a relative comparison of chromatograms of PPA, VTB, and Asphalt A, and the control before and after aging in the standard RTFOT. Before aging, the shape of the chromatograms for PPA, VTB, and sample A are quite similar. On the other hand, the shape of the chromatogram for the control asphalt is quite different than that of sample A. In asphalt A, the amount of micelles is higher and some agglomerates are present. After the RTFOT aging, the amount of micelles has increased in both sample A and the control asphalt, but more so in the latter. Also, there is a significant increase in the amount of agglomerates in the control asphalt after aging.

In the "ultra-fast" condition, only one 10^3 Å column of μ-styragel is used. A relative comparison of chromatograms of the same asphalts before and after RTFOT, using ultra-fast conditions is shown in Figure 3-21. Using the single 10^3 Å column, all the larger molecular weight compounds are eluted in a very small range of elution volumes at the bottom of the exclusion volume of the column. Hence the "interaction index" (see Section 3.3--Brûlé et al., 1986), which is the detector response for the exclusion volume, is linked to the amount of heavy compounds in the asphalt cement, and therefore with the amount of agglomerates. In Figure 3-21, the "interaction index" for PPA, VTB and sample A before aging is very close to zero, i.e., the amount of micelles is quite low. These asphalts have very few compounds with high molecular weight. As in Figure 3-20, the control asphalt cement is different showing a large amount of micelles and a significant "interaction index". These observations agree with those from Figure 3-20, but the "ultra-fast" GPC allows a sharp distinction of the difference in the amount of high molecular weight among the different samples.

After RTFOT aging, an increase both in the "interaction index" and in the amount of micelles for VTB and Sample A is observed. The same is also seen for the control sample, but the increase in the content of micelles is more significant. These results agree with the long-term age hardening behavior of these asphalts.

Ishai et al. (1988) concluded that the evolution of the colloidal structure either between different types of asphalts possessing different sensitivities to aging or as caused by aging, is clearly reflected in the molecular weight distribution as obtained by GPC. It was found that GPC can

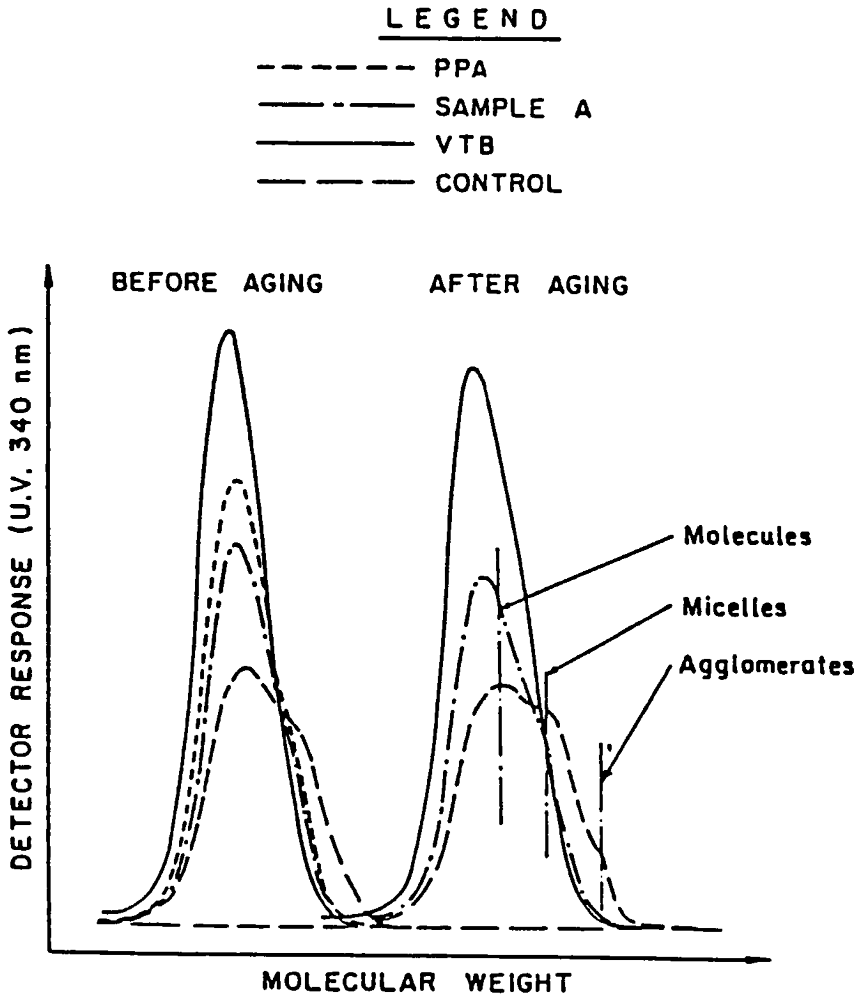


Figure 3-20. GPC characterization of the asphalt samples in "fast" conditions before and after RTFOT (Ishai et al., 1988).

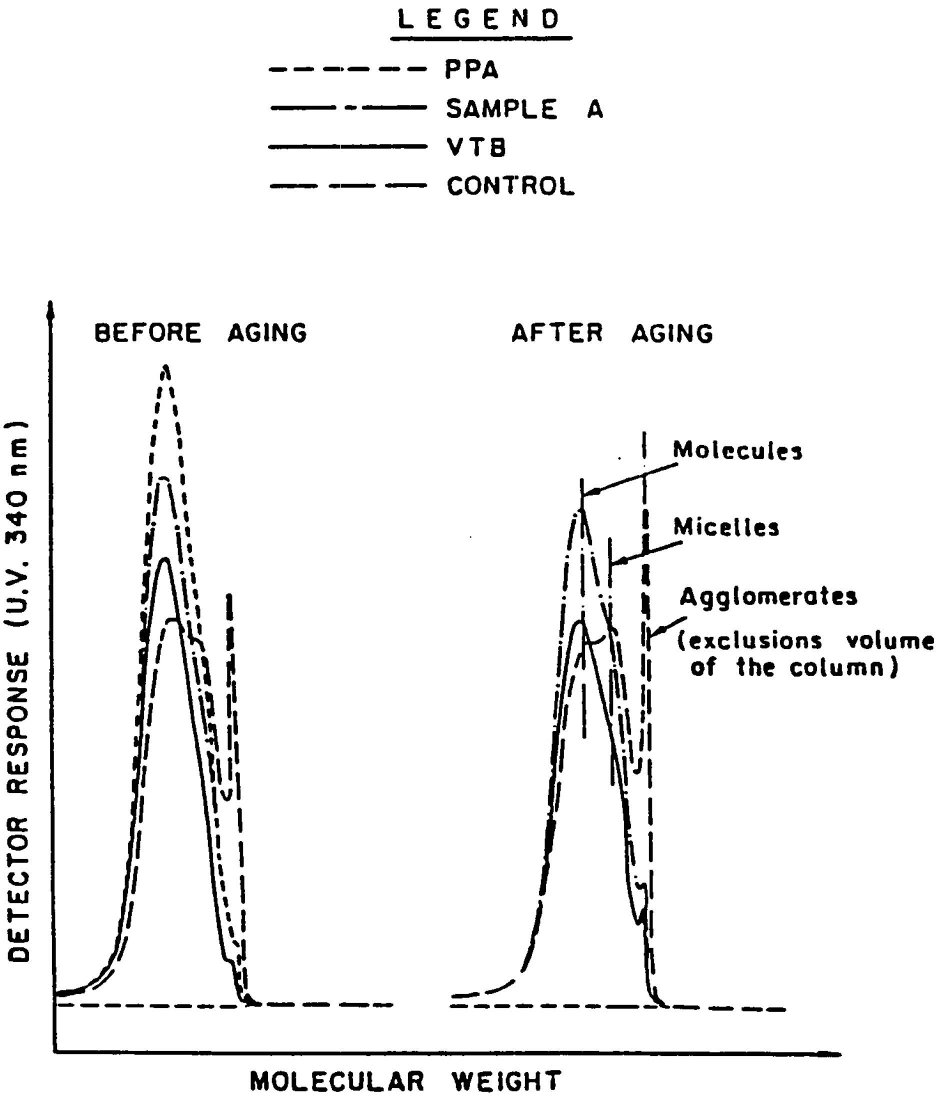


Figure 3-21. GPC characterization of the asphalt samples in "ultra-fast" conditions before and after RTFOT (Ishai et al., 1988).

provide valuable information on the changes occurring in the colloidal structure of the different asphalt types during aging.

3.5 PRICE AND BURATI (1990)

In this study, Price and Burati (1990) used HP-GPC to characterize ten modified asphalts and one control AC-20. The ten modified asphalts included four rubber modifiers, three plastic modifiers, two hard (harder grade) asphalts and one oxidant modifier. Table 3-7 summarizes the eleven binders studied. Their principal objective was to demonstrate the value of HP-GPC in predicting performance of asphalts and modified asphalts in laboratory tests for asphalt cement, Marshall mix design and asphaltic concrete mixes.

Laboratory test data were divided into three groups. Test data on the parent asphalt cement included specific gravity, penetration, absolute and kinematic viscosities and absolute viscosity of the Thin Film Oven Test (TFOT) residue. Mix design data included optimum asphalt content, Marshall stability and Marshall flow (no information was provided on the type of aggregate used). Physical test data on the asphalt concrete mix specimen included indirect tensile strengths at four different temperatures; resilient modulus at four temperatures; and creep-rebound test data at two temperatures. The properties measured are described in Table 3-8. The mean values for all variable data for modified asphalts is summarized in Table 3-9. HP-GPC analysis was performed on all of the modified asphalts and the control AC-20. The HP-GPC chromatograms were partitioned into thirds (LMS, MMS, SMS) after work by Jennings et al. (1980), and into tenths. Partitioning into tenths was used because partitioning into thirds did not provide sufficient resolution to establish correlations between HP-GPC and the laboratory tests. These partitions were called HP-GPC group variables. Tables 3-10 and 3-11 summarize the HP-GPC data for the modified asphalts using three and 10 partitions, respectively.

The authors (Price and Burati, 1990) presented five strong (significance level of less than 0.10 and an R^2 value of 0.75 or greater) correlations between test data and HP-GPC characterization. These relationships are as follows:

1. $\text{SG} = 1.3937 - 0.0096\,(\text{TEN1}) + 0.0189\,(\text{TEN2})$
   $- 0.0218\,(\text{TEN6}) + \text{Type constant}$ $(R^2 = 0.98)$
2. $\text{TS39} = -3031.74 + 180.08\,(\text{TEN5}) + 220.86\,(\text{TEN9})$
   $- 141.62\,(\text{TEN10}) + \text{Type constant}$ $(R^2 = 0.98)$

Table 3-7. Modified asphalt codes and descriptions (Price and Burati, 1990).

CODE	NAME	DESCRIPTION
		Control
C	Parent AC-20	Control and basis for all mixes
		Hard Asphalts
H1	AC-40	Straight run AC-40 for comparison
H2	45% Trinidad	45% Lake Trinidad Asphalt in AC-20
		Rubbers
R1	Rubber 1	Ground reclaimed tire rubber
R2	Rubber 2	SBS* Rubber Latex
R3	Rubber 3	SBS* oil extended copolymer rubber
R4	Rubber 4	Polychloroprene homopolymer rubber
		Plastics
P1	Plastic 1	Ethyl vinyl acetate
P2	Plastic 2	Polyethylene with 5% LDPE**
P3	Plastic 3	Two component polymer
		Oxidant
O1	Oxidant	Oil based soap and soluble manganese

*SBS = styrene butadiene styrene.
**LDPE = low density polyethylene

Table 3-8. Data variables and their descriptions (Price and Burati, 1990).

VARIABLE	DESCRIPTION
PEN	Standard penetration test value
SG	Specific gravity
OAC	Optimum asphalt content by Marshall method
STAB	Marshall stability
FLOW	Marshall flow
STRN77	Strain measured at 77° F for creep-rebound
STRN104	Strain measured at 104° F for creep-rebound
CREEP77	Measured creep in inches at 77° F
CREEP104	Measured creep in inches at 104° F
REB77	Measured rebound in inches at 77° F
REB104	Measured rebound in inches at 104° F
PCRB77	Percent rebound at 77° F
PCRB104	Percent rebound at 104° F
RM0	Resilient modulus at 0° F
RM39	Resilient modulus at 39° F
RM77	Resilient modulus at 77° F
RM104	Resilient modulus at 104° F
TS0	Indirect tensile strength at 0° F
TS39	Indirect tensile strength at 39° F
TS77	Indirect tensile strength at 77° F
TS104	Indirect tensile strength 104° F

Table 3-9. Mean values for all variable data for modified asphalts (Price and Burati, 1990).

Code	TYPE	SG	PEN .1mm	TS0 psi	TS39 psi	TS77 psi	TS104 psi	RED77 %	RED104 %
C	Control	1.037	85	583.6	345.9	96.7	38.5	32.3	61.5
H1	Hard	1.020	39	450.9	445.1	197.7	50.2	29.3	40.0
H2	Hard	1.174	23	600.1	516.5	209.7	60.7	24.3	34.6
R1	Rubber	1.054	50	599.1	349.2	99.3	44.4	38.7	29.8
R2	Rubber	1.030	67	526.5	387.9	131.6	41.3	23.1	45.0
R3	Rubber	1.029	65	476.7	330.0	117.5	48.2	25.4	24.7
R4	Rubber	1.045	80	630.4	366.0	124.8	43.7	29.6	25.3
P1	Plastic	1.035	54	610.5	391.3	140.9	53.3	31.2	28.0
P2	Plastic	1.025	53	600.3	419.2	156.3	55.0	12.3	35.2
P3	Plastic	1.028	108	561.6	159.9	97.1	32.1	34.2	30.2
O1	Oxidant	1.038	89	493.4	386.6	161.9	98.3	15.9	33.3

Code	Type	RM0 psi	RM39 psi	RM77 psi	RM104 psi	CM77	RMC77
C	Control	3143888	3030308	316513	76251	375.9	841.9
H1	Hard	2792331	3041043	451148	125440	294.1	1533.9
H2	Hard	1575560	1405298	791644	113794	721.2	1097.8
R1	Rubber	2150855	2021732	595207	205194	480.8	1238.0
R2	Rubber	1548690	1235363	329850	125085	468.8	703.7
R3	Rubber	1146040	1366029	373305	155819	496.7	751.6
R4	Rubber	1624240	489017	266380	120091	413.2	644.6
P1	Plastic	2286823	1078911	347476	150905	700.9	495.7
P2	Plastic	877121	898425	372100	161594	635.6	585.4
P3	Plastic	2860852	1614363	625545	93485	441.2	1417.9
O1	Oxidant	3247483	1682085	653892	243172	1694.9	385.8

Code	Type	OAC %	STAB lbs	FLOW .01"	STRN77 in/in	STRN104 in/in
C	Control	5.0	2160	11	0.133	0.088
H1	Hard	4.8	2240	9	0.170	0.074
H2	Hard	5.6	3200	9	0.104	0.104
R1	Rubber	5.4	2040	12	0.156	0.227
R2	Rubber	5.1	2780	10	0.160	0.096
R3	Rubber	5.1	2480	11	0.151	0.117
R4	Rubber	5.2	2040	11	0.121	0.111
P1	Plastic	4.8	2640	9	0.107	0.110
P2	Plastic	5.0	2570	11	0.118	0.090
P3	Plastic	4.9	2080	10	0.170	0.094
O1	Oxidant	4.8	3850	10	0.059	0.064

Table 3-10. HP-GPC data for modified asphalts using partitions into thirds (% area) (Price and Burati, 1990).

Code	Type	LMS	MMS	SMS
C	Control	12.65	49.83	37.52
H1	Hard	4.51	47.31	48.18
H2	Hard	19.70	40.80	39.49
R1	Rubber	15.00	49.15	35.85
R2	Rubber	14.24	50.35	35.41
R3	Rubber	16.54	46.67	36.80
R4	Rubber	12.77	50.45	36.78
P1	Plastic	13.25	50.06	36.69
P2	Plastic	13.08	49.46	37.45
P3	Plastic	15.52	49.17	35.31
O1	Oxidant	12.75	50.11	37.15

Table 3-11. HP-GPC data for modified asphalts using partitions into tenths (% area) (Price and Burati, 1990).

Code	Type	TEN1	TEN2	TEN3	TEN4	TEN5	TEN6	TEN7	TEN8	TEN9	TEN10
C	Control	0.2	2.2	6.4	10.7	11.6	17.8	18.9	17.5	9.4	5.3
H1	Hard	0.2	0.7	2.0	5.5	9.2	18.2	23.0	24.0	11.9	5.3
H2	Hard	3.6	6.0	6.8	9.4	10.2	14.3	14.6	17.3	12.0	5.9
R1	Rubber	1.3	3.2	6.8	10.6	11.3	17.6	18.8	17.2	8.8	4.5
R2	Rubber	0.9	2.3	7.0	11.2	11.6	17.9	19.2	17.4	8.5	4.0
R3	Rubber	4.5	2.1	6.3	10.2	10.8	16.6	17.9	17.1	9.6	4.9
R4	Rubber	0.4	2.0	6.5	10.8	11.6	18.0	19.6	17.9	8.9	4.4
P1	Plastic	0.3	2.3	6.7	10.9	11.6	17.9	19.0	17.5	9.0	4.7
P2	Plastic	0.2	2.2	6.7	10.9	11.6	17.5	18.7	17.5	9.4	5.2
P3	Plastic	2.2	3.4	6.4	10.1	11.0	17.8	19.2	16.8	8.5	4.5
O1	Oxidant	0.1	2.1	6.6	10.8	11.6	18.0	19.2	17.8	9.1	4.7

3. TS77 = - 85.45 + 22.73 (TEN9) + Type constant ($R^2 = 0.87$)

4. RM39 = 3,458,500 - 327,600 (TEN3) + Type constant ($R^2 = 0.77$)

5. RM77 = - 1,232,000 + 174,300 (TEN2) + 64,200 (TEN7)
+ Type constant ($R^2 = 0.89$)

where: SG = Specific Gravity
TS39 = Indirect tensile strength @ 39°F
TS77 = Indirect tensile strength @ 77°F
RM39 = Resilient modulus @ 39°F
RM77 = Resilient Modulus @ 77°F
TENi = Area under curve of i^{th} tenth of elution time ($i = 1$ to 10)
Type constant = Constant dependent upon type of modified asphalt sample (Table 3-12).

No strong or significant correlation was found between HP-GPC parameters for modified asphalts and the following properties: penetration, optimum asphalt content, Marshall stability, Marshall flow, percent rebound, indirect tensile strength at 0°F and 104°F, and resilient modulus at 0°F and 104°F. In conclusion, Price and Burati (1990) were able to develop a quantitative method to analyze HP-GPC profiles. This method involves partitioning the HP-GPC profile into tenths (based on elution time). They were also able to obtain regression equations to predict physical properties of asphalts and modified asphalts from HP-GPC parameters.

3.6 GARRICK AND BISKUR (1990)

Garrick and Biskur (1990) detail the research done at the University of Connecticut with regard to developing a procedure for classifying asphalts on the basis of their GPC profiles in this report. (This is an expansion of some of Garrick's earlier work (see Section 2.4) from 1986 and 1988.) The procedure was successfully evaluated for GPC profiles of various asphalt research. The results of this evaluation suggest that this classification process is accurate for a wide range of paving grade asphalts. In addition, the process also appears to be applicable to profiles obtained using many variations of the GPC procedures.

Fifteen different asphalts from six suppliers were obtained for this project. Table 3-13 presents information on the identity of these asphalts. Table 3-14 summarizes the physical properties of these asphalts and Table 3-15 contains the results of the GPC analyses. The elution time for each partition (twelve partitions) are listed for all the asphalts tested. The following GPC system was used:

Table 3-12. HP-GPC Data Regression Analysis Coefficients for Modified Asphalts: TS39, TS77 AND SG (N = 11) (Price and Burati, 1990).

HP-GPC Parameter	TS39	TS77	SG
TEN1			-0.0096
TEN2			0.0189
TEN3			
TEN4			
TEN5	180.08		
TEN6			-0.0218
TEN7			
TEN8			
TEN9	220.86	22.73	
TEN10	- 141.62		
constant	-3031.74	- 85.45	1.3937
Type C	- 45.85	- 31.12	-0.0086
H	- 81.76	17.08	0.0115
O	- 10.73	39.92	-0.0036
P	- 3.91	12.50	-0.0198
R	0	0	0
R-squared	0.93	0.8693	0.9830
C.V.	11.72	14.26	0.98

HP-GPC Parameter	RM39	RM77
TEN1		
TEN2		174300
TEN3	-327600	
TEN4		
TEN5		
TEN6		
TEN7		64200
TEN8		
TEN9		
TEN10		
constant	3458500	-1232000
Type C	1674600	- 47000
H	192800	56300
O	395100	286300
P	- 98100	1900
R	0	0
R-squared	0.7690	0.8897
C.V.	33.81	19.39

Table 3-13. List of asphalts used in project (Garrick & Biskur, 1990).

Asphalt No.	Grade	Supplier	State
NE5	AC-5	New Bituminous	Rhode Island
NE10	AC-10	New Bituminous	Rhode Island
NE20	AC-20	New Bituminous	Rhode Island
D5	AC-5	Diamond Shamrock	Texas
D10	AC-10	Diamond Shamrock	Texas
D20	AC-20	Diamond Shamrock	Texas
A5	AC-5	Ashland	Kentucky
A10	AC-10	Ashland	Kentucky
A20	AC-20	Ashland	Kentucky
E5	AC-5	Edgington	California
E20	AC-20	Edgington	California
CAG5	AC-5	Guyott	Connecticut
CAG20	AC-20	Guyott	Connecticut
CP10	AC-10	Chevron	New Jersey
CP20	AC-20	Chevron	Connecticut

Table 3-14. Physical properties of test asphalts (Garrick & Biskur, 1990).

	Original Asphalt			TFOT Residue	
Asphalt No.	Penetration 0.1 dm, 77°F	Viscosity p, 140°F	Viscosity cst, 275°F	Pentration 0.1 dm, 77°F	Viscosity p, 140°F
NE5	187	586	230	109	1344
NE10	110	1035	319	79	2155
NE20	68	1945	436	56	3957
D5	203	424	311	133	753
D10	122	896	476	78	1551
D20	70	2237	654	57	3859
A5	114	538	240	97	1033
A10	96	1096	333	58	1816
A20	74	2023	432	54	3837
E5	140	547	163	88	1107
E20	55	1711	275	38	3572
CAG5	177	481	260	126	1224
CAG20	77	2149	479	54	4452
CP10	117	1089	330	78	2947
CP20	91	1926	442	55	5449

Table 3-14. Continued.

Asphalt No.	PVN'(77-140°F)	PVN(77-275°F)	VTS(140-275°F)	VisRatio(140°F)
NE5	-0.30	-0.35	3.46	2.29
NE10	-0.58	-0.46	3.42	2.08
NE20	-0.67	-0.52	3.42	2.03
D5	-0.54	+0.30	3.05	1.78
D10	-0.56	+0.30	3.03	1.73
D20	-0.48	+0.09	3.16	1.73
A5	-1.24	-0.87	3.38	1.92
A10	-0.73	-0.55	3.41	1.66
A20	-0.50	-0.45	3.45	1.90
E5	-0.89	-1.27	3.75	2.02
E20	-1.11	-1.37	3.76	2.09
CAG5	-0.64	-0.21	3.26	2.54
CAG20	-0.38	-0.25	3.39	2.07
CP10	-0.42	-0.33	3.41	2.71
CP20	-0.22	-0.18	3.41	2.83

Table 3-15. Results of GPC analyses (Garrick & Biskur, 1990).

Asphalt No.	X1	X2	X3	X4	X5	X6	X7	X8	X9	X10	X11	X12
N5	5.02	12.65	14.58	16.87	16.17	13.83	10.25	6.29	3.40	1.05	0.28	0.05
TN5	5.38	13.80	15.14	16.54	15.91	13.33	9.69	5.89	3.08	0.87	0.17	0.03
N10	4.18	12.62	15.28	17.80	17.15	13.94	9.70	5.53	2.82	0.86	0.19	0.03
TN10	10.92	15.97	14.95	15.81	14.84	11.92	8.20	4.85	2.20	0.63	0.11	0.01
N20	3.95	12.50	15.44	18.42	17.93	14.04	9.20	5.03	2.45	0.80	0.20	0.04
TN20	8.59	16.01	15.46	16.43	15.89	12.42	8.03	4.33	2.01	0.69	0.13	0.02
D5	5.11	14.87	19.57	21.07	17.84	11.35	5.98	2.58	1.03	0.45	0.14	0.03
TD5	5.98	16.42	20.01	20.46	17.01	10.71	5.54	2.36	0.94	0.41	0.12	0.02
D10	5.02	15.10	19.67	20.83	17.63	11.28	6.01	2.65	1.09	0.43	0.14	0.03
TD10	6.38	16.65	19.92	20.12	16.69	10.62	5.60	2.44	1.00	0.44	0.14	0.03
D20	5.44	15.38	19.63	20.63	17.35	11.19	5.98	2.66	1.11	0.45	0.15	0.03
TD20	7.01	17.38	20.25	20.19	16.24	10.00	5.30	2.22	0.89	0.38	0.12	0.03
A5	1.11	10.40	14.95	21.47	22.04	15.12	8.42	4.00	1.74	0.54	0.13	0.03
TA5	3.11	11.74	15.48	20.61	20.94	14.35	7.87	3.88	1.58	0.53	0.13	0.02
A10	2.84	10.30	14.10	19.15	20.40	15.60	9.60	4.95	2.30	0.74	0.16	0.03
TA10	3.34	11.54	14.63	18.79	19.70	14.92	9.14	4.71	2.14	0.87	0.19	0.03
A20	4.55	12.38	14.99	18.21	18.44	14.21	9.10	4.90	2.29	0.74	0.16	0.03
TA20	5.40	13.27	15.42	18.11	18.10	13.78	8.70	4.55	2.03	0.57	0.07	0.00
E5	1.00	5.84	11.90	18.20	20.41	18.64	13.80	6.71	2.66	0.69	0.13	0.02
TE5	2.28	9.25	13.74	17.57	18.81	17.01	12.43	5.85	2.25	0.68	0.12	0.02
E20	1.27	6.18	12.41	18.83	20.98	18.73	12.88	5.80	2.20	0.59	0.12	0.02
TE20	2.54	8.86	13.71	18.08	19.50	17.35	11.98	5.31	1.95	0.67	0.13	0.02
CAG5	4.22	12.32	15.11	17.87	17.44	14.06	9.84	5.48	2.77	0.88	0.19	0.03
TCAG5	5.35	13.49	15.15	17.28	16.77	13.51	9.22	5.23	2.60	1.12	0.23	0.04
CAG20	4.18	12.11	14.54	17.00	16.58	14.02	10.44	6.36	3.35	1.04	0.25	0.05
TCAG20	5.47	13.88	15.11	16.60	15.90	13.31	9.77	5.85	3.01	0.89	0.19	0.03
CP10	5.38	13.13	15.72	17.20	15.81	13.03	9.65	5.75	3.01	0.98	0.23	0.05
TCP10	9.28	15.22	15.48	15.88	14.83	12.02	8.84	5.15	2.58	0.80	0.15	0.02
CP20	4.73	12.93	15.64	17.21	16.21	13.52	9.84	5.70	2.94	0.94	0.27	0.05
TCP20	8.95	14.62	15.66	16.64	15.44	12.64	9.14	5.26	2.64	0.80	0.18	0.03

Columns: Three ultra-styragel columns–1000 Å, 500 Å, 500 Å;
Solvent: Tetrahydrofuran (THF)
Detector: Multiwave-length ultraviolet detector set at 290 nm.
Flow Rate: 1 ml/min.

The GPC parameters were obtained from the GPC profiles using a modified form of a procedure developed by Garrick and Wood (1986). Instead of partitioning the profiles into eights, twelve equal time segments were used. The GPC parameters, designated X1 to X12, are the percentage of total area under the curve in each segment. Molecular size can be assumed to increase from X1 to X12. These parameters are a measure of the properties of asphalt molecules of a given size.

Regression analyses were then performed in an attempt to find relationships between the HP-GPC parameters and physical properties. No relationship was found between GPC parameters and either penetration (at 77°F) nor viscosity (at 140°F). These findings conflict with those from Garrick and Wood (1988), but Garrick and Biskur speculate that in the earlier study, the asphalts analyzed were from two sources only, which might explain the discrepancy.

Three measures of temperature susceptibility were calculated: PVN' (penetration viscosity number, 77°F to 140°F); PVN (77°F to 275°F) and VTS (viscosity temperature susceptibility, 140°F to 275°F). In all cases, an excellent correlation was found between GPC parameters and temperature susceptibility. Figures 3-22 to 3-24 illustrate the close fit between GPC parameters and temperature susceptibility. Since each value correlates with a different GPC slice, this suggests that temperature susceptibility in different temperature ranges are independent of each other. In all three cases, the temperature susceptibility became less severe as the GPC parameter decreased. In general, an asphalt with a very narrow GPC profile (narrow molecular size distribution) will have extreme (very high or very low) values of temperature susceptibility depending on the location of the peak. Conversely, an asphalt with a broader GPC profile will have moderate values of temperature susceptibility (Garrick and Biskur, 1990).

Figure 3-25 shows that viscosity ratio increases with an increase in the GPC parameter, X_{10}. This result supports the hypothesis that asphalts with more volatiles (small molecules) are more likely to show significant heat hardening. However, the correlation between GPC parameters and viscosity ratio was poor, indicating that loss of volatiles is not the only mechanism contributing to heat hardening (Garrick and Biskur, 1990). Table 3-16 summarizes the regression equations that were developed.

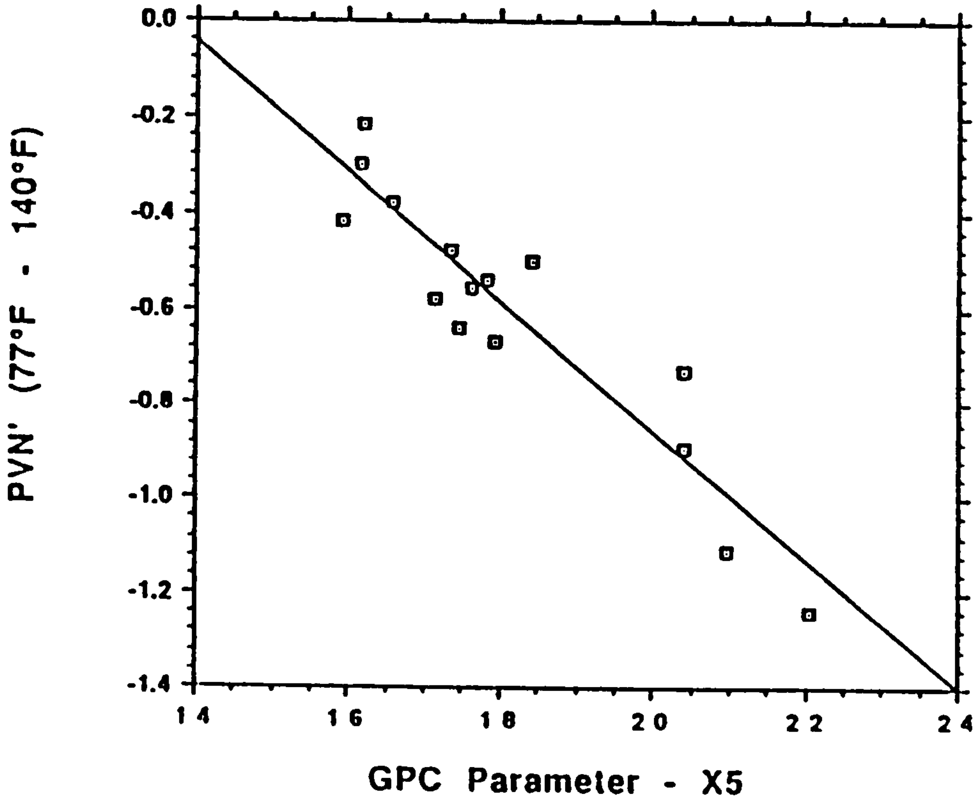


Figure 3-22. PVN vs. GPC parameter X5 (Garrick & Biskur, 1990).

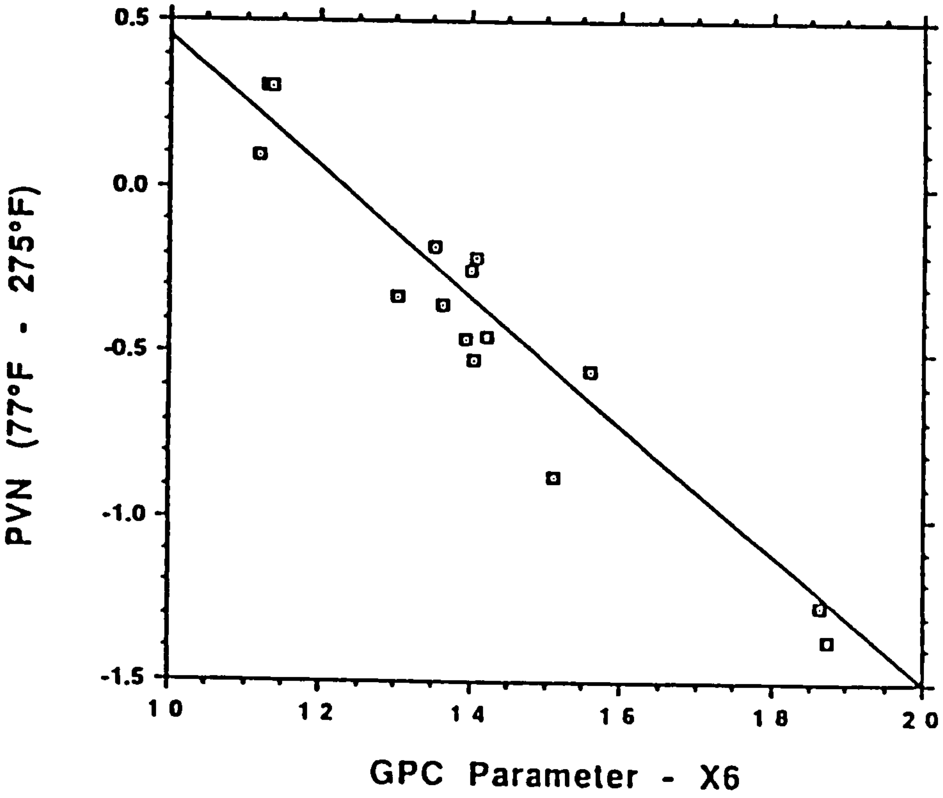


Figure 3-23. PVN vs. GPC parameter X6 (Garrick & Biskur, 1990).

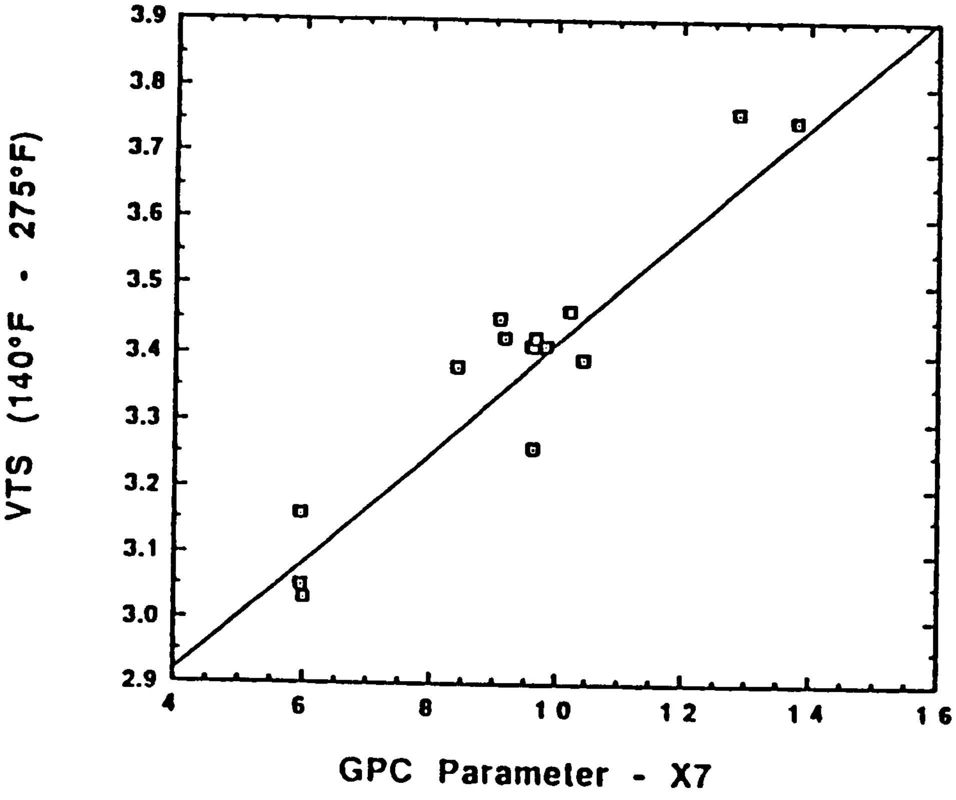


Figure 3-24. VTS vs. GPC parameter X7 (Garrick & Biskur, 1990).

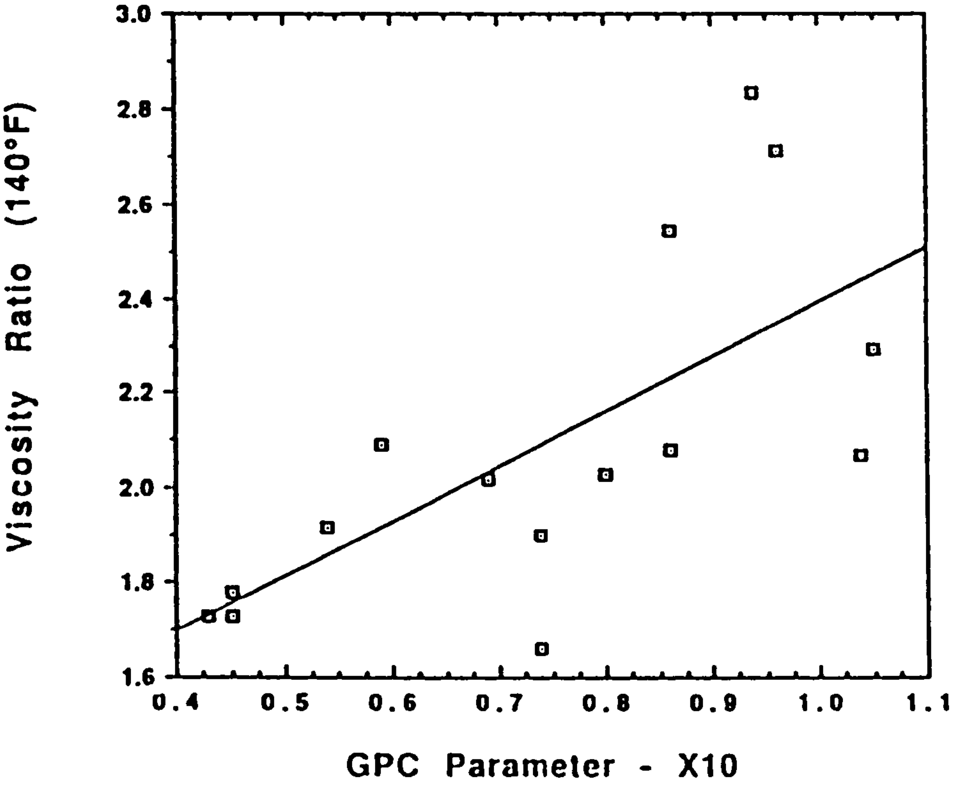


Figure 3-25. Viscosity ratio vs. GPC parameter X10 (Garrick & Biskur, 1990).

Table 3-16. Results of regression analyses (Garrick & Biskur, 1990).

Property	Regression Model	R-squared
PVN' (77°F - 140°F)	PVN' = -0.138 X5 + 1.890	0.87
PVN (77°F - 275°F)	PVN = -0.207 X6 + 2.528	0.92
VTS (140°F - 275°F)	VTS = 0.087 X7 + 2.565	0.89
Vis. Ratio (140°F)	VR = 1.160 X10 + 1.230	0.48

Garrick and Biskur also found that the asphalts in the project could be divided into four different groups on the basis of their GPC profiles. Also, the asphalts in each group had similar temperature susceptibility and heat hardening properties. The classification is based on two characteristics of the GPC profile--the distribution (broad or narrow) and the location of the peak. The authors believe that the framework provided in their paper will make it easier to understand the relationships between asphalt composition and some of its physical properties.

Finally, the authors concluded that GPC parameters correlate well with temperature susceptibility and to some extent with the viscosity ratios. Using the relationships developed between GPC parameters and physical properties, a procedure for classifying asphalts on the basis of their GPC profiles was derived. Under this system the asphalts are divided into four groups with each group having similar temperature susceptibility and heat hardening properties. This classification system may be used to predict physical properties of an asphalt from the shape of its GPC profile.

4.0 CONCLUSIONS

Before drawing any specific conclusions, it will be worthwhile to review the HP-GPC process. Chromatographic separation for asphalt compositional analysis can be broken down into:

- Gas Chromatography
- Inverse gas-liquid chromatography
- Liquid Chromatography (adsorption, ion exchange, coordination, thin layer, size exclusion - mostly HP-GPC)

Size exclusion chromatography (GPC, HP-GPC) separates asphalt constituents based on their associated sizes in dilute solutions. Smaller molecular aggregations diffuse into and out of the porous media in the column, with the larger structures unable to enter the pores and so they pass quickly through the column. It separates asphalt based on the apparent size (hydrodynamic volume) of molecules and molecular aggregations/associations in dilute solution (Altgelt & Gouw, 1975). The chromatogram defines the molecular size distribution (MSD) or profile of an asphalt. However, what the profile represents is influenced by several factors, as discussed previously in Section 1.3.

Despite the many factors that can influence HP-GPC results and their interpretation, three basic conclusions may be made from this literature review:

1. HP-GPC vs. Physical Properties of Asphalt - The molecular size distribution (MSD) of an asphalt has a definite effect on its physical properties. However, these effects are not easily characterized, although several studies have been performed in an effort to quantify these effects.
   a. According to Chollar et al. (1985), the LMS content of an asphalt has a minor influence on the physical properties such as ductility, specific gravity, shear susceptibility since the regression model that was developed only had a R^2 of 0.39.
   b. After measuring the physical properties such as viscosity, penetration and softening point, before and after TFOT's, Glover et al. (1987) concluded that the changes in these properties are reflected by their respective GPC chromatograms.
   c. Garrick & Wood (1986) found viscosity (@ 60°C and @ 135°C) and penetration (@ 25°C) to be directly related to HP-GPC parameters. In 1988,

they obtained similar regression relationships with viscosity ratios, retained penetration (after TFOT), resilient modulus (@ 50°F, 72°F) and indirect tensile strengths of asphalt sand mixtures.

d. According to Brûlé et al. (1986), asphalt cements of the same grade can have substantially different chemical compositions and rheological behavior. GPC enables a characterization of the complex colloidal equilibrium of an asphalt cement. At the same time, Brûlé et al., found that no relationship existed between the interaction index (see Section 3.3) and the consistency of the asphalt cement as evaluated by, for example, penetration. However, a model was obtained to predict the degree of medium organization within asphalt using asphaltene content and the interaction index.

e. Price and Burati (1990) were able to predict physical properties (such as specific gravity, indirect tensile strength, and resilient modulus) of <u>modified</u> asphalts using HP-GPC parameters. Regression equations were developed.

f. Garrick and Biskur (1990) concluded that GPC parameters of an asphalt cement correlate well with temperature susceptibility and, to some extent, with the viscosity ratios. Regression equations were also developed.

2. <u>HP-GPC vs. Field Performance</u> - There are conflicting results on whether HP-GPC analysis can help to identify the performance of asphalt-aggregate mixtures.

a. Jennings et al. (1985) report that road cracking (primarily transverse cracking) is related to the LMS fraction determined from the HP-GPC chromatogram. Recommendations on the range of LMS and asphaltenes needed for good performance were obtained for Montana and other states. No asphalts with more than 36 percent LMS have given excellent cracking performance in studies limited to a minimum LMS value of 18%.

b. Kinnison's (1986) statistical approach led to his conclusion that the LMS and SMS portions did <u>not</u> show any association with pavement performance. However, although his data was based on Jennings et al.'s (1985) work, climate was not included as a variable.

c. Zenewitz & Tran (1987), however, concluded that there was statistical significance in Jennings et al.'s data between LMS, SMS and rutting and cracking. Although no quantifiable results were presented, they were able to report some trends in the data.

d. Glover et al. (1987) were able to report that there is a general increase in LMS as aging occurs. A correlation between LMS and the tenderness rating was obtained; generally, a low LMS content led to asphalts with tenderness problems.

e. Bynum and Traxler (1970) showed that virgin asphalt cements which contain considerable amounts of high molecular size compounds have a greater resistance to hardening in the asphalt course of a pavement. However, Goodrich et al. (1986) superimposed their chromatograms (Figure 4-1) and some interesting contradictions were shown. Although Asphalts 8-3 and 6-14 (See top half of figure) were rated as excellent, the chromatograms do show distinct differences. Conversely, Asphalts 3-9 and 11-10 (see bottom half of figure) had very similar chromatograms despite differences in their condition. Similarly, Figure 4-2 shows chromatograms based on data collected by Jennings et al. (1977). Although the roads had different conditions, their chromatograms were very similar.

f. Hattingh (1984) concluded that insufficient high molecular mass components in the asphaltenes of the virgin asphalts leads to poor performance in terms of setting (curing) of asphalt and bleeding.

g. Brûlé et al. (1986) showed that GPC can be used to evaluate the blowing rate of new asphalt cements as well as the degree of in-situ weathering.

h. Ishai et al. (1988) concluded that the evolution of the colloidal structure as caused by aging is clearly reflected in the molecular weight distribution as obtained by GPC. For an asphalt cement, the HP-GPC interaction index (as defined by Brûlé et al., 1986) increases with aging.

3. HP-GPC as an Asphalt Identification Tool - HP-GPC can be used to identify differences in crude sources between various asphalts, between asphalts of the same grade having different aging characteristics, and between asphalts from various refinery processes. It is possible to detect the presence of modifiers or fillers as the MSD will change. Zenewitz & Tran (1987) also indicate that it could be used to monitor the quality (uniformity) of asphalt during the production/refinery process.

a. According to Glover et al. (1987), the GPC procedure is a tool for asphalt characterization. They also point out that changes in asphalt composition caused by changes in processing and feedstock can be detected by GPC. In most instances, the differences between asphalts from various sources are distinguishable.

b. Bynum and Traxler (1970) concluded that GPC is a useful method for determining differences in MSD of various road building asphalts. Asphalts from different crude sources have different GPC profiles and so do asphalts from various methods of processing.

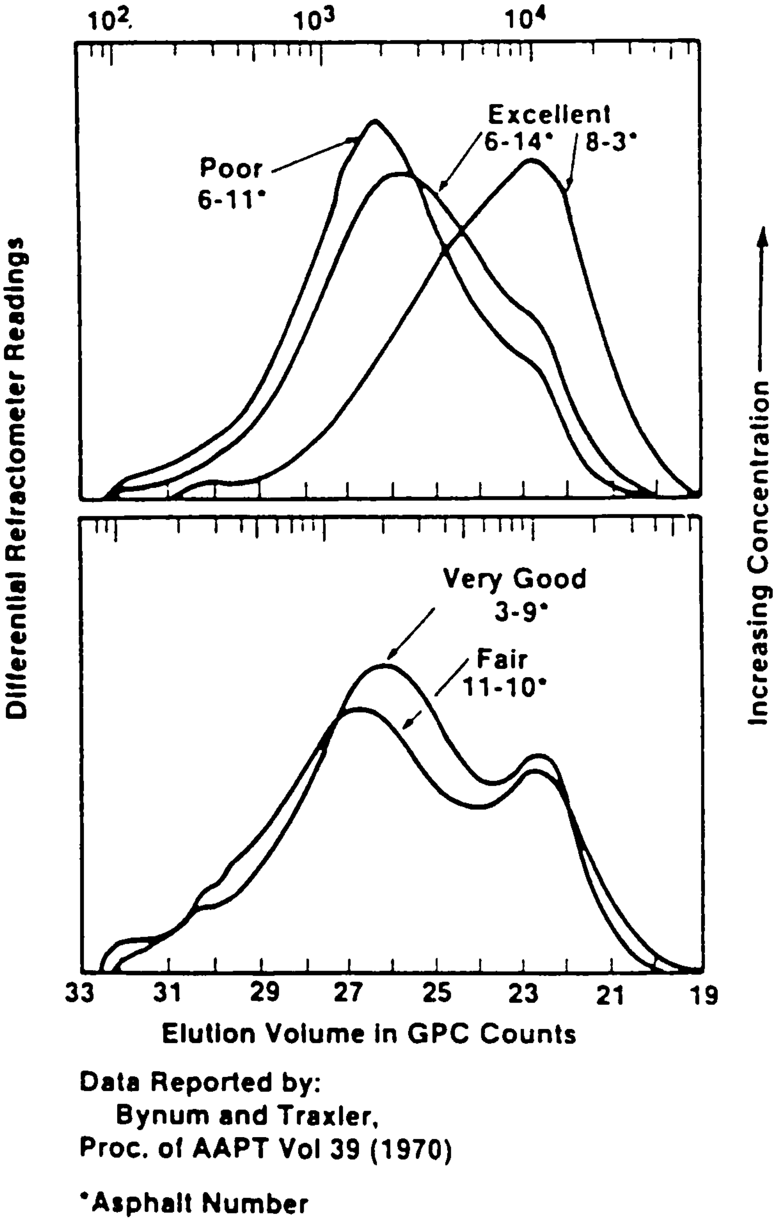
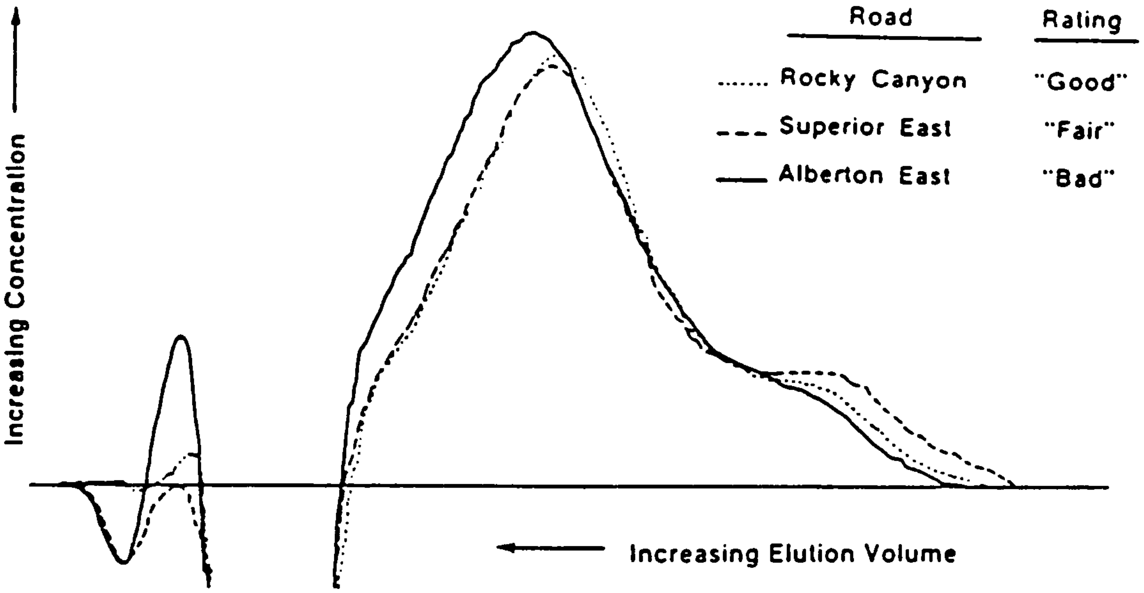


Figure 4-1. HP-GPC chromatograms of asphalts: Texas Test Roads 1963-66 (Goodrich et al., 1986).



Data Reported by:

P. W. Jennings
Report No. FHWA-MT-7929, 1977

Figure 4-2. HP-GPC chromatograms of asphalts recovered from aged roads (Goodrich et al., 1986).

c. GPC enables a characterization of the complex colloidal equilibrium of an asphalt cement (asphalt cements of the same grade can have substantially different chemical compositions and rheological behavior) (Brûlé et al., 1986). The shifting of the colloidal equilibrium towards the formation of aggregates due to the interactions between asphaltenes can be characterized by the GPC "interaction index" (defined by Brûlé as the height of the signal at the exclusion volume for the ultraviolet detector). The interaction index, or the interaction peak (molecular weights exceeding 100,000), is an image of the fraction of the dispersed phase giving the binder its gel-character.

d. The evolution of the colloidal structure between different types of asphalts possessing different sensitivities to aging is clearly reflected in the molecular weight distribution as obtained by GPC (Ishai et al., 1988).

Because of extensive efforts to relate information from HP-GPC to pavement performance, a special effort has been made to determine its potential application to the development of performance-based specifications. Based on the information summarized in this report, it is concluded that:

1. HP-GPC can be used to "finger-print" asphalts produced from a specific crude source of refinery, i.e., to determine when sources or procedures change and a different product is produced.
2. Physical tests incorporated in current asphalt specifications do not characterize the chemical properties (aggregations) as measured by HP-GPC.
3. Relationships have been shown between HP-GPC parameters and performance of asphalt concrete pavements. However, the relationships are not consistent and are likely to be confounded by test method, methods of interpretation of the HP-GPC test data, and relationship to different types of pavement distress, i.e., transverse cracking, fatigue cracking, rutting or tender mixes.

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APPENDIX A: GLOSSARY OF STATISTICAL TERMS

This appendix contains the description of some common statistical terms used in this review. There are three sources for this information:

1. Highway Research Board (1962), Special Report 61E, The AASHO Road Test: Report 5 - Pavement Research, Washington, D.C.
2. Neter, J., W. Wasserman & M. K. Kutner (1983), Applied Linear Regression Models, Richard D. Irwin, Inc., Homewood, Illinois.
3. Benjamin, J. R. & C. A. Cornell (1970), Probability, Statistics and Decision for Civil Engineers, McGraw-Hill Book Co.

Mathematical Model (model): An assumed algebraic form for the relationship among particular experimental variables. The model includes constants whose values are to be determined by analysis procedures, and may also include constants whose values are assumed. In many cases, the models involve logarithms.

Residual: The real difference between the observed value of an experimental variable and the value computed for this variable from a model in which all constants are determined and specific values are assigned to all remaining variables.

Root Mean Square Residual: the square root of the average squared residual. In general, the divisor for this average is equal to the number of residuals less the number of constants determined for the model by the data.

rms*r* or rms error

Average Residual (mean residual): The average of the absolute values of all residuals. In general, the divisor for this average is equal to the number of residuals..*r*

Mean Log Residual: Whenever an equation is derived for the logarithm of a variable, *Y*, instead of for *Y* itself, residuals and mean residuals represent discrepancies between observed and calculated logarithms of *Y*. Because it is generally assumed that about 90 percent of individual residuals are less than twice the mean residual, nine-tenths of the scatter of the observations log *Y*, around the calculated values, Log ^ *Y*, is contained in the bank whose limits are $\log Y = \log {}^\wedge Y + 2\underline{r}$, where $\log {}^\wedge Y$ is calculated from the derived equation and where $\underline{r}$ is the mean log residual.

It is often useful to express the error limits in the original units of *Y*. By taking antilogarithms these limits are given $= (10^{\pm 2r}) (\hat{Y})$. Thus nine-tenths of the scatter of *Y* around $\hat{Y}$ is expressed as two percentages of $\hat{Y}$ (10^{-2r}) (Y) and (10^{2r}) $(\hat{Y})$. For example, if $r = 0.16$, then $10^{-0.32} = 0.48$ and $10^{0.32} = 2.09$, so that approximately nine-tenths of the observed values for *Y* are found between 0.48 and 2.09 times the corresponding calculated values for *Y*. Roughly speaking, it would be unusual, in this example, to find an observation less than one-half or more than twice the corresponding value calculated from the equation.

If only one mean log residual is used to establish the error band, it can be expected that the band will contain about 60 percent of the residuals in log *Y*.

Effects (explained effects): Changes, or average changes, in an observed variable that are attributed to changes in one or more of the controlled factors of an experiment.

Residual Effects (unexplained effects, residual variation): Changes in an observed variable that are attributed to changes in unidentified variables. Usually expressed in terms of average residuals.

Statistical Significance: An (explained) effect is said to be statistically significant if its magnitude relative to an appropriate average residual is so large that there is little risk that the unexplained effect is actually a residual effect. The assumed risk that the explained effect is really a residual effect is called the significance level, usually selected to be no more than 5 percent.

Linear Model: A model whose general form is $A_0 + A_1X_1 + A_2X_2 ... + A_kX_k = 0$, where $X_1, X_2, ..., X_k$ are functions of one or more experimental variables, and at least one of the constants, $A_0, A_1, ..., A_k$ is to be determined through data analysis.

Least Squares Linear Regression Analysis (regression analysis): A mathematical procedure for evaluating the undetermined constants in a linear model when it is assumed that the best coefficients are those which lead to a minimum for the sum of squared residuals for a particular experimental variable.

Total Variation: For a particular experimental variable, the sum of squared deviations of the values for the variable from the mean value of the variable.

Squared Correlation Coefficient: For linear models, the difference between unity and the ratio of total squared residuals to total variation for a particular variable. Sometimes said to be that fraction of the total variation which is explained by the regression equation...r^2

Correlation Index: For the case of nonlinear models, the correlation index serves to indicate the degree of correlation between observed values of an experimental variable and corresponding values of an experimental variable and corresponding values predicted from a derived equation. Thus, the correlation index is a generalization of the squared correlation coefficient that is used for linear models. The correlation index is computed by subtracting from one the ratio of sum of squared residuals to the total variation in the observations for the variable.

APPENDIX B

DESCRIPTION OF HEITHAUS PROCEDURE

This appendix contains a brief description of the Heithaus state of peptization test that was used to determine the flocculation ratio by Glover et al. (1987) in Section 2.3 of this report. Also, some terms used in that study are defined in this appendix.

In Glover et al.'s (1987) study, an abbreviated version of the Heithaus state of peptization test was used for determining the flocculation ratio. The procedure is described below:

1. Add 1 ± 0.1g of asphalt to a 250 ml Erlenmeyer flask.
2. Add 5 ± 0.05 ml toulene from a burette.
3. Heat gently on a steam bath or hot plate set at 200°F, the Erlenmeyer flask, asphalt and toulene until asphalt softens.
4. Stir with a glass stirring rod until asphalt is well mixed into a uniform cutback. CAUTION-be careful not to lose toulene. It may be helpful to weigh flask, asphalt toulene and rod before heating and then replace any evaporation after cutback is made.
5. Cool in a water bath at 70°F-80°F.
6. With a magnetic stirrer, mixing constantly, add heptane slowly. Intermittently stop mixing and place a drop of mix on a slide, cover with a cover glass and observe under a microscope at 100 or more power. Continue examination after additional increments of addition. With continued heptane addition, small individual transparent asphaltene particles will be seen in suspension.
7. No change will be observed with further heptane addition for a few ml. then, suddenly, with addition of another increment, a definite change will be observed as the individual asphaltene particles begin to agglomerate or clump into loose flocculus. Additional heptane (1-3 ml) completes flocculation of the asphaltenes.
8. On initial evaluation, large increments of heptane, perhaps 10 ml, should be added. After the approximate volume for flocculation has been determined, another sample should be taken and the heptane added in smaller increments as the volume is approached where flocculation occurs.

The weight of asphalt, volume of toulene and volume of heptane required to initiate precipitation are recorded. The flocculation ration (FR) is computed as follows:

$$FR = \frac{\text{(volume of toulene)}}{\text{(volume of toulene + volume of heptane)}}$$

The full procedure may be used to compute additional parameters such as: (1) peptizability of asphaltenes, (2) peptizing power of asphaltenes, and (3) state of peptization of asphaltenes.

Peptize: This means to cause to disperse in a medium or to bring into colloidal solution.

Compatibility: As used by Glover et al., it relates to the mutual solubility of the molecular components in asphalt to produce homogeneity in the asphalt system and is thus a function of the state of peptization of the asphalt. By definition, as highly associated molecular agglomerates in the asphalt become separated from their dispersing or solubizing components, the system will have reduced component compatibility.

APPENDIX C

STREITER CHEMICAL ANALYSIS

This appendix contains a description of the Strieter analysis referenced in Section 2.4 by Garrick & Wood (1986) for determining the components of asphalts and crude oils. This is produced verbatim from Research Paper RP1387, National Bureau of Standards, U.S. Department of Commerce (Vol. 26, Journal of Research of the National Bureau of Standards, May 1941).

METHOD FOR DETERMINING THE COMPONENTS OF ASPHALTS AND CRUDE OILS

By O. G. Strieter

ABSTRACT

The ordinary procedure for the analysis of asphalts, which uses petroleum naphtha and carbon bisulfide as solvents, does not yield satisfactory results. Recently it has been found that by substituting pentane for the petroleum naphtha and ether for the carbon bisulfide, accurately reproducible results can be obtained for the content of asphaltenes, resins, and the oily constituents.

1.0 Introduction

The components of asphalt, according to Marcusson, are the asphaltic acids and their anhydrides, oily constituents, resins and asphaltenes. The asphaltic acids and their anhydrides are determined by saponifying with cold and hot alcoholic potash, respectively, but owing to the formation of troublesome emulsions and to the fact that they are present in the asphalt only in small amounts, their determination is usually omitted, so the ordinary procedure is:

1. The asphaltenes are precipitated with 88° Bé petroleum naphtha.
2. The petroleum naphtha filtrate, which contains the oily constituents and the resins, is reduced in volume by evaporation and then is completely absorbed by fuller's earth.
3. The oily constituents are extracted from the fuller's earth with petroleum naphtha.
4. After the oily constituents are removed from the fuller's earth, the resins are extracted with carbon bisulfide or benzol.

Petroleum naphtha is not a definite compound, but a mixture of hydrocarbons that varies with the nature of the crude petroleum from which it is obtained. A naphtha that consists chiefly of hydrocarbons of the paraffin series will precipitate the asphaltenes more completely than will a naphtha of the same boiling range but composed of naphthenes and aromatics. The revised method substitutes n-pentane for the petroleum naphtha. Because n-pentane is of nearly constant composition, it has the advantage over petroleum naphtha that different lots of it will precipitate the same percentage of asphaltenes from a given sample of asphalt or crude oil. In addition, because it is a paraffin hydrocarbon, it will precipitate the asphaltenes almost completely, and will give more accurate results than are possible to get with petroleum naphtha.

For the extraction of the resins from the fuller's earth, the revised method substitutes ethyl ether for the carbon bisulfide or benzol ordinarily used. On a given sample, it was found that extraction of the resins with carbon bisulfide yielded 8.3 percent and with benzol 13.2 percent, but extraction with ethyl ether according to the revised procedure yielded 22.7 percent. In these cases, the sums of the components of the asphalt when using carbon bisulfide, benzol, and ether, were 88.1, 94.7, and 99.4 percent respectively.

2.0 Revised Procedure

Weight 5.000 g of asphalt in small pieces on a tared watchglass and transfer to a 400-ml wide-mouthed Erlenmeyer flask. Add 100 ml of normal pentane, and rotate the Erlenmeyer flask until the asphalt is partially disintegrated. Add an additional 75 ml of pentane, and again rotate until the asphalt is completely disintegrated. Then add 50 ml of pentane, lightly cork the flask, and allow to settle overnight.

2.1 Asphaltenes

Filter the pentane solution through a tared Gooch crucible, with slight suction. Catch the filtrate, without attempting to transfer all the asphaltenes to the Gooch crucible, in a 600-ml beaker under a bell jar. Wash the residue in the flask and on the crucible with successive small portions of pentane until the filtrate is colorless. Dry the Gooch crucible in an oven at 105°C, cool in a desiccator, and weigh. Dissolve in carbon tetrachloride the residue adhering to the walls of the Erlenmeyer flask, and transfer the solution to a 250-ml beaker. Evaporate to dryness by allowing the beaker to stand in a warm place, dry at 105°C and weigh. The combined weights of the residue divided by 5 and multiplied by 100 gives the percentage of asphaltenes.

2.2 Oily Constituents

Allow the filtrate containing the oily constituents and the resins (600-ml beaker) to evaporate slowly to dryness at room temperature under the hood. Wash the sides of the beaker with pentane, and dissolve the residue in a total volume of 25 ml of pentane.

To the 25-ml pentane solution in the 600-ml beaker add 20 g of fuller's earth which passes a 100-mesh screen and thoroughly mix with a steel spatula. Add 15 g of 30- to 60-mesh fuller's earth, and mix with the finer fuller's earth to make the latter more porous.

Transfer the fuller's earth mixture, not too wet but before it becomes dusty, to a Soxhlet extraction thimble (43 mm in diameter and 123 mm high). Plug the top of the thimble with cotton to prevent washing the fuller's earth out of the thimble during the subsequent extraction. Let the thimble with its contents stand for 4 hours, then place it in a Soxhlet extraction apparatus, cover with pentane, and allow the thimble to soak overnight. Then extract for an additional 6 hours. (Place glass beads in the distilling flask to prevent bumping). Transfer the pentane solution, a little at a time, to a 250-ml beaker and evaporate at room temperature under the hood. The beaker must never be more than half-filled, otherwise the evaporation of the pentane will cause the oily constituents to creep over its rim. Place the beaker on the steam-bath and then in an oven at 105°C to drive off the last traces of pentane, cool in a desiccator, and weigh. The weight of the oily constituents divided by 5 and multiplied by 100 gives the percentage of them in the sample. The oily constituents should be amber colored. If darker they must be treated again with fuller's earth and re-extracted.

2.3 Asphaltic Resins

After the removal of the oily constituents, extract the fuller's earth in the thimble with ethyl ether in the manner described for the oily constituents. Evaporate the ether solution to dryness, heat in an oven at 105°C, cool, and weigh. The weight of the residue divided by 5 and multiplied by 100 gives the percentage of asphaltic resins.

3.0 Analytical Data

Table C-1 illustrates the type of analytical results obtained with the revised method, using pentane and ether as solvents.

The results given in Table C-1 are the average of two determinations. The duplicate asphaltene determinations varied by less than 0.3 percent. The maximum difference between determinations of the oil constituents was 1.5 percent and of the resins, 1.0 percent.

TABLE C-1. COMPOSITION OF FOUR ASPHALTS DETERMINED BY THE REVISED METHOD

Components	A	B	C	D
Asphaltenes	40.1	48.3	36.7	44.9
Oil Constituents	41.0	33.2	40.0	39.0
Resins	18.2	17.8	22.7	15.5
Total	99.3	99.3	99.4	99.4

The revised method is applicable not only to asphalts but to crude oils as well. Hence, every crude oil can be classified with respect to the proportion of asphaltenes, resins, and oily constituents that it contains. This is illustrated by the analysis of various crude oils as shown in Table C-2. In this table the percentages of the oily constituents were obtained by difference. The oily constituents of the crude oils are volatile and so can not be determined directly without a slight change in technic.

TABLE C-2. ANALYSIS OF CRUDE OILS BY THE REVISED METHOD

Specimen	Source	Asphaltenes	Oily Constituents	Resins
1.	Arkansas	% 4.3	% 79.9	% 15.8
2.	Texas	7.2	76.6	16.2
3.	"	5.5	80.7	13.8
4.	"	7.7	77.9	14.4
5.	California	6.7	74.7	18.6
6.	"	17.5	63.7	18.8
7.	"	9.8	75.4	14.8
8.	Kentucky	0.1	95.8	4.1