[redacted]

FOREWORD

Public Law 102-240, the Intermodal Surface Transportation Efficiency Act (ISTEA) of 1991, directed the Federal Highway Administration in Section 6016 to enter into a 5-year contract research program with the Western Research Institute (WRI) of the University of Wyoming. The title of this research program is Fundamental Properties of Asphalts and Modified Asphalts, Contract No. DTFH61-92-C-00170. As part of this contract, "Fundamental Properties of Asphalts and Modified Asphalts – Volume II – Final Report: New Methods" is hereby presented.

This report presents 10 new test methods developed during a comprehensive study of the physical and organic chemistry of petroleum asphalts. The comprehensive study is reported in Volume I of this report. The mission of the study was to improve the Long Term Pavement Performance (LTPP), predictability of asphalts by developing an understanding of effects of differing chemical reactions on the physical properties of asphalts in pavements. The new test methods that were developed during this project are reported in this volume in a ready-to-use format. This report is of interest to asphalt users who want to improve the selection of asphalts for roadway construction, to producers to improve the predictability of their products, and to highway research personnel who seek to develop more distinctive test methods to classify asphalts by their long-term performance characteristics. This report also contains modifications of six test methods that were in use before the beginning of this study. Some test results obtained after the submission of Volume I of this report for review also are described here.

T. Paul Teng

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Director, Office of Infrastructure
Research and Development

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16. Abstract

Sixteen new methods that distinguish behavioral characteristics of compositionally diverse petroleum asphalts were developed or refined into new methods during this project. These methods include an automated Heithaus titration (AHT), high performance liquid chromatography/size exclusion chromatography (HPLC/SEC), large scale plant mix simulation (after the German rolling flask method), modulated differential scanning calorimetry (MDSC) to predict low temperature properties, fast ion exchange chromatography, asphalt aging using a microwave oven, non-aqueous potentiometric titration (NAPT) for acids in asphalt, supercritical fluid extraction (SFE) of asphalt concrete cores, a shale oil modified asphalt demonstration site near Jackson, Wyoming, effects of moisture on rheology and aging of asphalt, ion exchange chromatography of asphalts using inexpensive resins, precipitation of waxes from asphalt neutrals, mastics penetration test, fast inverse gas liquid chromatography to predict long term aging, multiple size exclusion chromatography (SEC) to improve definition of associated materials, and a sliding plate microviscometer using aggregate plates to examine asphalt thin film behavior.

This volume is the second in a series. The other volume in the series is:
FHWA-RD-99-212 Volume I: Interpretive Report

Authors: Raymond E. Robertson, Jan F. Branthaver, P. Michael Harnsberger, J. Claine Petersen, Samuel M. Dorrence, John F. McKay, T. Fred Turner, A. Troy Pauli, Shin-Che Huang, Jung-Do Huh, Jane E. Tauer, Kenneth P. Thomas, Daniel A. Netzel, Francis P. Miknis, Theresa Williams, John J. Duvall, F. Alan Barbour, Christine Wright, Stephen L. Salmans, and Alana F. Hansert

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SI* (MODERN METRIC) CONVERSION FACTORS

APPROXIMATE CONVERSIONS TO SI UNITS

Symbol	When You Know	Multiply By	To Find	Symbol
		LENGTH		
in	inches	25.4	millimeters	mm
ft	feet	0.305	meters	m
yd	yards	0.914	meters	m
mi	miles	1.61	kilometers	km
		AREA		
in^2	square inches	645.2	square millimeters	mm^2
ft^2	square feet	0.093	square meters	m^2
yd^2	square yards	0.836	square meters	m^2
ac	acres	0.405	hectares	ha
mi^2	square miles	2.59	square kilometers	km^2
		VOLUME		
fl oz	fluid ounces	29.57	milliliters	mL
gal	gallons	3.785	liters	L
ft^3	cubic feet	0.028	cubic meters	m^3
yd^3	cubic yards	0.765	cubic meters	m^3

NOTE: Volumes greater than 1000 l shall be shown in m^3.

Symbol	When You Know	Multiply By	To Find	Symbol
		MASS		
oz	ounces	28.35	grams	g
lb	pounds	0.454	kilograms	kg
T	short tons (2000 lb)	0.907	megagrams (or "metric ton")	Mg (or "t")
		TEMPERATURE (exact)		
°F	Fahrenheit temperature	5(F-32)/9 or (F-32)/1.8	Celcius temperature	°C
		ILLUMINATION		
fc	foot-candles	10.76	lux	lx
fl	foot-Lamberts	3.426	candela/m^2	cd/m^2
		FORCE and PRESSURE or STRESS		
lbf	poundforce	4.45	newtons	N
lbf/in^2	poundforce per square inch	6.89	kilopascals	kPa

APPROXIMATE CONVERSIONS FROM SI UNITS

Symbol	When You Know	Multiply By	To Find	Symbol
		LENGTH		
mm	millimeters	0.039	inches	in
m	meters	3.28	feet	ft
m	meters	1.09	yards	yd
km	kilometers	0.621	miles	mi
		AREA		
mm^2	square millimeters	0.0016	square inches	in^2
m^2	square meters	10.764	square feet	ft^2
m^2	square meters	1.195	square yards	yd^2
ha	hectares	2.47	acres	ac
km^2	square kilometers	0.386	square miles	mi^2
		VOLUME		
mL	milliliters	0.034	fluid ounces	fl oz
L	liters	0.264	gallons	gal
m^3	cubic meters	35.71	cubic feet	ft^3
m^3	cubic meters	1.307	cubic yards	yd^3
		MASS		
g	grams	0.035	ounces	oz
kg	kilograms	2.202	pounds	lb
Mg (or "t")	megagrams (or "metric ton")	1.103	short tons (2000 lb)	T
		TEMPERATURE (exact)		
°C	Celcius temperature	1.8C + 32	Fahrenheit temperature	°F
		ILLUMINATION		
lx	lux	0.0929	foot-candles	fc
cd/m^2	candela/m^2	0.2919	foot-Lamberts	fl
		FORCE and PRESSURE or STRESS		
N	newtons	0.225	poundforce	lbf
kPa	kilopascals	0.145	poundforce per square inch	lbf/in^2

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* SI is the symbol for the International System of Units. Appropriate rounding should be made to comply with Section 4 of ASTM E380.

(Revised September 1993)

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LIST OF ABBREVIATIONS

The abbreviations listed below are what are commonly known as acronyms. Symbols for scientific terms (e.g., V for volts, η for viscosity, etc.) or chemical formulae are not included. Neither are abbreviations used to describe models of commercial equipment. The Strategic Highway Research Program (SHRP) asphalts are described by a three letter code system usually followed by a hyphen and number (AAA-1, AAB-1, etc.) and are not considered to be acronyms. The SHRP aggregates are described by a two letter code (RA, RB, etc.). With the exception of such widely used acronyms as SHRP, United States (U.S.), and WRI (Western Research Institute), the terms that the acronyms refer to are spelled out on first use in each chapter of this report.

AAT	Advanced Asphalt Technologies
AASHTO	American Association of State Highway and Transportation Officials
AHT	automated Heithaus titration
ASTM	American Society for Testing Materials
ATR	attenuated total reflectance
CRM	crumb rubber modifier
DAD	diode array detector
DRID	differential refraction index detection
DSC/MDSC	differential scanning calorimetry/modified differential scanning calorimetry
EPA	U. S. Environmental Protection Agency
ETG	Expert Task Group
FHWA	Federal Highway Administration
FTIR	Fourier transform infrared
GRF	German rolling flask
HPLC/SEC	high pressure liquid chromatography/size exclusion chromatography
IEC	ion exchange chromatography
IGLC	inverse gas-liquid chromatography
KDOT	Kansas Department of Transportation
LVDT	linear variable differential transformer
MGRF	modified German rolling flask
MSD	molecular size distribution
NAPT	non-aqueous potentiometric titration
NCE	Nichols Consulting Engineers
NIST	National Institute of Standards and Testing
NR	natural rubber
PAV	pressure aging vessel
RAP	recycled asphalt pavement
RBF	round bottom flask
RI	refractive index
RTFO/PAV	rolling thin film oven/pressure aging vessel
SFE	supercritical fluid extraction
SHRP	Strategic Highway Research Program

LIST OF ABBREVIATIONS (continued)

SOM	shale oil modifier
SOMAT	shale oil modified asphalt
TBAH	tetrabutyl ammonium hydroxide
TFO/PAV	thin film oven/pressure aging vessel
THF	tetrahydrofuran
UV	ultraviolet
WFLHD	Western Federal Lands Highway Division

PROJECT MANAGEMENT

The project management at Western Research Institute was as follows: Dr. Raymond E. Robertson, Principal Investigator; Dr. Jan F. Branthaver, Co-Principal Investigator for chemical studies; P. Michael Harnsberger, Co-Principal Investigator for physical property studies; Dr. J. Claine Petersen, Consultant; Dr. Samuel M. Dorrence, Technical Administrator for Subcontracts; Jane E. Tauer, Computerized Database Manager; David C. Coletti, Subcontract Manager; Dawn K. Geldien, Program Administrator; and Jackie Greaser, Project Secretary.

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INTRODUCTION

Several new methods and unique applications of existing methods were developed during this project. In many cases these methods have shown that the important role of asphalt composition on pavement performance is overlooked in the current Superpave® binder specification. Physical properties of binders that are graded alike by Superpave® were observed to change unpredictably when exposed to any of a variety of service conditions. This volume presents detailed operating instructions for use of the newly developed and the modified existing methods. Also included is a considerable amount of information supplementary to what is given in Volume I. Some of the methods are briefly described below. Full details are given in separate chapters.

A new version of the Heithaus titration test, used to study the compatibility characteristics of asphalt, has been developed into an automated, closed system. This new method is less operator dependent, less sensitive to crude source than the original method, and insensitive to air oxidation.

The HPLC/SEC was developed to obtain SEC chromatograms of asphalts and asphalt-like materials very rapidly. The method requires toluene as the carrier and the results can be obtained in terms of gravimetric data and/or differential refractive index data. The column combination in use has an effective separation range of around 1,200 to 14,000 daltons. This extends measurement of molecular weight into the range of the molecular associations present in asphalts.

The introduction of modulated differential scanning calorimetry (MDSC) to the study of asphalts has improved the understanding of the complex thermal behavior of asphalts near their glass transition. It is now possible to deconvolute end points for the overlapping thermal phenomena of many asphalts and to predict the glass transition temperature at different lengths of time after storage at low temperature.

The "fast" IEC technique requires much less resin than the conventional IEC separation and is, therefore, both much faster and less expensive than the conventional method. A 2-gram sample of asphalt is separated by each run and this is enough to acquire "fingerprint" IEC data.

The rolling thin film oven test (RTFOT) is the current standard for plant mix aging simulation used in the Superpave® binder specification. However, the RTFOT produces small amounts of aged asphalts among several bottles and the recovery of material is somewhat tedious. At the request of the FHWA Superpave® binder expert task group (ETG), the German Rolling Flask method was scaled up and developed into a method that gives a 190-gram single sample of aged asphalt that is essentially identical to material produced by RTFOT. The method was presented to and accepted by the Chair of the binder ETG.

A uniaxial constitutive model of nonaging asphalt-aggregate mixtures has been developed to predict hysteretic stress-strain behavior of asphalt concrete under different loading histories, varying rates of loading, different modes-of-loading (controlled-stress vs. controlled-strain), various stress-strain amplitudes, and the beneficial effects of healing during random rest periods.

The technique of supercritical fluid extraction (SFE) was examined as an alternate method to isolate screenable aggregate from asphalt-aggregate mixtures without the use of hydrocarbons or chlorinated hydrocarbon solvents. This continuous extraction method uses the environmentally friendly, dischargeable supercritical fluid carbon dioxide as the extraction solvent. Unfortunately, the dissolution kinetics and equilibria are unfavorable for "complete" extraction of asphalt from aggregate.

A nonaqueous potentiometric titration (NAPT) method was developed for the semi-quantitative analysis of acids in asphalt. This method can be used to measure quantities and strengths of acids in whole asphalt. Some, but not all, asphalts have been shown to contain small amounts of newly formed, very strong acids after the asphalts were oxidized. The method is fast (30 minutes/sample), user-friendly, and repeatable.

The Kansas Department of Transportation developed a microwave method, with partial support from this contract, to oxidatively age asphalts. The method requires use of a controlled-power microwave unit and operates at elevated pressure. The current version of this method generates aged asphalts that have the same properties as PAV-aged asphalts. The microwave method requires about 7 hours whereas the PAV requires 20 hours. This method is published as a Kansas DOT report.

NEW METHODS DEVELOPED DURING FHWA CONTRACT DTFH61-92C-00170

METHOD 1. THE AUTOMATED HEITHAUS TITRATION TEST (AHT W/ TITRANT)

ABSTRACT

The Heithaus test, which models asphalt explicitly as a colloidal system, was developed in the early 1960's by J. J. Heithaus [Heithaus 1960] to study compatibility characteristics of petroleum residua used in the roofing industry. Since then, the Heithaus test has found use in the paving industry as a method to study rutting propensity and oxidative age hardening. The original method, which suffered from operator dependency and poor data repeatability, has recently been automated. The automated Heithaus titration (AHT) test is based on light transmitting/scattering detection of the onset of flocculation using ultraviolet (UV)-visible spectrophotometry. The AHT test has been found to significantly reduce operator dependency and improve data repeatability, in some cases, by an order of magnitude. As a result of the improved repeatability of data, Heithaus parameters are found to measure physical properties that relate to rheological properties of asphalt.

INTRODUCTION AND APPLICABILITY

Historically, asphalts have been classified into gel-type asphalts and sol-type asphalts [Traxler 1961]. Gel-type asphalts usually are characterized by non-Newtonian rheological behavior, relatively low variation of viscosity with temperature, and low ductility. Sol-type asphalts exhibit more Newtonian rheological behavior, are highly temperature susceptible, and are more ductile. The two classifications represent extremes, and most asphalts are of intermediate nature. Sol-type asphalts have been designated as compatible asphalts, while gel-type asphalts have been designated as incompatible asphalts.

The terms "compatible" and "incompatible" (or sol-gel) arose from what became known as the colloidal model of asphalt structure. This model considers asphalts to be dispersions of what are termed "micelles," consisting of polar, aromatic molecules in viscous oils. The degree to which the so-called "micelles" form extended gel structures (which can be broken up by heat and shear) will determine the relative degree of compatibility. In a compatible asphalt, the dispersed materials are believed to be well peptized by the solvent, either because the dispersed materials are small in amount and/or tend not to form strong associations, and/or because the solvent effectively disperses the "micelles." In an incompatible asphalt, associations of dispersed materials presumably are more extensive and are not so efficiently peptized by the solvent.

The colloidal model has been subjected to much criticism in recent years. The principal objection is that there is no evidence for "micellar" structures, either classical or inverse, in asphalts. The term "micelle," which implies existence of a separate phase with distinct boundaries, may be inappropriate. Recently, a microstructural model of asphalt structure has been proposed [SHRP 1994a], and has been refined in this program (Volume I, chapters 1, 3, and 4). In this model, associations of polar, aromatic molecules of varying sizes are considered to be dispersed in a solvent moiety composed of less polar, relatively small molecules. However, no distinct phase boundaries are believed to be present. Regardless of the validity of the model, the concept of compatibility as a measure of mutual miscibility of different chemical components of asphalts is useful. Compatible asphalts differ from incompatible asphalts in their physical properties and therefore may be expected to behave differently in pavements. Changes in the degree of compatibility often have opposing effects on important performance related properties. For example, a change that may result in better rutting resistance may also result in more embrittlement resulting from oxidative age hardening. Thus, compromises in compatibility are sometimes necessary for optimum overall pavement performance.

Asphaltenes are solid materials that precipitate when asphalts are treated with solvents such as n-pentane, n-hexane, n-heptane, iso-octane, etc. Maltenes are the components of asphalts not precipitated by the above alkane solvents. Asphaltenes are more aromatic than maltenes and contain more heteroatoms. Thus intermolecular interactions are more extensive in asphaltenes than in maltenes. This is reflected in the greater molecular weights of asphaltenes compared with maltenes [Koots and Speight 1975]. In the colloidal model of asphalt structure, asphaltenes are believed to correspond to the dispersed materials and maltenes to the solvent. Therefore, asphaltenes will be mainly responsible for the internal structure of asphalts and will dominate many physical properties [Boduszynski 1981]. Thus the amount of asphaltenes in an asphalt is one measure of compatibility. Compatible asphalts will have smaller amounts of asphaltenes than incompatible asphalts. The ease with which asphaltenes are dispersed is dependent on their peptizability and on the dispersing power of maltenes. Oxidative aging of an asphalt would be predicted to influence compatibility by formation of polar molecules, which results in more extensive molecular associations, but also may result in a better solvent.

The best known measurement of compatibility of asphalts that takes all the above factors into account is the Heithaus test [Heithaus 1960, 1962]. Heithaus observed that for straight-run asphalts, measuring asphaltene contents provided a reasonably good estimate of compatibility. However in blended asphalts from different sources, weight-averaging asphaltene contents did not provide reliable estimates of compatibility. It proved necessary to test each blend and develop a different method that took into consideration factors other than asphaltene content. In Heithaus' original "classical" test, solutions of various concentrations containing different weights of asphalt (W_a) dissolved in a constant volume of solvent (V_S), e.g., toluene, are titrated with normal alkane solvents, e.g., n-heptane, until flocculation (asphaltene precipitation) is observed. Flocculation is detected by spotting a drop of the solution onto filter paper, resulting in an observable phase separation of precipitated material from material remaining in solution, or by use of a microscope, where precipitated material is directly observed. The volume of titrant (V_T) required to initiate flocculation in each solution is used to determine flocculation ratios (FR), calculated as $FR = V_S/(V_S + V_T)$. Values of flocculation ratio are plotted versus dilution concentration (C), calculated as $C = W_a/(V_S + V_T)$ and a best fit straight line connecting the points is extrapolated to the x and y-axes. The x and y intercepts determined from the extrapolation, referred to as the dilution concentration minimum (C_{min}) and the flocculation ratio maximum (FR_{max}), respectively, are used to calculate three Heithaus parameters, defined below. The theoretical significance of the quantity C_{min} is that it is the quantity of titrant (n-heptane for the classical method) that would be just enough to cause asphaltene precipitation in the neat asphalt, undissolved in toluene, assuming it would be possible to do so. FR_{max} is a measure of the solubility parameter, δ (see discussion in Volume I, chapter 3), at which asphaltene flocculation occurs in the asphalt as a whole. Thus, the Heithaus method measures some fundamental properties of asphalts and blends that asphaltene concentration values do not measure.

The Heithaus parameters are: $p_a = 1 - FR_{max}$, which measures the peptizability of the asphaltene fraction; $p_o = FR_{max}(C_{min}^{-1} + 1)$, which measures the solvent power of the maltene fraction, and $P = p_o/(1 - p_a)$, which measures the overall compatibility of the asphalt. Larger values of p_a, p_o, and P represent peptizable asphaltenes, maltenes that are a good solvent, and a compatible asphalt overall. Smaller values of p_a, p_o, and P represent the reverse. The p_a and p_o values do not necessarily vary directly with one another among asphalts. An asphalt may be composed of asphaltenes that are not readily peptizable, but which are dispersed in maltenes that have good solvent characteristics, or the reverse.

The method is tedious and yields highly variable results with waxy asphalts, so a study of asphaltene flocculation behavior to develop an improved compatibility test was implemented. As a result, an automated Heithaus titration procedure was developed [Pauli 1996], based on a method published by Hotier and Robin [1983] for determining asphaltene precipitation characteristics. The advantages of the automated method are that it monitors asphalt flocculation by observing sharp changes in transmittance at 740 nm of the solution being titrated and is not as operator dependent as the original method. The automated Heithaus method may be used for the testing of neat asphalts, asphalt crossblends, and oxidatively aged asphalts.

It has been speculated that the Heithaus asphaltene peptizability parameter p_a may be related to asphalt rheological properties in terms of the Pal-Rhodes equation. A detailed discussion, presented in chapter 3 of Volume I, suggests that p_a values directly measure the volume fraction (α) of the continuous (maltene "solvent") phase immobilized by the flocs of solvated asphaltene particles in an asphalt. Thus, reasonable Pal-Rhodes solvation parameters (K_S) values (which measure the size of the solvation shell, and may be related to the stability of the asphalt system), may be determined based on p_a data.

STANDARD OPERATING PROCEDURE

Apparatus

Equipment

Hach DR/3000 UV-visible spectrophotometer
(Hach Co., P.O. Box 389, Loveland, CO 80539-0389)

Spectra-Physics SP4270 integrator
(Spectra-Physics Inc., 5475 Kellenberger Rd., Dept. TR, Dayton, OH 45424)

ChronTrol®, Model XT-4 power switch timer
(ChronTrol Corp., 9675 Business Park Avenue, San Diego, CA 92131)

two CGS® 200 mL water jacketed reaction vessels
(CGS/Thermodynamics, 123 Willowbrook Lane, Willowbrook Industrial Park, West Chester, PA 19380)

two FMI® metering pumps, Models: QG-50 w/ R405 pump head (circulation pump; P1) & QG-20 w/ RH00 pump head (titrant dispersion pump; P2)
(Fluid Metering, Inc., 29 Orchard St., P.O. Box 179, Oyster Bay, NY 11771)

two Magnetic stirring plates

NesLab RTE-110 Temperature controlled circulating water bath
(NesLab Instruments, Inc., 25 Nimble Hill Rd., Newington, NH 03801)

Starna® 0.1 mm pathlength flow cell
(Starna Cells, Inc., P.O. Box 1919, Atascadero, CA 93423)

30 mL vials adaptable to Teflon® flow cell cover (figure 1-1)
(VWR Scientific Products Corp., P.O. Box 1002, So. Plainfield, NJ 07080)

0.056 cm ID (0.022") and 0.159 cm ID (1/16") Viton® tubing
(VWR Scientific Products Corp., P.O. Box 1002, So. Plainfield, NJ 07080)

Reagents

Toluene LC grade (VWR Scientific Products Corp., P. O. Box 1002, So. Plainfield, NJ 07080)

Iso-octane (2,2,4-trimethylmethane) LC grade (EM Sciences, P. O. Box 70, Gibbstown, NJ 08027)

Configuration

Figures 1-1 and 1-2 show a schematic of the apparatus used currently to perform automated Heithaus titration tests. Power supplies running from the spectrophotometer, integrator, and water bath, circuits A, B, and C respectively, are connected to a ChronTrol® power switch timer. This permits programmable activation of the instruments. Two CGS® 200 mL reaction vessels with water jackets arranged in series are attached to the water inlet and outlet of the NesLab RTE-110 circulating water bath. An FMI® metering pump, Model QG-50 w/ R405 pump head (P1) is connected to the Starna® 0.1 mm pathlength flow cell (housed inside of the spectrophotometer) via a 15 cm long, 0.159 cm (1/16") ID piece of Viton® tubing. A second and third piece of 0.159 cm (1/16") ID Viton® tubing, 10 cm and 20 cm long, respectively, extend from the metering pump and from the flow cell to a 30 mL reaction vial screwed into a

Teflon® cover. The reaction vial w/ Teflon® cover is positioned inside of one of the CGS® 200 mL water jacketed reaction vessels (WJ2, figures 1-1 and 1-2). A second FMI® metering pump (P2), Model QG-20 w/ RH00 pump head (titrant dispersion pump) is connected to the other CGS® 200 mL water jacketed reaction vessel, which acts as a titrant reservoir (TR, figure 1-2), via a 25 cm long piece of 0.056 cm (0.022") ID Viton® tubing. A second, 20 cm long piece of 0.056 cm (0.022") ID Viton® tubing extends from the titrant pump (P2), through a predrilled hole in the Teflon® cover to the reaction vial positioned inside of a CGS® 200 mL water jacketed reaction vessel (WJ2).

Setup

The spectrophotometer, temperature bath, and integrator are activated (circuits A, B and C) at least 1 hour before testing of samples begin. All three devices are connected to a ChronTrol® power switch timer and may be activated by typing "**CIRCUIT**", "**1**", and "**ON**", "**CIRCUIT**", "**2**", and "**ON**", and "**CIRCUIT**", "**3**", and "**ON**"on the ChronTrol power switch timer key pad.

The temperature bath is set to a temperature of 25°C (77°F). Fine tuning of the temperature control may be required once the temperature of the water bath has stabilized (approximately 1 hour).

LC-grade iso-octane (titrating solvent) is added to the titrant reservoir (TR, figure 1-2). The level of titrating solvent is added to within 1 cm of the top of the reservoir. Titrant is added to the reservoir prior to activation of the water bath, allowing the titrant to come to temperature equilibrium.

The spectrophotometer and integrator parameters are set once the spectrophotometer has warmed up. The UV-visible spectrophotometer is set in percent transmittance detection mode by depressing "**4**", "**signal**", and the "**%T**" keys on the spectrophotometer soft key pad. The wavelength selection knob is set to λ_D (nm) = 740 nm. The zero scale and full scale settings of the spectrophotometer are initially set at 0 percent transition and 10 percent transition, respectively, by depressing the following keys on the soft key pad of the spectrophotometer:

"**zero**", "**0**", and "**full**", "**1**", "**0**".

(NOTE: The full scale and zero scale settings may need to be reset for each sample, depending on the sample response once testing has begun.)

The spectrophotometer signal average is set to 10 by keying in:

"**signal**", "**1**", "**0**".

The integrator, when activated, prompts the user for the date and time. Once the date and time are entered the following settings are entered on the soft key pad:

"shift", **"shift"**, **"P"**, "W", "=", **"shift"**, **"2"**, **"0"**, **"0"**, "enter", which sets the peak width to 200,

"shift", **"shift"**, **"P"**, **"T"**, "=", **"shift"**, **"1"**,**"0"**, **"0"**, "enter", which sets the peak threshold to 100,

"atten", **"1"**, **"0"**, **"2"**, **"4"**, "enter", which sets the attenuation to 1024, and

"chtsp", **"1"**, **"enter"**, which sets the chart speed to 1.0 cm/min.

The following procedure is used to re-zero the spectrophotometer relative to a toluene reference blank prior to sample testing. Two 30 mL vials are taped together and toluene is added to one of the vials. The two taped-together vials are placed in a ring stand clamp next to the solution circulating pump (P1). Toluene is drawn from the first vial and deposited into the second (empty) vial, via Viton® tubing attached to the circulating pump (P1, figure 1-2). When approximately one half of the toluene has been pumped into the second (empty) vial, the "re-zero" key on the spectrophotometer key pad is depressed. The reading on the spectrometer should read 100.0 percent transmittance, and may fluctuate; ± 0.5 percent transmittance. During the re-zeroing of the spectrophotometer, the solution circulating pump (P1) is adjusted to a flow rate of 8 mL/min. The end of the Viton® tubing in the vial containing toluene is removed and the circulating pump system is pumped clear of solvent.

Sample Preparation

Samples of asphalt are weighed into 30 mL vials adaptable to a custom design Teflon® cover (figure 1-1). Care should be taken during weighing not to deposit asphalt on the sides of the vials. Two sets of the following sample weights are prepared; 0.200 g, 0.400 g, 0.600 g, and 0.800 g (all ± 0.002 g). The actual measured weight of each sample, measured to an accuracy of ± 0.0002 g, is recorded in a notebook under the heading W_a. Samples are labeled: *Operator initials; notebook number; page number; sample set letter; sample number.* Several sets of samples may be weighed into vials at one sitting. If dry samples are to be stored for any length of time, i.e., more than a day, they should be capped under a blanket of argon gas.

Samples to be tested within 1 day of weighing are dissolved in 1.000 ± 0.002 mL of LC-grade toluene, which is added to each vial using a 2.500 ± 0.002 cc syringe. The volume of solvent added to each sample is recorded in the notebook under the heading V_S. Approximately 1 to 2 hours may be required to completely dissolve all samples at room temperature.

(NOTE: Samples dissolved in solvent should be tested on the same day they are prepared.)

Testing (Procedure)

Sample runs are performed by loading vials (30 mL) of sample into the second water jacket (WJ2), generally from least to most concentrated in solution, by carefully placing a small stir bar into a vial of the solution and screwing the vial into the Teflon® cover. The vial/cover is placed into the second water jacket (WJ2). The two ends of the Viton® tubing, which run from the circulating pump (P1) and from the flow cell, respectively, are placed through holes in the cover down into the solution. As the asphalt solution circulates through the flow cell, the percent transmittance reading of the spectrophotometer decreases, then stabilizes at some minimum value of percent transmittance, corresponding to the percent of light transmitted through a solution of asphalt in toluene with no titrant added. One end of the Viton® tubing running from the titrant pump (P2) is placed down into the vial well above the surface of the asphalt solution. A probe thermometer (not shown in figures 1-1 and 1-2) is also placed down into the test solution and used to monitor the temperature of the solution as the titration proceeds. To begin the titration, the titrant pump (P2) and the integrator are started at the same time. As the titration proceeds a flocculation peak develops. The initial increase in percent transmittance (%T) of the flocculation peak plotted as a function time in which titrant is added at a constant flow rate is due to the dilution of the test solution as iso-octane is added. During this time period dispersed phase molecular associations remain in solution. A maximum %T value is then reached and the integrator prints out a retention time. The %T value versus time plot then decreases due to the scattering of light as dispersed phase molecular associations begin to precipitate from the test solution. The flocculation onset point is then taken as the retention time value recorded at maximum %T. At the flocculation onset point the temperature of the solution is recorded. Figure 1-3 shows a plot of percent transmittance versus time for a flow rate of υ_T (mL/min) for four samples of SHRP core asphalt AAD-1 dissolved in toluene at four different concentrations. At the completion of a run, the Viton® tubing running from the circulating system is drawn up out of solution and the remaining solution in the circulating system is pumped out into the sample vial. The tubing is then placed into a vial containing toluene. Clear toluene is circulated through the pump (P1), tubing, and flow cell clearing the system. The Viton® tubing running from the titrant pump (P2) is placed into the top of a graduated cylinder and the flow rate of the titrant is timed with a stop watch. A second sample is then loaded into the system and the procedure is repeated.

When testing is completed, all glassware used during the procedure is rinsed with wash toluene and allowed to dry in a vented hood. The circulation pump is flushed with fresh LC-grade toluene, pumped dry of solvent, and all components of the system are shut down.

Data Calculation

Sample weights, W_a (g)
Volume of solvent (toluene), V_S (mL)
Detection wavelength, λ_D (nm)
Titrant flow rate, υ_T (mL/min)
Retention time at peak apex (flocculation onset), t_R (min)
Solution temperature at flocculation onset, T_{sln} (°C)

The volume of titrant (V_T, mL) added to each sample to initiate flocculation is calculated as the product of the time (reported as the peak retention time t_R, min) required to deliver titrant at a flow rate of υ_T (mL/min) to the test solution. V_T (mL) is calculated as follows:

$$V_T = t_R \upsilon_T \qquad (1\text{-}1)$$

Values of V_T, V_S, and W_a are used to calculate flocculation ratios and dilution ratio concentrations, FR and C, for each run (which consists of a set of test solutions of different concentrations of a given asphalt) using the following relationships;

$$FR = \frac{V_S}{V_S + V_T} \tag{1-2}$$

and

$$C = \frac{W_a}{V_S + V_T} \tag{1-3}$$

A linear analysis is used to derive the equation for the line FR = aC + b using values of FR_i plotted versus values of C_i . Heithaus parameters are calculated by extrapolating the line to the x and y axis, where the x and y intercepts are formally referred to as the dilution ratio minimum (C_{min}) and the flocculation ratio maximum (FR_{max}), respectively:

$$b = FR_{max} \ @ \ C = 0 \tag{1-4}$$

and

$$-\frac{a}{b} = C_{min}^{-1} \ @ \ FR = 0 \tag{1-5}$$

Using values of FR_{max} and C_{min}, Heithaus parameters p_a, p_o, and P are calculated as follows:

$$p_a = 1 - FR_{max} \tag{1-6}$$

$$p_o = FR_{max} \left[\left(\frac{1}{C_{min}} \right) + 1 \right] \tag{1-7}$$

$$P = \frac{p_o}{1 - p_a} \tag{1-8}$$

Precision

Table 1-1 lists Heithaus parameters, their averages, and standard deviations measured using the automated method (AHT with titrant iso-octane) for an incompatible asphalt, AAD-1, and for a compatible asphalt, AAG-1, with two different operators. Standard deviations in Heithaus parameters p_a, p_o, and P measured in four different experiments for asphalt AAD-1 were found to be 0.002, 0.01, and 0.03, respectively. Standard deviations in Heithaus parameters p_a, p_o, and P measured in four different experiments with two different operators for asphalt AAG-1 were found to be 0.003, 0.02, and 0.07, respectively. For comparison, standard deviations in Heithaus parameters calculated for the same two asphalts using the original method were found to be 0.01, 0.02, and 0.04 for AAD-1, and found to be 0.03, 0.08, and 0.4 for AAG-1, constituting almost an order of magnitude improvement in precision using the automated method. These results must be tempered with the observation that the standard deviations calculated for data obtained using the original method are based on experiments where n-heptane was used as the titrating solvent. Consequently, this point may be considered moot based on the finding that Heithaus parameters, specifically p_a values measured using iso-octane as titrant, are found to relate to asphalt rheological properties in terms of the Pal-Rhodes model (Volume I, chapter 3, section 1).

Results and Discussion

Identification of Variables Influencing Test Repeatability and Operator Dependence

It has been determined that the spot test, used as the method for detecting the onset of flocculation in the classical procedure, is the most probable cause of operator error. The spot test is performed by removing several drops of sample from the test solution and spotting them onto filter paper over the course of the experiment. The appearance of the spot test method is that of a brown circle with a darker brown circle inside of the first circle. Often the contrast between these two spots is difficult to resolve at the flocculation onset, thus different operators will judge the flocculation onset at different times by adding more titrant to the solution, effectively "over shooting" the end point. It is speculated that removal of drops of solution from the sample for the purpose of spot testing also introduce error into the measurement. Both of the problems encountered with the "classical" method are overcome in the automated method, where the test solution is in a closed solution circulating system, and the onset of flocculation is detected using light transmitting/scattering spectrophotometry.

Both titrant flow rate and flow rate consistency in the automated procedure influence data repeatability for the following reasons. First, titrant flow rate consistency is necessary for accurately calculating values of titrant volume (V_T). Flow rate consistency of ± 0.005 mL/min over a complete testing period (e.g., several weeks) has been achieved using a dispersion pump. Second, the actual rate of titrant flow will affect data repeatability because titrant flow rates that are too fast may result in the onset of flocculation being missed. Also, the potential to flocculate only a part of the solution is greatly increased, a condition referred to as premature flocculation. Finally, very slow titrant flow rates limit the number of samples that may be tested in a given period of time. A maximum titrant flow rate was determined from a simple experiment where a

1.0000 g ± 0.0002 g sample of SHRP core asphalt AAM-1 was dissolved in 1.000 mL ± 0.005 mL toluene. As the sample was circulated through the flow cell/UV visible detection system, a 1.000 mL ± 0.005 mL aliquot of iso-octane was rapidly (2 to 3 seconds for addition of iso-octane) added to the solution with the percent transmittance response to the addition of the 1.000 mL of iso-octane plotted on a stripchart recorder. It was observed that the percent transmittance response of the 1.00 g/mL asphalt in toluene solution to a 1.000 mL addition of iso-octane required approximately 2.0 minutes to achieve a stable percent transmittance reading. Figure 1-5 shows the plot that was recorded on a stripchart recorder where percent transmittance is plotted as a function of the time required for the sample to come to light transmitting equilibrium. From this plot a maximum flow rate of 0.5 mL/min (i.e., 1.000mL/~2 min, figure 1-5) was decided upon. In the present test method, the titrant flow rate ranges between 0.330 mL/min and 0.380 mL/min, with a flow rate tolerance of ± 0.005 mL/min.

Constant temperature control of test solutions in the automated procedure is important for obtaining repeatable data. An asphalt solution is maintained at a constant temperature of 25.0°C ± 0.1°C (77.0°F ± 0.1°F) by using a probe thermometer that is placed down into the test solution and adjusting the water bath temperature as needed. Sample stirring rate consistency is also accounted for. All samples are stirred at a constant rate of 2 revolutions/second to adequately homogenize the solution but not to heat the solution to any appreciable degree.

Finally, replacing n-heptane with iso-octane (2,2,4-trimethyl pentane) as the titrant of choice is important for obtaining repeatable data, in that highly compatible asphalts, e.g., AAM-1, AAG-1 and AAC-1 were difficult, and in the case of AAM-1 impossible to titrate using n-heptane as the titrating solvent. This is because AAM-1 has almost no n-heptane asphaltenes. Iso-octane, however, precipitates enough asphaltenes from AAM-1 so that flocculation is detectable. It was also observed that automated Heithaus titration experiments performed using iso-octane as the titrating solvent are less susceptible to temperature fluctuations that may occur in the system during testing. Furthermore, based on the aforementioned assumption that p_a directly measures the volume fraction of solvent (α) immobilized by the solvated particles, the use of iso-octane in deriving p_a values may be theoretically supported (chapter 3, Volume I).

AHT with Titrant Iso-Octane Testing of 19 SHRP Core and Non-Core Asphalts

Table 1-2 lists Heithaus parameters p_a, p_o, and P measured in duplicate for 19 SHRP asphalts using the automated Heithaus titration test for asphalt/toluene solutions titrated with iso-octane. An average titrant flow rate (υ_T) of 0.35 ± 0.01 mL/min and an average solution temperature at the flocculation onset (T_{sln}) of 25.0 ± 0.2°C (77 ± 0.4°F) are applicable to all 38 sets of tests that were performed. From the data in table 1-2, p_a (asphaltene peptizability parameter) values were found to range from 0.576 for asphalt AAE-1 to 0.902 for asphalt AAM-1. Values of p_o (maltene solvent power parameters) were found to range from 0.56 for asphalt ABM-1 to 1.52 for asphalt AAE-1, and values of P (state of peptization parameters) were found to range from 2.32 for asphalt AAF-1 to 7.96 for asphalt AAM-1. Table 1-3 lists average values in p_a, p_o, and P, calculated from table 1-2 and n-heptane asphaltene natural abundance levels. Table 1-4 lists rankings of 19 SHRP asphalts from low to high in values of p_a, P, p_o, and n-heptane asphaltene natural abundance levels. Asphalts listed in table 1-4 are ranked from least to most compatible in terms of the natural asphaltene abundance levels starting with AAM-1 (least amount of asphaltenes-compatible) followed by AAG-1, etc., and ending with incompatible asphalts AAD-1 and AAE-1. Asphalts in terms of P values are ranked somewhat differently, starting with AAM-1 followed by AAG-1, etc., but ending with AAW-1 and AAF-1. Thus the Heithaus test does not merely duplicate information that could be obtained simply by precipitating asphaltenes.

Based on these results, it is of interest to note characteristics of the air blown asphalt AAE-1. Asphalt AAE-1, which is ranked 19th (incompatible) in terms of asphaltene content and ranked 1st in terms of p_a (least peptizable asphaltenes), is ranked as a compatible asphalt in terms of its P value (P-ranked 13th). The higher p_o-ranking of AAE-1 may suggest that the air blowing process improves the solvent power of the maltenes resulting in a compatible system, even though the asphaltenes are difficult to disperse. Data from oxidatively aged asphalts obtained by AHT also show an increase in p_o, suggesting that the air blowing process would have a similar effect on the asphalt as does oxidative aging (see below).

Asphalts AAG-1, ABD, and ABM-1 were compared based on the rankings in table 1-4. Asphalt ABM-1, which is a replacement for asphalt AAG-1 (AAG-1 is lime treated ABD), is p_a-ranked similarly to AAG-1. On the other hand, ABD is p_a-ranked much lower. It is further observed that ABM-1 is p_o-ranked lower than either AAG-1 or ABD. In fact ABM-1 is shown to have the poorest solvent based on its p_o value. Based on these observations, the p_o value would appear to influence the overall value in P for ABM-1, designating it much less compatible compared with AAG-1 and ABD. When solutions of AAG-1 and ABM-1, prepared in toluene, are visually inspected, undissolved material, probably lime, is observed in ABM-1 samples but not in AAG-1 samples. Furthermore, the asphaltene content of ABM-1 (7.7 percent by mass) is not much different compared with AAG-1 (5 percent) or ABD (7 percent). It is speculated that the low P-value of ABM-1 (incompatible), which is largely influenced by the poor solvent power of the maltenes, is a result of the excess amount of lime present in the asphalt.

AHT with Titrant Iso-Octane Testing of TFO-PAV Oxidatively Aged SHRP Core Asphalts

Figures 1-6 and 1-7 show plots of Heithaus parameters p_a, p_o, and P measured using the AHT with iso-octane method versus aging time for TFO/PAV aged SHRP core asphalts AAD-1 (aged up to 20 hr) and AAM-1 (aged up to 50 hr) at 100°C (212°F), respectively. It is observed in figure 1-6 (asphalt AAD-1) that the line of a third order polynomial, which is used to connect the data points, shows an inflection in the line for all three parameters after approximately 15 hr aging. Figure 1-7, oxidatively age hardened AAM-1, shows an inflection of the line for values of p_a, and p_o after approximately 20 hr aging. It has been observed that the inflection of these lines corresponds to the sulfoxide production "spurt" observed by Petersen et al. [1996] (and discussed at length in chapter 4, Volume I) for the same two asphalts aged at the same temperatures. It has been speculated, based on the assumption that p_a measures α (the volume fraction of immobilized solvent within a floc), that the p_a versus aging time curves reflect the small increase in amount and size of asphaltene flocs as a consequence of oxidation of solvent to produce more resins and asphaltenes. This results from direct conversion of non-polar maltenes into polar resins and asphaltenes and further immobilization of solvent from the continuous phase. Further, it is observed that the changes in p_o (the solvent power of the maltenes) more strongly influence the overall change in the asphalts' state of peptization (P) over longer periods of aging. Based on the above observations it is speculated that the production of sulfoxides improves the compatibility of an asphalt, but ketone production may not. This hypothesis is based on the observation that values of P begin to decrease after the initial spurt when ketones begin to form in large quantities.

AHT with Titrant Iso-Octane Testing of Blends of TFO/PAV Oxidatively Aged SHRP Core Asphalts with Neat SHRP Core Asphalts

Mixtures of aged asphalt blended with neat asphalt were prepared in an attempt to simulate the effects of adding fresh asphalt to recycled asphalt to develop a method to predict changes in compatibility of recycled asphalt paving materials (RAP) presently used in roadway construction. Mixtures of aged AAD-1 with neat AAG-1 were prepared by weighing 10 g of neat AAG-1 and 0.5 g to 2.5 g of aged AAD-1 to a large petri dish. The petri dish was gently heated on a hot plate to soften both materials. Once heated, the materials were mixed together with a spatula, allowed to cool and then weighed out in sample sets for AHT testing. Figure 1-8 shows plots of Heithaus parameters p_a, p_o, and P, measured using the AHT (with iso-octane), versus mass percent of 144 hr, 60°C (140°F) TFO/PAV age hardened SHRP core asphalt AAD-1 mixed with neat SHRP core asphalt AAG-1. In these plots, 0 mass percent data corresponds to 100 percent neat AAG-1 (no aged AAD-1 added), and 100 mass percent data correspond to 100 percent aged AAD-1. Other mixtures range from 4.85 to 33.3 mass percent aged AAD-1 per total mass of sample. The most striking observation is that the numerical values of the Heithaus parameters p_a and P decrease, and the numerical value of p_o increases as the percentage of aged AAD-1 in the mixtures increases. Obviously as a greater amount of aged AAD-1 is added to neat AAG-1 the compatibility of the mixture (measured by P) diminishes with the greatest amount of change in P occurring in mixtures ranging between 0 percent and 35 percent in aged AAD-1. Based on these results, it is speculated that this type of study may be useful for predicting RAP mixture concentration limits and rheological properties of RAP roadways.

SUMMARY

A standard operating procedure for an automated Heithaus titration test, described above, is shown to decrease operator dependency and increase data repeatability compared with previous methods. Nineteen neat SHRP asphalts and several oxidatively age-hardened asphalts, aged using the thin film oven/pressure aging vessel (TFO/PAV) method, were analyzed using the AHT method. Data obtained from these studies have shown that changes in Heithaus parameters plotted as functions of aging time correspond to the initial spurt in oxidative aging observed by Petersen et al. [1996]. A pilot study of AHT analyses of crossblends of aged and unaged asphalts has been conducted in order to develop a method for predicting compatibility characteristics of RAP. Preliminary data obtained for crossblends of aged SHRP core asphalt AAD-1 mixed with neat SHRP core asphalt AAG-1 suggest that the method may be used in the RAP mix design recommendation process.

Table 1-1. Heithaus parameters p_a, p_o, and P measured for SHRP core asphalts AAD-1 (incompatible) and AAG-1 (compatible) for different operators using the automated Heithaus titration test for test samples titrated with iso-octane ($\upsilon_T = 0.35 \pm 0.01$ mL/min).

Asphalt	p_a	p_o	P
AAD-1	0.658	0.88	2.57
Operator 1	0.658	0.90	2.63
	0.662	0.88	2.60
	0.658	0.87	2.55
$\bar{x}$	0.659	0.88	2.59
σ	0.002	0.01	0.03
AAG-1			
Operator 1	0.802	0.80	4.03
	0.801	0.84	4.20
Operator 2	0.803	0.81	4.11
	0.808	0.79	4.11
$\bar{x}$	0.804	0.81	4.11
σ	0.003	0.02	0.07

Table 1-2. Heithaus parameters p_a, p_o, and P measured in duplicate for 19 SHRP asphalts using the automated Heithaus titration test for test samples titrated with iso-octane (AHT with titrant iso-octane, $\upsilon_T = 0.35 \pm 0.01$ mL/min).

Asphalt	p_a	p_o	P
AAA-1	0.702 0.701	0.84 0.83	2.82 2.78
AAB-1	0.693 0.701	0.91 0.84	2.95 2.81
AAC-1	0.763 0.767	0.77 0.75	3.24 3.23
AAD-1	0.662 0.658	0.88 0.90	2.60 2.63
AAF-1	0.687 0.683	0.73 0.74	2.32 2.33
AAG-1	0.798 0.836	0.69 0.70	4.03 4.20
AAK-1	0.685 0.698	1.04 0.91	3.31 3.01
AAM-1	0.901 0.902	0.79 0.73	7.96 7.50
ABM-1	0.818 0.816	0.56 0.57	3.05 3.12
ABD	0.714 0.703 0.715	1.24 1.20 1.08	4.36 4.03 3.78
AAE-1	0.609 0.576	1.19 1.52	3.04 3.58
AAH-1	0.761 0.760	0.68 0.70	2.86 2.93
AAJ-1	0.763 0.741	0.92 0.98	3.89 3.80
AAN-1	0.695 0.688	0.92 0.98	3.01 3.13
AAS-1	0.701 0.706	0.93 0.91	3.11 3.09
AAV-1	0.762 0.757	0.80 0.83	3.34 3.43

Table 1-2. Heithaus parameters p_a, p_o, and P measured in duplicate for 19 SHRP asphalts using the automated Heithaus titration test for test samples titrated with iso-octane (AHT with titrant iso-octane, $\upsilon_T = 0.35 \pm 0.01$ mL/min) (continued).

Asphalt	p_a	p_o	P
AAW-1	0.621 0.627	0.95 0.92	2.49 2.45
AAX-1	0.740 0.742	0.90 0.88	3.46 3.40
AAZ-1	0.769 0.771	0.72 0.76	3.11 3.30

Table 1-3. Average p_a, p_o, and P values and values of mass % n-heptane asphaltene content for the 19 SHRP asphalts listed in table 1-2.

Asphalt	p_a	p_o	P	Mass % n-heptane asphaltenes
AAA-1	0.701	0.84	2.80	15.8
AAB-1	0.697	0.87	2.88	17.3
AAC-1	0.765	0.76	3.23	9.9
AAD-1	0.660	0.89	2.61	20.2
AAE-1	0.592	1.35	3.31	22.9
AAF-1	0.685	0.73	2.32	13.4
AAG-1	0.802	0.82	4.12	5.0
AAH-1	0.760	0.69	2.90	15.9
AAJ-1	0.752	0.95	3.84	10.6
AAK-1	0.692	0.98	3.16	20.1
AAM-1	0.902	0.76	7.73	3.7
AAN-1	0.692	0.95	3.07	15.7
AAS-1	0.704	0.92	3.10	18.4
AAV-1	0.759	0.81	3.38	9.7
AAW-1	0.624	0.93	2.47	17.9
AAX-1	0.741	0.89	3.43	12.0
AAZ-1	0.770	0.74	3.20	9.2
ABD	0.715	1.08	3.78	7.0
ABM-1	0.817	0.57	3.09	7.7

Table 1-4. Ranking of 19 SHRP asphalts from low to high in values of average p_a, P, p_o, and in values of mass % n-heptane asphaltene content.

Ranking in p_a [1]	Ranking in p_o [2]	Ranking in P [3]	Ranking in mass % n-heptane asphaltenes
AAE-1	ABM-1	AAF-1	AAM-1 (lowest)
AAW-1	AAH-1	AAW-1	AAG-1
AAD-1	AAF-1	AAD-1	ABD
AAF-1	AAZ-1	AAA-1	ABM-1
AAN-1	AAC-1	AAB-1	AAZ-1
AAK-1	AAM-1	AAH-1	AAV-1
AAB-1	AAV-1	AAN-1	AAC-1
AAA-1	AAG-1	ABM-1	AAJ-1
AAS-1	AAA-1	AAS-1	AAX-1
ABD	AAB-1	AAK-1	AAF-1
AAX-1	AAD-1	AAZ-1	AAN-1
AAJ-1	AAX-1	AAC-1	AAA-1
AAV-1	AAS-1	AAE-1	AAH-1
AAH-1	AAW-1	AAV-1	AAB-1
AAC-1	AAN-1	AAX-1	AAW-1
AAZ-1	AAJ-1	ABD	AAS-1
AAG-1	AAK-1	AAJ-1	AAK-1
ABM-1	ABD	AAG-1	AAD-1
AAM-1	AAE-1	AAM-1	AAE-1 (highest)

[1] Asphalt AAE-1 asphaltenes least peptizable; asphalt AAM-1 asphaltenes most peptizable.
[2] Asphalt ABM-1 maltenes poorest solvent; asphalt AAE-1 maltenes best solvent.
[3] Asphalt AAF-1 least compatible; asphalt AAM-1 most compatible.

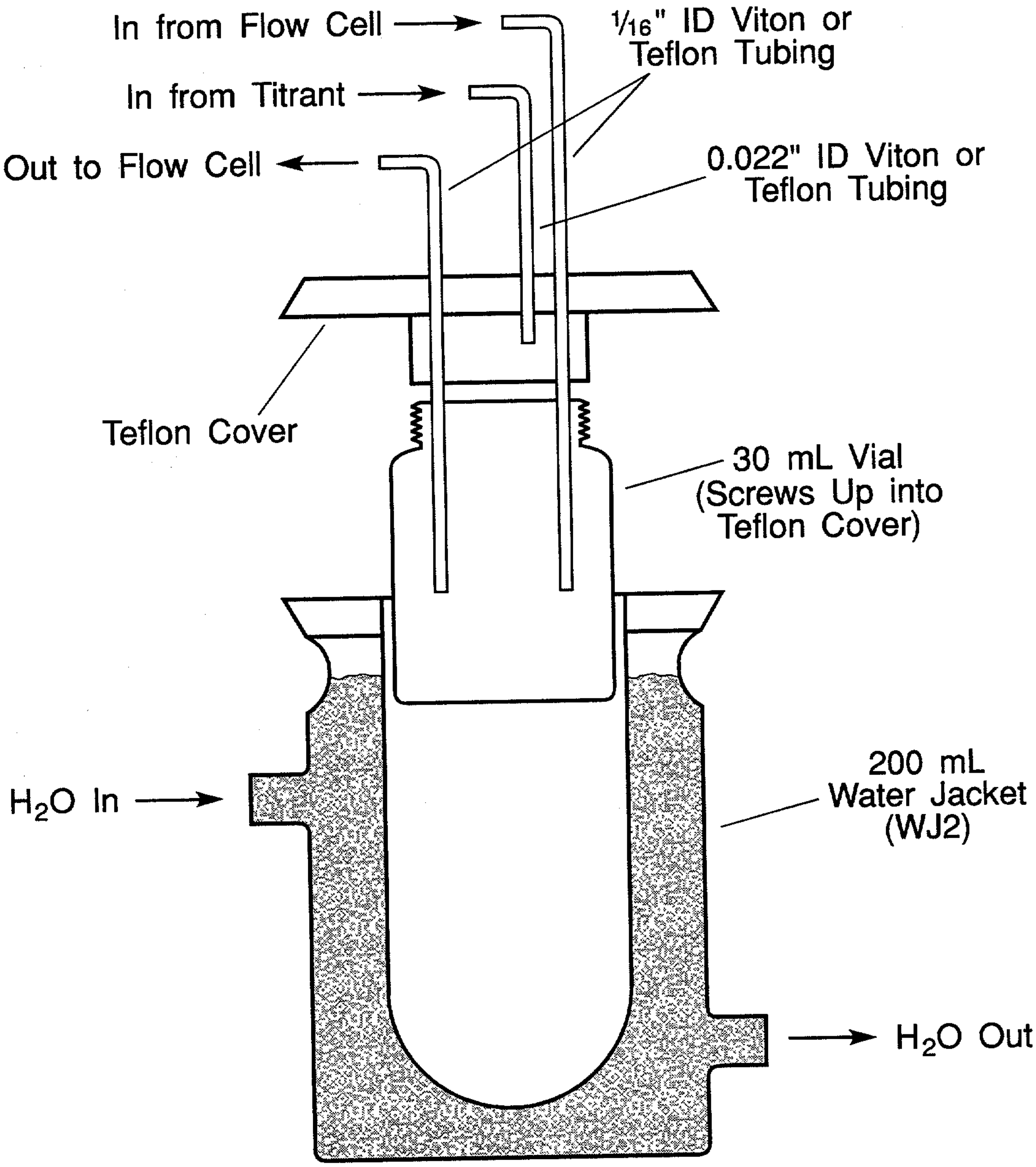


Figure 1-1. AHT w/iso-octane reaction vessel consisting of a 100 mL (optional) or 200 mL water jacket, 30 mL sample vial, and a custom designed Teflon cover/vial holder.

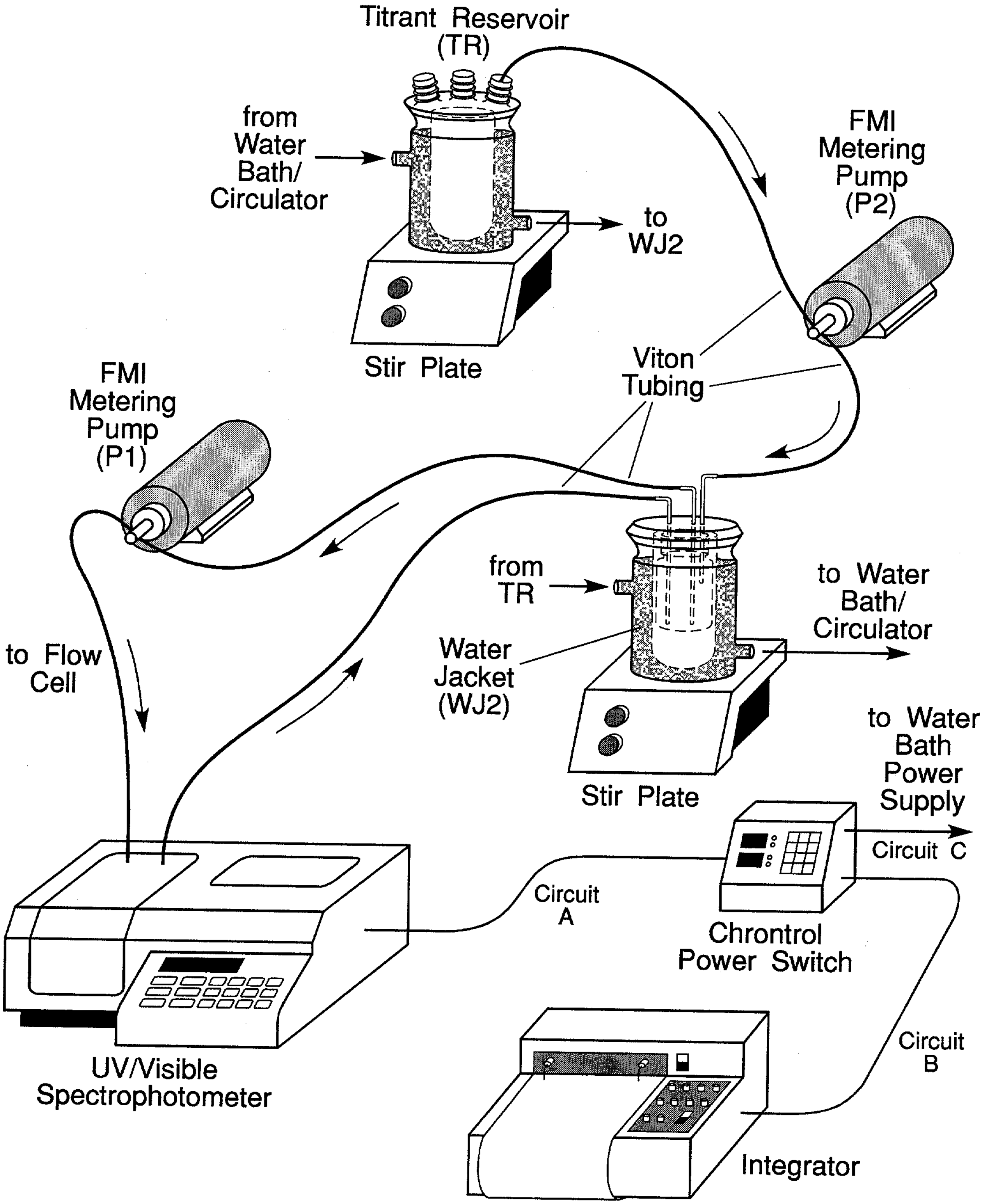


Figure 1-2. Present configuration of AHT apparatus.

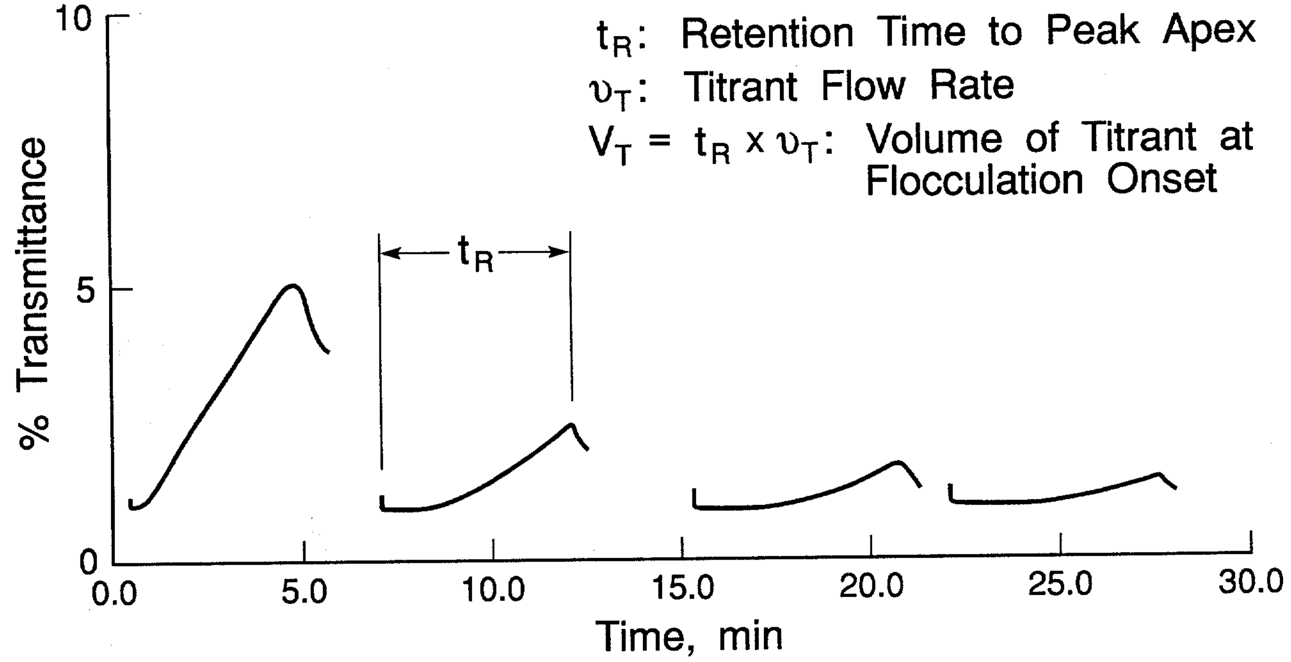


Figure 1-3. Percent transmittance versus titrant delivery time (flocculation curves) plotted for AAD-1 SHRP core asphalt solutions prepared at four different concentrations, titrated with iso-octane (titrant flow rate $\upsilon_T = 0.350 \pm 0.005$ mL/min).

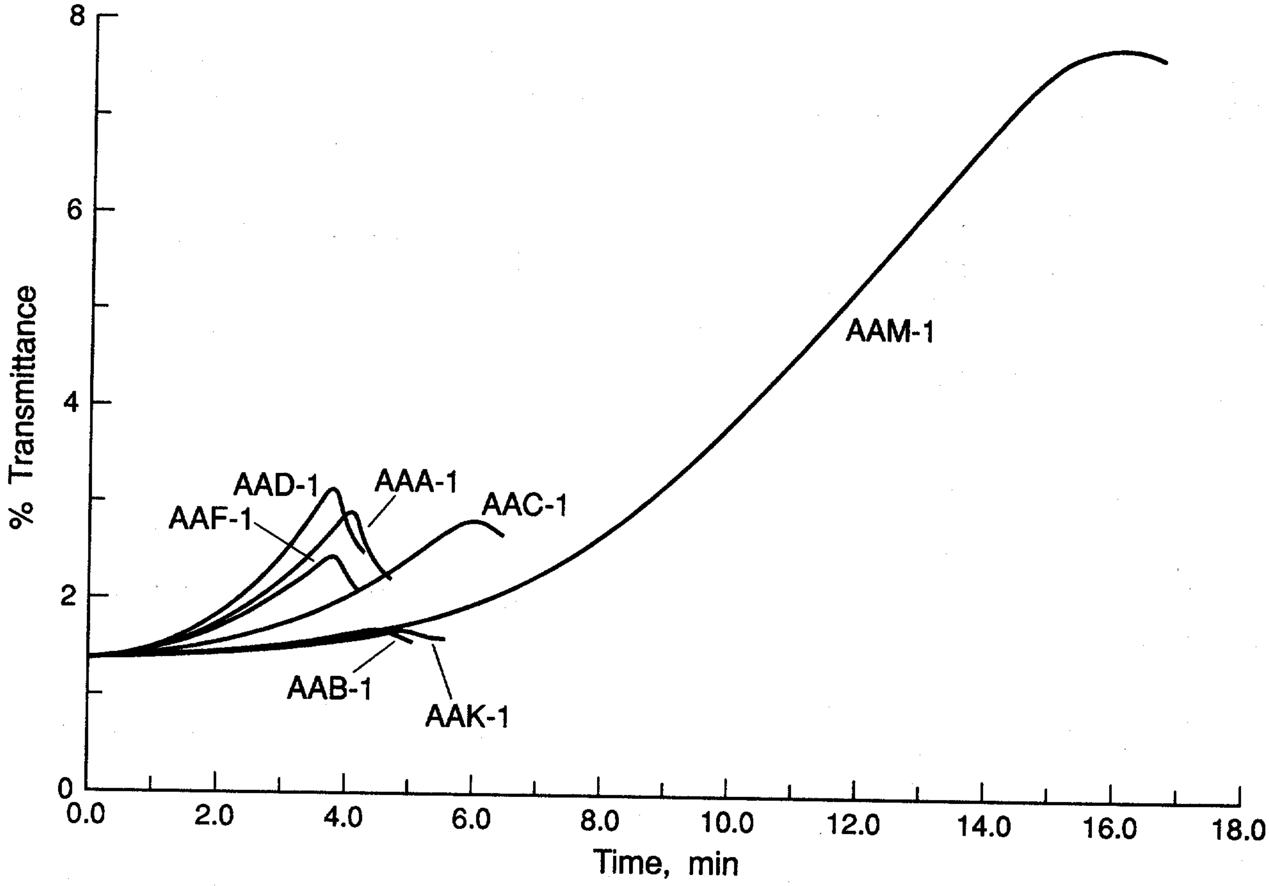


Figure 1-4. Percent transmittance versus titrant delivery time (flocculation curves) plotted for 7 SHRP core asphalt solutions prepared as 1.0000 ± 0.0005 g of asphalt dissolved in 1.000 ± 0.005 mL of toluene, titrated with iso-octane (titrant flow rate $\upsilon_T = 0.350 \pm 0.005$ mL/min).

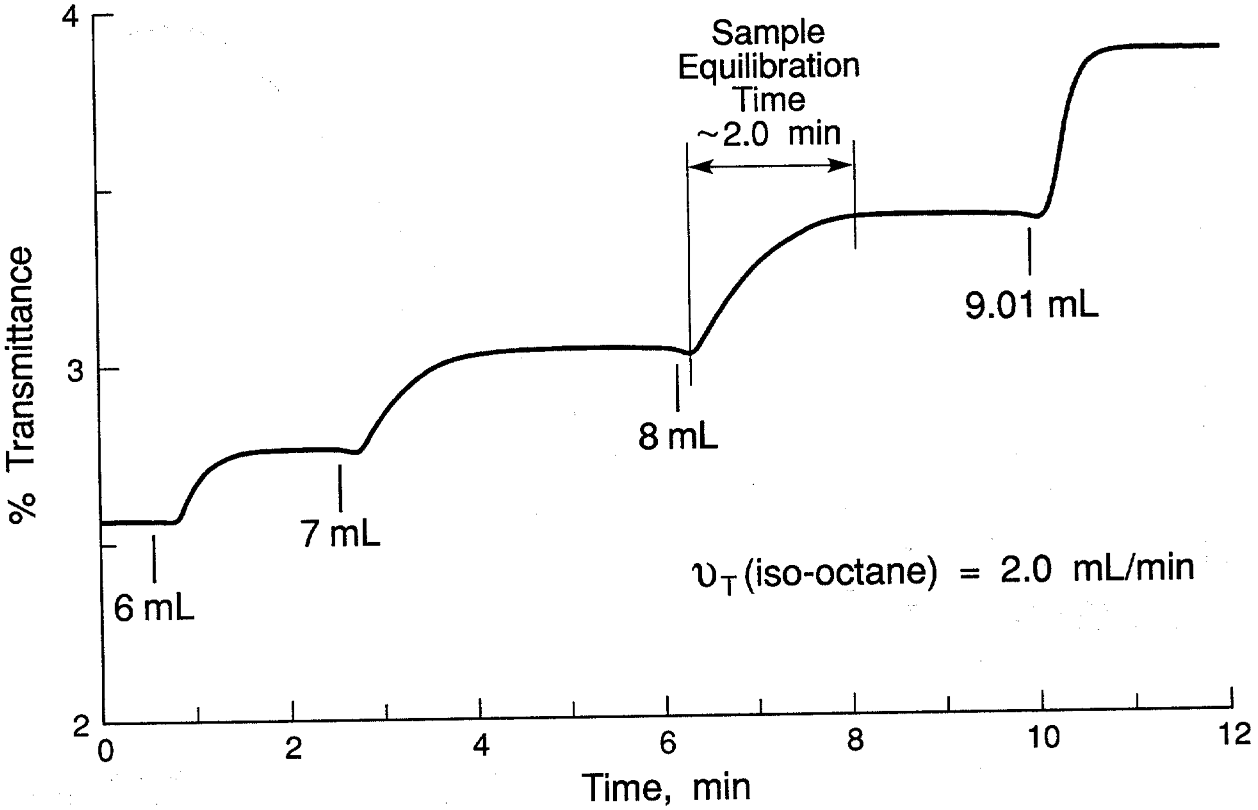


Figure 1-5. Percent transmittance versus time plotted on a strip chart recorder for a solution of SHRP core asphalt (AAM-1) dissolved in toluene, continuously circulated through a UV-visible spectrophotometric detection system as 1.0 mL aliquots of iso-octane are added intermittently.

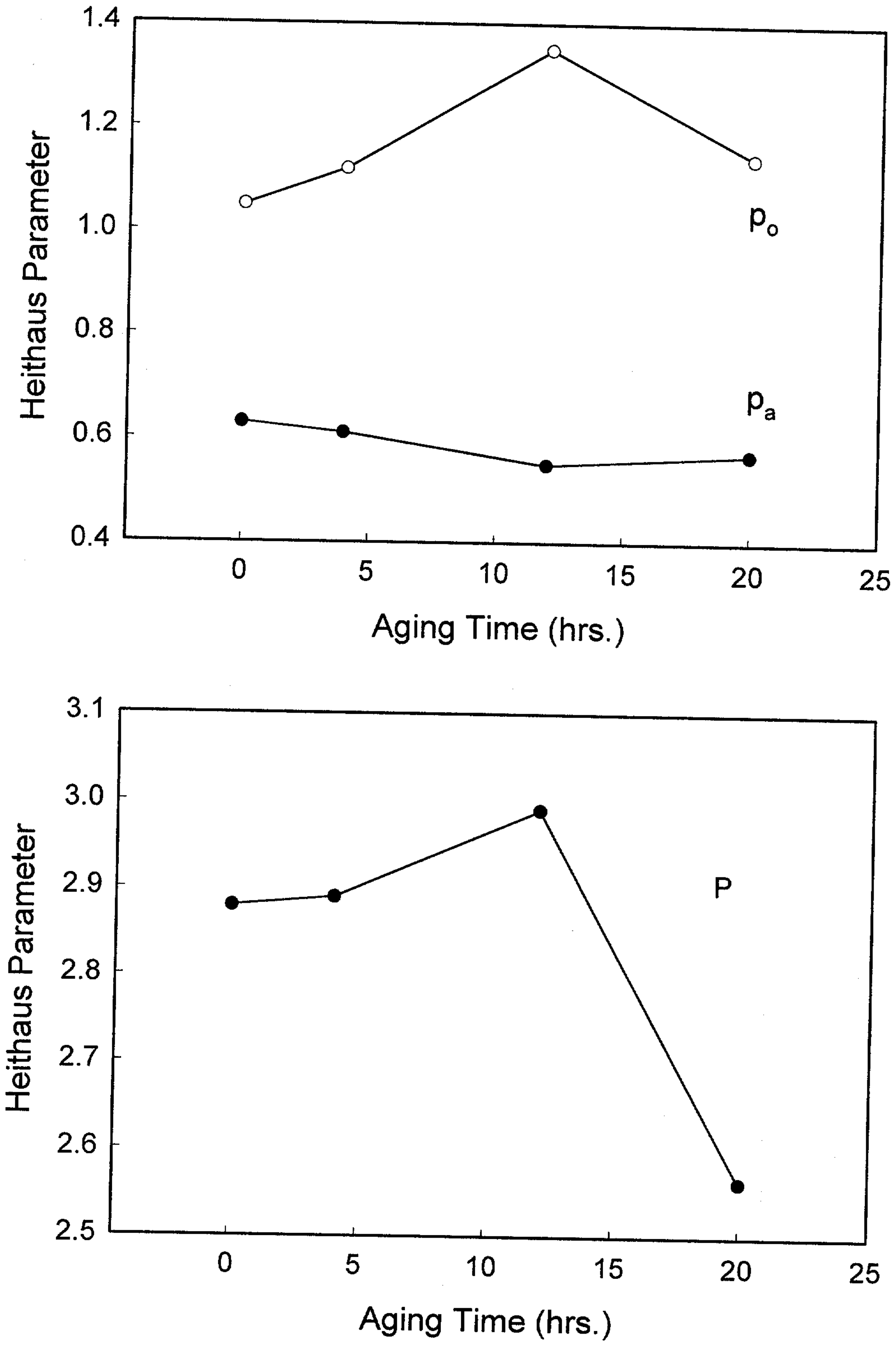


Figure 1-6. Heithaus p_a and p_o parameters and Heithaus P parameters plotted versus aging time for samples of 100°C (212°F) TFO/PAV aged SHRP core asphalt AAD-1.

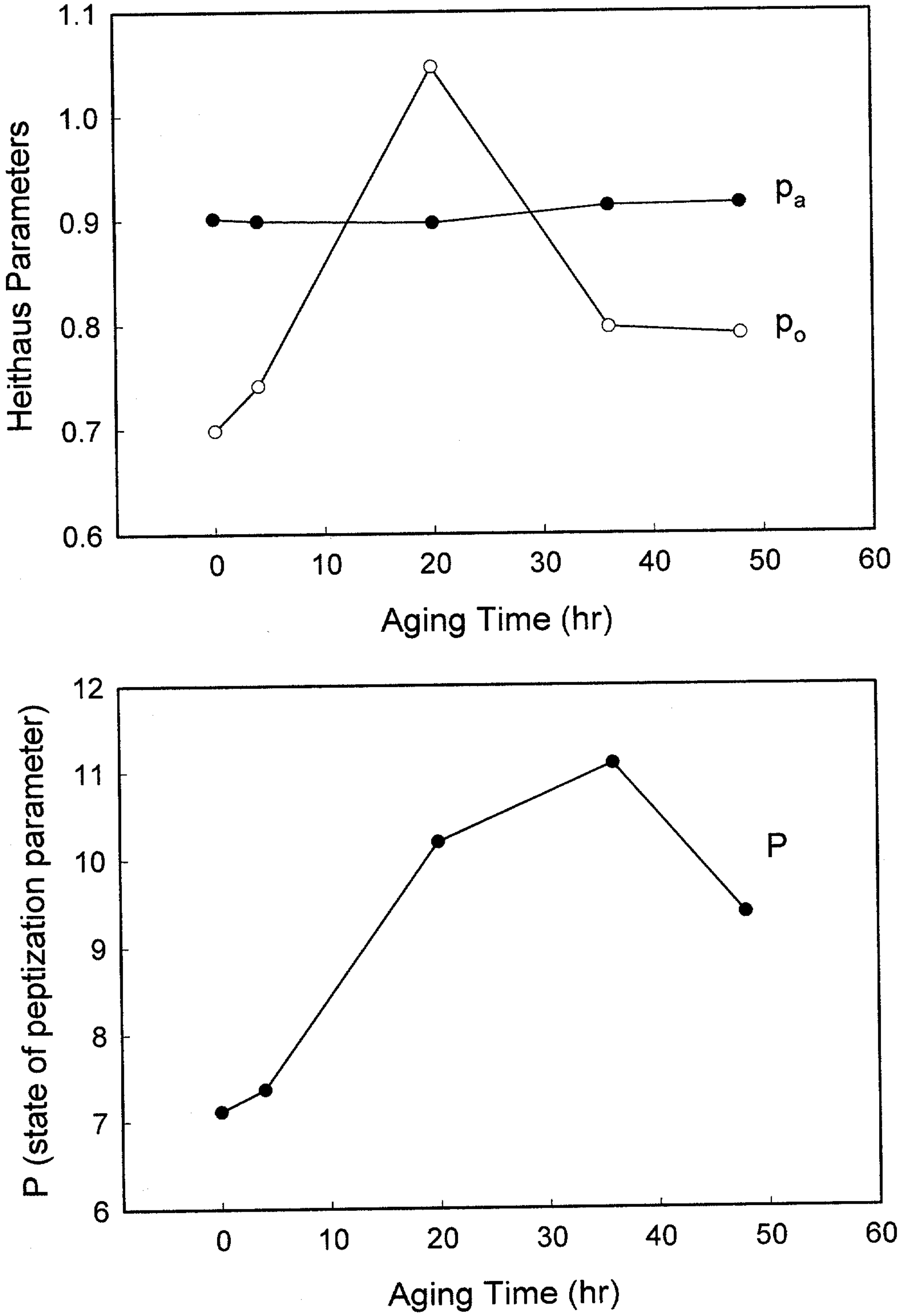


Figure 1-7. Heithaus p_a and p_o parameters and Heithaus P parameters plotted versus aging time for samples of 100°C (212°F) TFO/PAV aged SHRP core asphalt AAM-1.

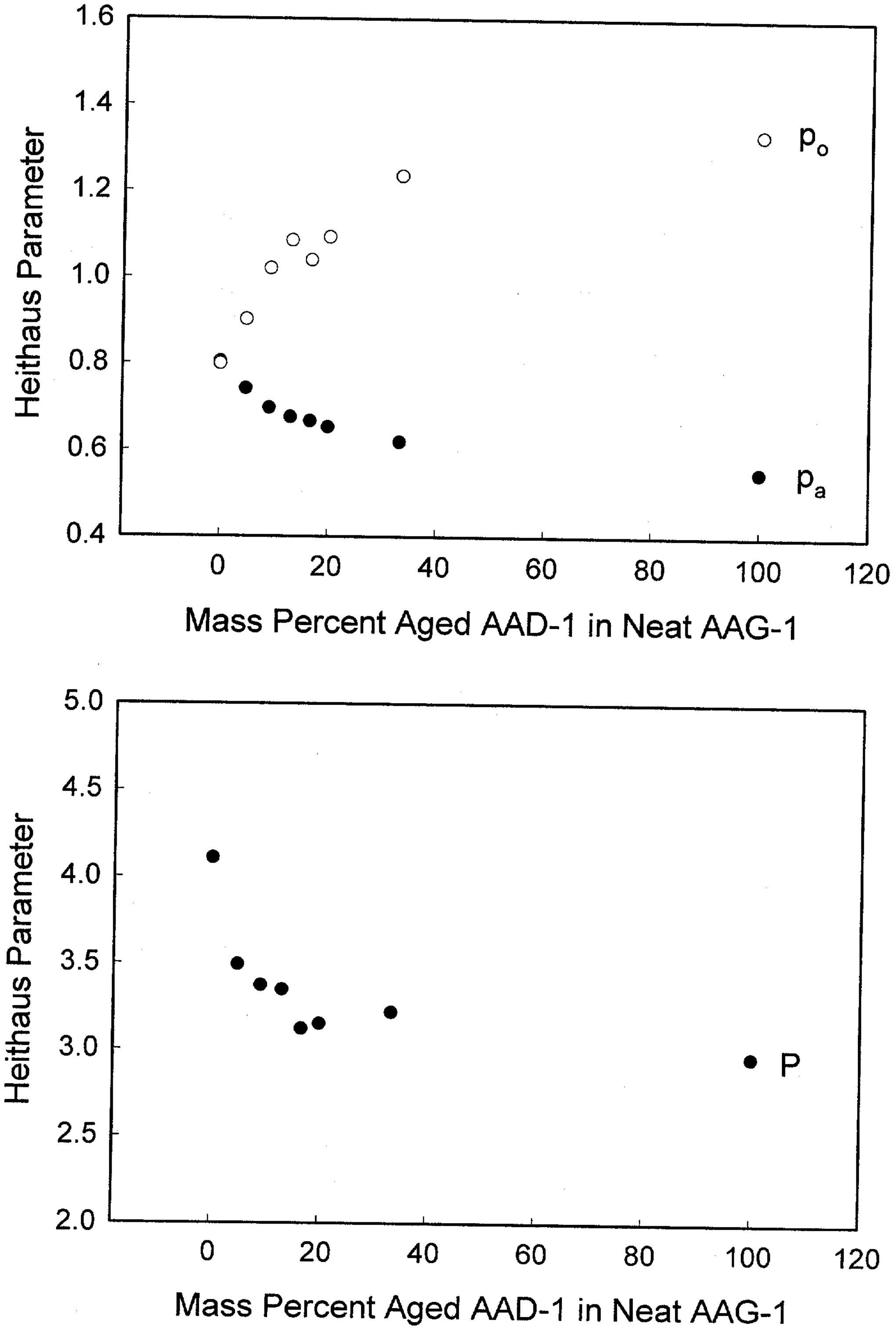


Figure 1-8. Heithaus p_a and p_o parameters and Heithaus P parameters plotted versus mass % SHRP core asphalt AAD-1 aged for 144 hr at 60°C (140°F) TFO/PAV added to neat SHRP core asphalt AAG-1.

METHOD 2. HIGH PERFORMANCE LIQUID CHROMATOGRAPHY/SIZE EXCLUSION CHROMATOGRAPHY (HPLC/SEC) ANALYSIS OF ASPHALTS

ABSTRACT

An HPLC/SEC (high performance liquid chromatography/size exclusion chromatography) technique has been developed that yields results similar to those obtained from preparative SEC. The column combination used consists of a guard column followed by two 500 Å columns followed by one 100 Å column. The columns are packed with 5 μm Phenogel® and are maintained at 40°C (104°F) with a toluene flow of 1.00 mL/min. This combination was calibrated with polystyrene standards and other compounds of known molecular weight. The technique was applied to SHRP core asphalts (both unaged and aged to three levels), mixtures of two asphalts and a potential recycling agent, and crumb rubber modified asphalts. Molecular weights of peaks and shoulders in the chromatograms obtained were estimated using the calibration curve. Molecular weight values ranged from about 100,000 daltons at signal onset to 300 or 400 daltons for the last peaks in the chromatograms and varied from asphalt to asphalt. For some asphalts, the estimated molecular weights of the earliest peaks appeared to be multiples of later peaks, indicating some type of uniform intermolecular combinations. Investigation of the crumb rubber modified asphalts, heated for various lengths of time, showed that the reaction of the two crumb rubbers investigated (one contained natural rubber and the other was a mixture of natural rubber and synthetic rubber) was asphalt and rubber dependent. The changes in the chromatograms occurred first in the highest molecular weight region with the space between that region and following regions filling in as heating time increased, indicating that the rubber originally broke down into large molecular weight fragments followed by breaking down of those fragments into lower molecular weight material.

INTRODUCTION AND APPLICABILITY

Size exclusion chromatography (SEC), also referred to as gel permeation chromatography (GPC) is a chromatographic method that separates mixtures of materials on the basis of hydrodynamic size. This occurs because the SEC column packing contains pores of various sizes that some molecules can enter and thereby be slowed in their passage through the chromatographic column. Other molecules are too large to enter the column packing pore structure and so these larger molecules pass through the column between particles of packing material. SEC has been used to analyze asphalts by a number of investigators including those using column chromatography and those using HPLC, an instrumental method. Attempts have been made to relate SEC results to physical properties; for example, Garrick [1994] developed a mathematical model from SEC data that predicts SEC profiles from physical properties of asphalts and suggests that a strong relationship exists between SEC profiles and these physical properties, especially rheological properties. Most previous investigators have used tetrahydrofuran (THF) as the carrier for HPLC systems [Donaldson et al. 1988; Jennings et al. 1991; Bishara et al. 1991; SHRP 1993a; Brûlé et al. 1994].

The method described here uses toluene as the carrier and utilizes a differential refractive index detector (DRID) to obtain chromatograms of asphalts and asphalt-like materials that simulate results obtained using the preparative SEC method [SHRP 1993a]. A fraction collector is available for determination of gravimetric results, which are required in order to replicate the preparative SEC data. Samples are weighed, dissolved (in the case of crumb rubber modified asphalts the sample/solvent mixtures are also centrifuged), filtered, and brought to volume in a volumetric flask. The samples are then injected into the HPLC system at 40°C (104°F) with HPLC grade toluene as the carrier. Sample size is 24.0 ± 0.1 mg contained in about 220 μL solution. Software is available to determine areas under the curve for any desired combination of time segments of the DRID chromatograms in order to compare asphalts and asphalt mixtures. A calibration curve was constructed so that "ballpark" estimates of molecular weights at peaks, shoulders, valleys, or any other portion of the chromatograms can be obtained. This technique is applicable to analysis of asphalts, both unaged and aged, asphalt blends, and modified asphalts including asphalt/crumb rubber mixtures. It might possibly be used to predict time to pavement failure from the increase in area, on laboratory aging, in the large molecular size region of the molecular size distribution (MSD) for individual asphalts in common usage.

PROCEDURE

Apparatus

Equipment

Hewlett Packard (HP) Series II 1090 liquid chromatograph equipped with an HP UV/visible diode array detector (DAD), pumps, an automatic injection system, and a guard column followed by two 500 Å and one 100 Å 5 μ Phenogel® columns in series.

HP Vectra 486 66U computer equipped with a Maxtor® 72004AP/A 2.0 gigabyte hard drive, a Western Digital 850 megabyte hard drive, 40 megabytes of RAM, an Irwin BACKUP 2000 Series tape drive, a 3.5" floppy drive, and a Hewlett Packard D1196A 15" Ultra VGA monitor.

Waters Associates R401 differential refractive index detector (DRID).
ISCO Foxy 200 X-Y fraction collector.
HP 35900 multichannel interface (dual analog to digital converter).
HP 1046A fluorescence detector (this item is available but not in use).
HP LaserJet IIIp printer.
Bucchi rotary evaporator.
Miscellaneous Erlenmeyer flasks, volumetric flasks, filter flasks, filters, vials, and caps.
Centrifuge capable of at least 2,000 RPM and 100 mL centrifuge tubes.

Reagents

Toluene	HPLC grade (EM Sciences, P. O. Box 70, Gibbstown, NJ 08027)

Instrument Setup

The HPLC, with its pumps, automatic injection system, column oven, and UV/visible diode array detector (DAD), is an integrated unit. The eluant stream passes from the HPLC to the DRID and thence to the fraction collector. The fraction collector is used as a solvent conservation system when not in use, that is, eluate containing sample is collected separately from eluate that does not contain sample.

The HPLC and detectors are all operated through the computer through use of HP software, called Chemstation software, supplied with the system. The DRID signal goes through the multichannel interface to the computer and the multichannel interface and the fraction collector are started by a signal from the HPLC when a sample is injected. Run conditions and the mode of data gathering from the detectors are set up through use of a "Method" and the order of sample analysis, data storage, and data file naming are set up through use of a "Sequence". Samples are run in quadruplicate in the following order: (1) an unmodified asphalt as a control or standard, (2) three "unknown" samples, (3) the unmodified control asphalt again, and repeating steps (2) and (3) until all samples have been analyzed.

The columns are placed in the HPLC with a guard column first followed by the two 500 Å columns in series followed by the 100 Å column. Toluene should be passed through the columns for 2-3 hours prior to the first sample injection of a series/sequence. This will allow the columns to adjust to solvent flow and temperature, and will allow removal of any background materials that may have collected in the columns while the system was idle.

A "Sequence", the order in which the samples are to be run, is prepared using the HP software by entering the sample names, the number of analyses per sample, the sample vial number, and the "Method" to be used with the sample and is exemplified by the following example where the sequence file name is MHSULFDE.S (see Appendix).

If desired, the software can be set up to divide the chromatograms into specific time intervals by manually entering interval start and stop times and integrals can be determined for each of those time intervals (as shown in the example "Method" above in the manual integration event table). In addition, each data file can be recalled if and when desired and reanalyzed with different parameters.

Sample runs are performed by setting up the "Method" and "Sequence" and by loading the automatic injector table with the desired sample vial(s) in the order specified in the sequence. When everything is ready, the "Sequence" is started by pressing the appropriate button (Run Sequence) using the computer. All data are stored in the computer under file names assigned by the computer according to the information entered by the operator; the only information entered in the laboratory notebook is the sample name, date, time, and data file name. A report can be printed on completion of the individual sample analysis or, for more detailed reports that require some operator interaction, printed later at the operator's discretion.

Because the samples are quite concentrated, back pressure, probably caused by adsorption of asphalt components in the frits at the ends, especially the front end, of the columns, tends to build up after about 75 to 100 runs. Cleaning is accomplished by backflushing the columns with 25 mL of a 3 percent methanol in toluene solution at 80° C (176° F) followed by about 400 mL of toluene. Several samples of an asphalt are then run using the normal procedure to condition the columns.

The column combination is calibrated by determination of retention times of several polystyrene standards with known peak molecular weights. Several other compounds of known molecular weight also may be examined.

Data Calculation

The Chemstation software was designed by HP to analyze a chromatogram according to individual peaks. That is, it looks for increases in response, for changes in slope (as at peaks and shoulders), and return to baseline. This is a well established software and is primarily used to analyze fairly simple mixtures of compounds and not complex mixtures such as asphalts. In other words, when the software analyzes a chromatogram, it looks for onset of response, shoulders, peaks, valleys, and the end of detector response. In the "Method", the operator can set the "initial threshold", which determines the increase in response over baseline necessary for the software to recognize the onset of a peak. The operator also sets a "minimum area" to be recognized, i.e., when the signal has increased over baseline, changed slope, and returned to baseline, thereby setting the smallest peak that will be calculated and reported. "Peak width" is also set in the "Method" for each detector and this parameter determines the frequency of data point collection to be taken during an analysis. The frequency of data point collection determines how closely, timewise, the operator can set the cutpoints desired in the analysis of the data. The Chemstation software also has a function titled "Autointegrate" which is a useful place to start in the analysis of data from a new sample because it determines and sets the above mentioned parameters automatically. The operator also sets the time for onset and end of data collection. These settings, along with "peak width", determine the number of data points collected during a run. The operator also sets the beginning and end of integration time. The parameters can be adjusted, if necessary, to acquire results in the form desired by the operator.

There is a default "Method" that is used as a starting point for the analysis of chromatographic data. If a simple analysis of the data obtained from a single HPLC/SEC run of an asphalt is desired, the operator can use the default "Method" and the analytical report will appear as that shown in figure 2-1. Seen in that figure is a DRID chromatogram for SHRP core asphalt AAA-1. The software recognized three peaks in that chromatogram and also a shoulder on the initial peak. The report shows, among other things, retention times for the three peaks, their areas, the total area, and the area percent each peak is of the total with vertical lines drawn to the baseline from the valleys between the peaks.

The software also allows the operator to draw a baseline for the curve and get simply a total area under the whole chromatogram as shown in figure 2-2. The area varies somewhat according to the dexterity of the operator. In addition, the operator can set cutpoints for the chromatogram for whatever time periods are wanted. This is done by entering the cutpoints "manually" in the "Method". The results of such an analysis are shown in figure 2-3. In this report, the first cutpoint is comparable to that obtained from preparative SEC for F-I, i.e., the cutpoint was determined from a gravimetric HPLC/SEC series for AAA-1 and reflects the time in the HPLC/SEC necessary to get the same weight percent, for F-I, of the total material recovered as that previously determined using preparative SEC. The rest of the chromatogram was divided into eight equal time segments. It can be seen in the report in figure 2-3 that the columns labeled RT (retention time) and (peak) Width do not indicate equal time segments. This is a result of the software being designed to analyze simple mixtures and to look for peaks. The software apparently is "flummoxed" by the forcing (F in the report under Type) of cutpoints by entering them "manually" and prints erroneous numbers in the report. However, in table 2-1, a report obtained through an action separate from normal report generation in the Chemstation software, can be seen two additional columns labeled Start and End; the data in these columns show that the start and end times of each time segment are those desired. The reports shown in figures 2-1 through 2-3 and in table 2-1 are all from the same sample run.

Gravimetric cutpoints for F-I for the SHRP core asphalts for the HPLC/SEC were determined, as mentioned briefly in the previous paragraph, by running a gravimetric series, using the usual conditions and sample size, for each of these asphalts using the fraction collector. Each asphalt was fractionated 55 to 80 times, i.e., a total weight of 1.32 to 1.92 g of each asphalt was processed. Fractions were collected in the early part of the runs where the most distinctive peaks of the chromatograms were anticipated using the shortest collection times. The fractions were then divested of solvent. Weights were determined for each fraction, the total collected was determined, and the weight percents of each fraction were calculated. Fraction percents were then summed from the onset of sample emergence until fraction times were found that bracketed the weight percent for F-I determined by preparative SEC. Extrapolation between these two points gave the gravimetric cutpoint for F-I for HPLC/SEC that is equivalent to that for preparative SEC. Table 2-2 shows the SHRP core asphalts and the retention times for their gravimetric F-I's. This procedure was followed for each SHRP core asphalt and these cutpoints were then used to calculate time segment areas for the DRID chromatograms.

Precision

Data gathered from this technique are fairly precise for an HPLC method considering the complexity of the materials (asphalts) examined. Representative data are presented in table 2-3, which shows fraction area and area percent data for five consecutive runs of asphalt AAA-1, and figure 2-4 which shows overlaid chromatograms for the same runs. Standard deviations are less than 1 percent of the averages for the larger fractions, and gradually increase as the area of the fractions decreases. Fraction I in this table and figure is that time necessary to obtain gravimetrically that mass percentage of material equivalent to the mass percentage obtained from a preparative SEC separation.

Discussion

Calibration

A plot of retention time versus molecular weight was prepared using data (table 2-4) obtained for the standard model compounds of known molecular sizes. The calibration curve obtained (figure 2-5) shows that the main area of separation for this system lies in the molecular weight range from around 1,200 to 14,000 daltons. This is the range seen for SEC fractions F-I through F-IIb for the SHRP core asphalts as reported previously [SHRP 1993a]. This curve was then used to estimate molecular weights for peaks and shoulders for the SHRP core asphalts, unaged and aged, and for the crumb rubber modified asphalts. Examples will be shown below. Average retention times for the peaks and shoulders were determined using the computer and stored data for about 10 runs from the gravimetric series for each neat asphalt and for each of the runs for the aged and modified asphalts. These average retention times were then applied to the calibration curve to estimate molecular weights. Table 2-5 shows retention times and estimated molecular weights for unaged and aged asphalts. In table 2-5, many of the high molecular weight peaks are due to aged asphalts. However, in some asphalts, unaged and aged asphalts peaks coincide. Most low molecular weight peaks coincide for both aged and unaged asphalts (see figures 2-34 through 2-38). Table 2-6 shows similar data for crumb rubber modified asphalts. It is not suggested that the standards used have the same hydrodynamic volume to molecular weight ratio as the compounds and molecular associations that make up asphalts. It is rather suggested that the figures for molecular weights give only a rough estimate of what the actual molecular weights are. It should also be mentioned that molecular weights at the high end and low end are very rough estimates as small changes in retention time at the high end give large changes in estimated molecular weight while large changes in retention time are necessary to give small changes in molecular weight at the low end of the scale.

Early in this work it was necessary to determine the effect of sample size on the chromatogram. Figure 2-6 shows the results of this study in which it was found that a quite concentrated sample solution was necessary to achieve the desired result, i.e., emulate preparative SEC results. This is apparent in the shape of the first part of the chromatogram. With a sample of 1.12 mg a shoulder appears in the early part of the chromatogram that becomes a well defined peak when the sample concentration is increased by using a sample of 22.4 mg. Apparently molecular associations were broken up in the more dilute solutions of asphalt in toluene that occurred when smaller samples were run. The chromatogram obtained with the 22.4 mg sample more closely resembles that obtained with preparative SEC.

This very rapid HPLC/SEC procedure was developed to simulate the preparative SEC method, and chromatograms for neat asphalts AAD-1 and AAF-1, both from the preparative SEC procedure and the HPLC/SEC procedure, are shown in figures 2-7 and 2-8, respectively. These figures show the degree of similarity of the chromatograms from both methods for two asphalts that are characterized by dissimilar molecular size distributions and, therefore, yield quite different chromatograms.

Another technique for comparing the results of preparative SEC system and the HPLC/SEC system is through the results from the DRID, used to construct chromatograms in both systems. Figures 2-9a and b and 2-10a and b show the comparisons for SHRP core asphalts AAD-1 and AAF-1, respectively. Again, the chromatograms do not replicate each other exactly. The HPLC/SEC chromatogram for AAD-1 shows more detail than that from the preparative SEC. For AAF-1, just the opposite is true. For both asphalts, however, there seems to be a greater separation between the initial peaks and the main, later developing peak for preparative SEC than for HPLC/SEC. This is most likely due to the difference between the pore openings of the column packings. The pore opening for preparative SEC averages around 170 Å, which is not available in commercial HPLC/SEC columns. The combination of two 500 Å columns followed by one 100 Å column seems to be a fair compromise and provides similar results from HPLC/SEC to those from the preparative SEC.

Straight Run, New and Aged Asphalts

As mentioned in the experimental section, two types of detection systems were used in this work. The first was the DRID which is commonly used in HPLC and the second was the gravimetric finish involving the fraction collector. Two other detectors were available, a UV/visible diode array detector (DAD) and a fluorescence detector; however, both were swamped at the sample concentrations used in this work. Figures 2-11 and 2-12 show comparisons for those two detection systems for core asphalts AAD-1 and AAF-1, respectively. Both of these comparisons demonstrate that the gravimetric chromatograms show smaller responses in the first part of the trace, especially those for AAF-1, than the DRID. This is not unexpected because the first materials to emerge from the columns are those that are the largest molecules or molecular associations. These materials, especially the latter, would be those that are more polar, that is, contain larger amounts of heteroatoms such as oxygen, nitrogen, etc., and would differ more in refractive index from the carrier solvent toluene, an aromatic hydrocarbon. These materials would, therefore, be expected to exhibit the largest response to the DRID per amount of material present.

All of the SHRP core asphalts were run using this technique and the resulting chromatograms are shown in figures 2-13 and 2-14. These chromatograms show clearly the differences between these asphalts, especially in the region of large molecular size. They could even be classified into three categories according to the detail in the large molecular size region: (1) those with much detail including AAA-1, AAD-1, AAK-1, and AAM-1, (2) those with some detail such as AAB-1, AAC-1, and AAF-1, and (3) those with no detail such as AAG-1. Such a classification has been previously suggested [Jennings et al. 1991].

It was necessary to demonstrate the effectiveness of the technique on unaged and aged asphalts so the SHRP core asphalts, both unaged and aged, were all analyzed. Figures 2-15 through 2-22 show the overlaid chromatograms from the DRID (all chromatograms discussed from this point on are from the DRID) for all of the core asphalts unaged and aged to three levels from the technique described here. The chromatograms are drawn so that a large peak for all four chromatograms in each set is at the same level so that the change in the first part of the chromatogram is readily apparent. The figures also show the gravimetrically determined F-I cutpoint for each asphalt. The figures show how the amount of non-fluorescing associating material or F-I material increases with increased aging. This is in agreement with earlier reports [Jennings et al. 1991; Bishara et al. 1991; SHRP 1993a; Brûlé et al. 1994]. Also shown in these figures are the results of estimating molecular weights for peaks and shoulders present in the chromatograms. It is interesting to note for asphalt AAF-1 that, considering that these molecular weights are estimates only, molecular weight at shoulder 1 (see figure 2-19) is approximately 3 times that of the molecular weight at peak 2, which is approximately 10 times that of the molecular weight value at shoulder 3. In addition, for asphalt AAK-1 (see figure 2-21), molecular weight at peak 1 is double that of the molecular weight at peak 2, which is double that of the molecular weight at peak 3. Similar analyses could be made for all of the chromatograms shown in these figures. These results suggest that the materials responsible for some of the peaks in the chromatograms are the result of the combination of materials responsible for smaller peaks. This is what was anticipated, of course, but does also suggest that sometimes large associations aggregate two at a time and that in other cases, numerous smaller molecules or associations combine to make much larger aggregations.

Another way to portray data for unaged and aged asphalts is shown in figures 2-23 and 2-24 where normalized integrals for HPLC/SEC fractions for asphalts AAF-1 and AAM-1 are plotted versus aging time. The HPLC/SEC F-I fraction percents were determined by making the DRID area percent for F-I equal to the weight percent for preparative SEC F-I. The line for F-II is for the sum of the F-II subfractions and is complementary to F-I. For AAM-1, F-I is the sum of the F-I subfractions. Subfractions where the integrals are very small were not presented in these figures. It can be seen in these figures that the integrals for F-I increase and the integrals for F-II decrease on aging.

For asphalt AAF-1, it seems that fractions F-IIb and F-IIc decrease with increased aging while other F-II subfractions remain more or less constant. The time frames for F-IIb and F-IIc are 22.45 to 25.89 minutes and 25.89 to 29.32 minutes, respectively, and cover estimated molecular weight ranges from the calibration curve of 1,000 to 300 and 300 to 200 daltons, respectively. This time span encompasses the highest peak in both the gravimetric and the DRID chromatograms (see figures 2-19 and 2-21) and, therefore, seems the most logical source of materials that could be oxidized during aging. It should be pointed out, however, that it would take a number of units in this molecular weight range to combine in order to be transferred to F-I where the time span is 14.8 to 19.02 minutes and the molecular weight range is estimated to be ca. 90,000 (onset) to 4,400 daltons. For example, it would take about sixty 500 dalton units to make one 30,000 unit or as mentioned previously, ten 800 dalton units to make one 8,000 dalton unit.

A similar analysis of figure 2-24 shows that F-I for AAM-1 also grows at the expense of F-II and that includes both the initial spike and the rest of F-I. However, unlike AAF-1, fractions F-IIa, F-IIb, and F-IIc all decrease with increasing aging. The time range for these three fractions extends from 19.65 to 23.01 to 26.36 to 29.72 minutes with an estimated molecular weight range from 3,600 to 900 to 300 to 200 daltons. Again, a large number of these units would be needed to transfer these materials to F-I, which has an estimated molecular weight range of from ca. 100,000 to 3,600 daltons. For example, it would take approximately twenty 3,000 dalton units to reach a molecular weight of 59,000 daltons, which is the estimated molecular weight of the initial spike for asphalt AAM-1.

This study of these two asphalts indicates differences in the chemical makeup of these two materials. For example, there must not be materials in F-IIa of AAF-1 that will oxidize (during the aging process) to produce materials that will associate or react to produce materials that show up in F-I. These types of materials are present in F-IIb and F-IIc, however. On the other hand, these types of molecules are present in all three of those fractions in asphalt AAM-1. Why they are not present in F-IIa of AAF-1 is not readily apparent but does reconfirm the long standing position that asphalt behavior is highly source dependent. It would seem logical that these types of molecules would be distributed in the whole range of the MSD's for both asphalts.

Asphalt Fractions

Preparative SEC and ion exchange chromatography (IEC) are used to prepare asphalt fractions for analysis and for use in blending experiments, i.e., where fractions from the same or different asphalts are combined. HPLC/SEC runs were done on some of these fractions in order to learn more about their MSD's. For example, the preparative SEC Fraction-I (F-1) of core asphalt AAD-1 was reintroduced into a preparative SEC column using the same conditions under which it was obtained and four fractions were collected. These fractions were obtained by dividing the normal volume collected for F-I into three equal (100 mL) volumes (subfractions F-I-1, F-I-3, and F-I-3) as they emerged from the column and a fraction F-I-4 consisting of all other materials collected after the first 300 mL. Figure 2-25 shows chromatograms of the subfractions run at standard run concentration (24 mg samples), and figure 2-26 shows chromatograms of the same subfractions run at the concentration (0.33 to 5.4 mg samples depending on the subfraction) in which they would appear if 24 mg of the whole asphalt were run. In the concentrated chromatograms (figure 2-25), a leading edge spike appears at essentially the same retention time for each subfraction. In each case the second peak is the larger peak of the chromatogram. However, the spike for each subfraction has a different size relationship with its second largest peak than the others and also a different retention time relationship. That is, the retention time of the larger peak moved to a lower molecular weight realm (longer retention time), as expected, for succeeding fractions. The overlaid chromatograms of figure 2-26 are of a much different shape than those of figure 2-25. The difference is no doubt due to concentration effects as mentioned previously, i.e., molecular associations were disrupted by the greater dilution in toluene. The chromatograms for F-I-1 and F-I-2 show the initial peak followed by a shoulder. The chromatogram for F-I-3 is bimodal while that for F-I-4 is a single small peak at approximately the retention time of the shoulder of the two chromatograms of F-I-1 and F-I-2, and the second peak of the chromatogram of F-I-3. These chromatograms, especially those at the greater dilution, do show that many of the molecular associations are fairly stable in toluene or they would have been detected at much longer retention times.

Figures 2-27 and 2-28 show overlaid chromatograms of the eight SHRP core asphalts with their respective IEC neutral fractions. These comparisons show that the very large molecular weight compounds/molecular associations are missing from the IEC neutral fractions of all of the SHRP core asphalts. This is to be expected because the molecular associations are thought to consist of polar molecules and these have been removed by the IEC process. This is significant because the polar aromatic materials that have been removed in the IEC process have a great influence on the physical properties of asphalts. It is of interest that the chromatograms of four of the IEC neutral fractions, AAB-1, AAF-1, AAG-1, and AAM-1, are monomodal and those of the other four are bimodal. Despite the absence of molecular associations, the IEC neutral fractions contain some molecules of substantially large molecular weight.

Data in table 2-7 illustrate the change in the chromatograms for the SHRP core asphalts when the polar materials have been removed by IEC. In this table are shown the times of first detection of the sample by the DRID (onset time) and an estimated molecular weight, derived from the previously mentioned calibration curve, associated with that time. The changes in onset time (the time of initial response to asphaltic materials), between asphalt and neutral fraction, vary among the asphalts from 0.63 minutes, for asphalt AAM-1, to 2.26 minutes for asphalt AAD-1. The changes in estimated onset molecular weight, between asphalt and neutral fraction, vary from about 40,600 daltons for asphalt AAG-1 to 85,000 daltons for asphalt AAD-1. (Again, it must be remembered that these molecular weights are very rough estimates, especially at higher molecular weights.) These results once again confirm the individuality of asphalts and suggest that even when asphalts have the same physical properties, chemical composition can be quite different and that the change in physical properties on aging will be asphalt source dependent.

Recycling Agents

It was thought desirable to see if this technique could easily differentiate between an unmodified asphalt and that asphalt treated with a recycling agent such as a lower viscosity asphalt. Figure 2-29 shows the overlaid chromatograms of a recycling agent, an AC 2.5 asphalt, and unaged asphalt AAF-1 (AC 20). As is evident, the recycling agent has as wide an MSD as does the higher viscosity asphalt. The major difference is in the highest molecular size material where the lower viscosity asphalt seems to have more material. The lower viscosity asphalt also has more low molecular weight material. Therefore, addition of this recycling agent to the higher viscosity asphalt should show a difference in the high molecular weight region of the chromatogram. However, in figure 2-30, where mixtures (5, 10, 25, and 50 percent AC 2.5) of the recycling agent and AAF-1 are shown, no difference is apparent until the mixture reaches 25 percent recycling agent. Differences at the 50 percent level are easily seen in the figure. It is possible that small amounts of the molecular associations in the low viscosity asphalt become broken up when mixed with AAF-1.

Figure 2-31 and table 2-8 show data from the mixtures of the two grades of asphalt described above for the first five of nine SEC fractions. The curves in figure 2-31 show that SEC F-I does indeed grow with the addition of increasing concentrations of recycling agent while fractions F-IIa and F-IIb decrease somewhat but, again, the differences are only apparent at concentrations of 25 percent and above. This suggests that this particular column combination would not be useful to analyze mixtures of recycling agents with broad MSD's, such as low viscosity asphalts, and another asphalt except at high concentrations. It appears that only recycling agents that have a narrow MSD might be analyzed usefully by this system when the percentage of recycling agent is small.

Crumb Rubber Modified Asphalts

Mixtures of asphalts modified by addition of various crumb rubbers (CRM's) are being studied extensively in our laboratory and it was suggested that HPLC/SEC might be appropriate to determine the fate of the rubber in the CRM's, i.e., where in the MSD does any dissolved rubber appear? Figures 2-32 through 2-35 show chromatograms from the study of a mixture of asphalt ABD-1 with two CRM's, one crumb rubber consisting of natural rubber (NR) and the other consisting of both natural rubber and synthetic rubber (CRM4). For example, figure 2-32 shows overlaid chromatograms for the unmodified asphalt and mixtures with the two CRM's before they had been heated in a manner that simulates plant mixing. Each mixture had been heated only enough to mix the asphalt and crumb rubber thoroughly. It can be seen that the chromatogram of the CRM containing NR shows a small increase in the area of large molecular size, indicating that some high molecular size material had been incorporated into the asphalt. The other two chromatograms are essentially the same, showing no increment of soluble CRM4 to the asphalt prior to further heating. This suggests that the difference in the crumb rubbers is demonstrated very early in the heating regimen, i.e., that NR is solubilized more easily with asphalt ABD-1 than CRM4. As a control, figure 2-33 shows the effect of heating on the chromatograms of unmodified ABD-1. A very small change in the area of large molecular size is seen for unmodified ABD-1 on heating from 0 to 96 to 192 hours. Figure 2-34 shows chromatograms for the mixture of ABD-1 and NR. As can be seen, changes occur in the large molecular size region of the chromatograms. Heating this mixture for as little as an hour has made a significant change in the very large molecular size region of the chromatogram, that is, a peak is now seen at the front edge of the chromatogram that was not present prior to heating. Further heating of the sample gradually fills in the area between that peak and the rest of the chromatogram. This suggests that the rubber particles break down initially to yield a relatively large molecular size material followed by further breakdown to smaller molecular size material. Figure 2-35 shows chromatograms for the mixture of ABD-1 and CRM4. In this case, the 0 and 1 hour chromatograms are virtually identical, while the leading edge peak of the 24 hour chromatogram and those for higher levels of heating show that CRM4 does not begin to break down as early in the heating regimen with ABD-1 as does NR. The chromatograms are similar for the two crumb rubbers after 48 hours of heating, however, and a comparison with figure 2-33 shows that the material added in the front part of the chromatograms comes from the crumb rubbers and not from the asphalt.

Figures 2-36 through 2-38 show chromatograms for unmodified asphalt AAB-1 and mixtures of AAB-1 with NR and CRM4, respectively. In addition, figure 2-38 shows estimated molecular weights for the peaks and shoulders of the chromatograms. These estimated molecular weights apply to figures 2-36 and 2-37 also. Figure 2-36 shows chromatograms that illustrate how the unmodified asphalt reacted to different periods of heating at 200°C (392°F). Interestingly, the amount of large molecular size materials that had formed on heating unmodified AAB-1 for 24 hours gradually diminished on further heating, suggesting these materials broke down to lower molecular weight materials on sustained heating or became materials that are incapable of forming intermolecular associations. Of the asphalts studied so far, this result is unique. The chromatograms in figure 2-37 show that heating the AAB-1/NR mixture leads to an increase in large molecular size materials with increased heating time. Chromatograms are shown for a heating period of up to 168 hours. These chromatograms suggest that further breakdown of the rubber continues to occur by heating asphalt AAB-1 at 200°C (392°F) up to 168 hours. This is similar to the reaction of the same crumb rubbers with asphalt ABD-1 where an increase in the large molecular size region of the chromatograms continued through 96 hours for CRM4 and 168 hours for NR. These results demonstrate that asphalt behavior is highly source or composition dependent. The practitioner must be made well aware of this problem if there is to be any confidence in any given asphalt grading system. The chromatograms obtained for the AAB-1/CRM4 mixture (figure 2-38) show that for the first 48 hours of heating a peak formed in the very large molecular size region, estimated molecular weight of 46,000, that diminishes on further heating until it is only a shoulder after 192 hours of heating. In contrast a shoulder that was present in the unheated asphalt/CRM4 mixture at an estimated molecular weight of 9,000 grows through heating for 168 hours and diminishes on heating to 192 hours. A shoulder is also present in the chromatograms of the unmodified asphalt and in the asphalt/NR mixture. This shoulder grew through heating for 168 hours in the asphalt/NR mixture but began diminishing after 24 hours of heating of the unmodified asphalt. Once again these results show that the two crumb rubbers react differently to the same asphalt and that materials form in the asphalt crumb rubber mixtures that do not form from the asphalt itself during the same heating regimen. These differences are most likely due to the different chemical compositions of the crumb rubbers. It is also interesting to note that materials formed early in the heating period break down to lower molecular weight material on further heating.

Figures 2-39 through 2-41 show plots of normalized integrals for asphalt AAB-1 neat, with crumb rubber NR, and with crumb rubber CRM4, respectively, that have been heated at 200°C over time. Figure 2-39 demonstrates that the integrand for F-I increases initially and then decreases for unmodified AAB-1 as heating continues and that F-II does the opposite. Once again, composition driven behavior is obvious. Analysis of the graphs for the various fractions shows that subfractions F-IIa, F-IIb, and F-IIc decrease initially and then increase with continued heating. This data analysis corroborates what was seen in figure 2-37. Figures 2-40 and 2-41 show an initial increase in the integrand of F-I, with a corresponding decrease in F-II through about 48 hours of heating and a final decrease in F-I on continued heating above 168 hours, again corroborating the chromatograms shown in figures 2-37 and 2-38. In contrast to heating the neat asphalt, however, the mixtures show decreases after 1 hour heating in fractions IIa through IIe. This result differs from that of other asphalt/crumb rubber mixtures where fractions F-IId and F-IIe were unaffected. This suggests that the only change was addition of rubber material to F-I, which would cause an apparent relative diminution of the F-II subfractions.

Chromatograms similar to those shown for asphalt AAB-1 are shown for unmodified SHRP asphalts AAK-2 and ABL-3. Asphalt ABL-3 was supposed to be a replacement for SHRP asphalt AAK-2 but SEC chromatograms for the neat, untreated, unheated asphalts (figure 2-42) show significant differences. At any rate, the chromatograms for both the unmodified asphalts and the CRM's show a steady increase in the large molecular size region with increased heating time with the mixtures showing larger increases than the unmodified asphalts.

Figures 2-43 through 2-45 show chromatograms for asphalt AAM-1, asphalt AAM-1 with NR, and asphalt AAM-1 with CRM4, respectively. Included in the figures are estimated molecular weights for peaks and shoulders of the chromatograms. All three sets of chromatograms show peaks at 900 and 13,000 daltons and a shoulder in the unheated materials at 27,000 daltons. The chromatograms for the CRM's show an additional peak in the neighborhood of 40,000 daltons. This material must come from the crumb rubber and increases with increasing heating time. It is interesting that the estimated molecular weights are approximately multiples of 13,000 daltons, which suggests there is a pattern of molecular association similar to that discussed earlier. That is, molecular associations of ~13,000 daltons dimerize to make those of ~27,000 daltons, etc.

Figure 2-43 shows the chromatograms for the unmodified asphalt as a function of heating time and demonstrates that heating unmodified AAM-1 at 200°C (392°F) causes a small increase in the area of large molecular size material, that is, in the area of estimated molecular weights of 13,000 and 27,000 daltons. On the other hand, heating the AAM-1/NR mixture showed a shoulder at 39,000 daltons after 24 hours of heating that increased to a peak after 96 hours of heating.

The chromatograms for the AAM-1/CRM4 mixtures show a peak at 42,000 daltons after 24 hours of heating that increases with longer heating times up to 168 hours. Again, the chromatograms in figures 2-44 and 2-45, although one must remember that the molecular weights of 39,000 and 42,000 daltons have almost the same retention time, demonstrate the difference in the way the two crumb rubbers respond to the same asphalt.

SUMMARY

The HPLC/SEC technique described, i.e., the column combination, column temperature, solvent, and flow rate, has demonstrated the ability to provide chromatograms somewhat similar to those obtained by preparative SEC for unaged asphalts. The technique also provides chromatograms for aged asphalts that show that an increase of large molecular size material is produced on aging in the TFO/PAV. Calibration of the column combination with materials of known molecular weight shows the major separation occurs in the large molecular size material area of the molecular size distribution, that is, 14,000 to 1,200 daltons. In addition, analysis of the CRM's has shown that the breakdown products from the heating of the rubbers of the CRM's at 200°C (392°F) appear in the large molecular size region of the MSD. The response of the two crumb rubbers to heating with the asphalts varies in that NR seems to solubilize more rapidly than does CRM4 for the same asphalt. In addition, the two crumb rubbers respond differently to being heated with different asphalts, i.e., solubilizing more rapidly in one asphalt than in another. This HPLC/SEC system has easily shown these differences. Examples are given of the different separations discussed in the report.

Table 2-1. Integration results for core asphalt AAA-1, DRID.

Peak number	Ret. time, min	Peak type	Area	Start, min	End, min
1	22.28	FF[1]	11682	14.50	22.84
2	25.28	MF[2]	5602	22.84	25.84
3	25.84	MF	4260	25.84	28.85
4	28.85	FF	1671	28.85	31.85
5	31.85	FF	499	31.85	34.86
6	35.02	FF	217	34.86	37.86
7	37.86	FF	142	37.86	40.87
8	42.37	FF	97	40.87	43.87
9	43.87	FF	58	43.87	46.87

[1] F = Peak was forced by manual integration.

[2] M = Manually integrated.

Table 2-2. Core asphalt F-1 gravimetric cutpoint times.

Asphalt	F-1 cutpoint, min
AAA-1	22.84
AAB-1	23.61
AAC-1	22.60
AAD-1	22.87
AAF-1	22.59
AAG-1	23.47
AAK-1	22.95
AAM-1	21.85
Average	22.85
Standard Deviation	0.55

Table 2-3. HPLC/SEC DRID chromatographic fraction data for five consecutive runs for asphalt AAA-1.

Fraction	Area						
	Run 1	Run 2	Run 3	Run 4	Run 5	Average	Std. dev.
1	12450	12374	12269	12291	12325	12342	72
2	5638	5590	5547	5558	5577	5582	35
3	4303	4286	4272	4285	4302	4290	13
4	1696	1677	1680	1677	1702	1686	12
5	499	514	511	523	537	517	14
6	244	244	229	229	228	235	8
7	152	159	151	151	149	152	4
8	112	114	110	109	106	110	3
9	77	76	71	72	70	73	3
10	13	14	13	13	13	13	0
Total	25184	25048	24853	24909	25009	25001	128

Fraction	Area %						
	Run 1	Run 2	Run 3	Run 4	Run 5	Average	Std. dev.
1	49.44	49.40	49.37	49.44	49.40	49.41	0.03
2	22.39	22.32	22.32	22.39	22.32	22.34	0.04
3	17.08	17.11	17.19	17.08	17.11	17.12	0.04
4	6.73	6.70	6.76	6.73	6.70	6.72	0.03
5	1.98	2.05	2.06	1.98	2.05	2.02	0.04
6	0.97	0.97	0.92	0.97	0.97	0.96	0.02
7	0.60	0.64	0.61	0.60	0.64	0.62	0.02
8	0.45	0.45	0.44	0.45	0.45	0.45	0.01
9	0.31	0.30	0.29	0.31	0.30	0.30	0.01
10	0.05	0.06	0.05	0.05	0.06	0.05	0.00
Total	100.00	100.00	100.00	100.00	100.00	100.00	0.00

Table 2-4. Calibration data for the HPLC/SEC system.[1]

Peak molecular weight, daltons	Retention time, min	Standard deviation, min	Compound
206	31.67	0.01	2-Ethylanthracene
361	25.58	0.03	Phenyl stearate
761	23.93	0.04	Polystyrene standard
1202	21.15	0.01	Pentaerythrityl tetrastearate
2698	20.47	0.02	Polystyrene standard
4016	19.19	0.02	Polystyrene standard
7500	17.94	0.01	Polystyrene standard
13648	17.04	0.03	Polystyrene standard
25470	16.24	0.04	Polystyrene standard
30256	15.92	0.03	Polystyrene standard
48900	15.54	0.02	Polystyrene standard

[1] The system consists of 2 - 500 Å and 1 - 100 Å (7.8 by 300 mm) columns in series, toluene carrier, 40°C, 1.00 mL/min.

Table 2-5. Approximate molecular weights for peaks and shoulders in the HPLC/SEC chromatograms of unaged and aged SHRP core asphalts.

AAA-1		AAB-1		AAC-1		AAD-1	
Retention time, min	Molecular weight of peak, daltons	Retention time, min	Molecular weight of peak, daltons	Retention time, min	Molecular weight of peak, daltons	Retention time, min	Molecular weight of peak, daltons
15.78	36000	--	--	--	--	15.70	39000
--	--	16.42	23000	--	--	--	--
17.21	12000	17.53	10000	17.65	8600	17.08	13000
22.53	800	22.28	900	21.67	1000	22.41	800
25.57	300	24.76	400	24.12	600	26.65	300

AAF-1		AAG-1		AAK-1		AAM-1	
Retention time, min	Molecular weight of peak, daltons	Retention time, min	Molecular weight of peak, daltons	Retention time, min	Molecular weight of peak, daltons	Retention time, min	Molecular weight of peak, daltons
--	–	–	–	15.33	59000	--	--
--	--	--	--	15.95	29000	15.81	35000
16.38	23000	--	--	--	--	--	--
17.77	8100	--	--	16.95	15000	17.25	11000
22.59	800	21.35	1000	22.33	900	23.07	800
24.53	500	27.23	300	24.77	400	--	–

Table 2-6. Retention times and approximate molecular weights for peaks from the HPLC/SEC of asphalt/crumb rubber mixtures.

AAB-1 unmodified		AAB-1 with NR		AAB-1 with CRM4		ABL-3 unmodified		ABL-3 with NR		AAK-2 with CRM4	
						1 hour		1 hour			
Retention time, min	Molecular weight of peak, daltons	Retention time, min	Molecular weight of peak, daltons	Retention time, min	Molecular weight of peak, daltons	Retention time, min	Molecular weight of peak, daltons	Retention time, min	Molecular weight of peak, daltons	Retention time, min	Molecular weight of peak, daltons
–	--	–	–	15.58	46000	15.57	46000	15.52	48000	15.46	52000
--	--	16.37	24000	--	--	--	--	--	--	--	--
17.75	8300	17.50	9500	17.71	8500	17.28	11000	17.12	13000	17.06	13000
22.18	900	21.97	900	21.98	900	22.43	800	22.00	900	22.46	900
24.60	500	24.64	600	24.54	600	25.49	300	25.51	300	25.48	500

ABD-1 unmodified		ABD-1 with NR				ABD-1 with CRM4			
1 hour		1 hour		192 hour		24 hour		192 hour	
Retention time, min	Molecular weight of peak, daltons	Retention time, min	Molecular weight of peak, daltons	Retention time, min	Molecular weight of peak, daltons	Retention time, min	Molecular weight of peak, daltons	Retention time, min	Molecular weight of peak, daltons
--	--	15.38	55000	16.03	28000	15.45	52000	15.90	31000
18.44	5700	18.69	4900	18.15	6500	--	--	18.10	6800
23.31	800	23.46	700	23.35	700	23.54	700	23.50	700
25.11	400	25.19	300	25.17	300	25.14	400	25.07	400

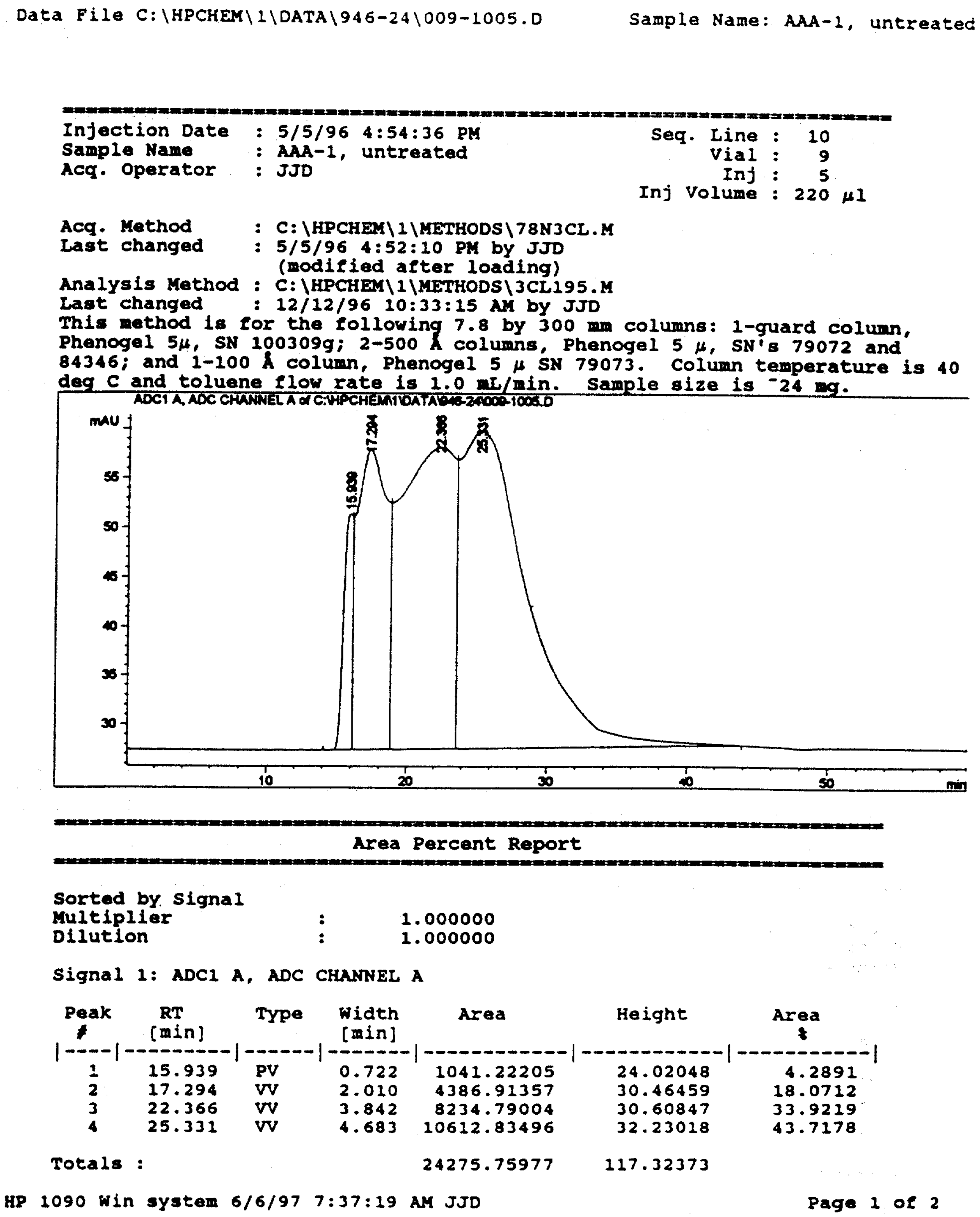
AAM-1 unmodified		AAM-1 with NR		AAM-1 with CRM4	
Retention time, min	Molecular weight of peak, daltons	Retention time, min	Molecular weight of peak, daltons	Retention time, min	Molecular weight of peak, daltons
–	--	15.74	39000	15.66	42000
16.06	27000	16.11	27000	--	--
17.11	13000	17.11	13000	17.06	13000
22.79	800	22.73	800	22.79	900

Table 2-7. Onset times and estimated molecular weights for SHRP core asphalts and IEC neutrals from DRID data.

Asphalt	Asphalts		IEC Neutrals	
	Onset time, min	Estimated molecular weight, daltons	Onset time, min	Estimated molecular weight, daltons
AAA-1	15.04	88000	16.33	24500
AAB-1	15.23	73000	16.92	15900
AAC-1	15.40	60000	17.20	12600
AAD-1	14.90	98000	17.17	13000
AAF-1	15.18	77000	17.06	14000
AAG-1	15.57	48000	18.06	7400
AAK-1	14.93	85000	16.76	18300
AAM-1	14.86	100000	15.48	51000

Table 2-8. HPLC/SEC fraction area percent data for core asphalt AAF-1 with Amoco-Wilmington AC 2.5.

Fraction	Unmodified	5% Amoco-Wilmington	10% Amoco-Wilmington	25% Amoco-Wilmington	50% Amoco-Wilmington
F-I	13.9	13.6	14.0	14.6	17.2
F-IIa	27.4	27.8	27.6	26.9	26.0
F-IIb	32.9	33.7	33.4	31.9	28.9
F-IIc	18.5	17.8	17.6	18.3	19.1
F-IId	5.1	5.0	5.0	5.5	6.1
F-IIe	1.2	1.3	1.4	1.5	1.3
F-IIf	0.6	0.5	0.5	0.7	0.8
F-IIg	0.3	0.3	0.3	0.4	0.4
F-IIh	0.1	0.1	0.1	0.2	0.2
Total	100.0	100.0	100.0	100.0	100.0



```
Data File C:\HPCHEM\1\DATA\946-24\009-1005.D          Sample Name: AAA-1, untreated

=====================================================================
Injection Date   : 5/5/96 4:54:36 PM                  Seq. Line :  10
Sample Name      : AAA-1, untreated                        Vial :   9
Acq. Operator    : JJD                                      Inj :   5
                                                     Inj Volume : 220 µl

Acq. Method      : C:\HPCHEM\1\METHODS\78N3CL.M
Last changed     : 5/5/96 4:52:10 PM by JJD
                   (modified after loading)
Analysis Method : C:\HPCHEM\1\METHODS\3CL195.M
Last changed     : 12/12/96 10:33:15 AM by JJD
This method is for the following 7.8 by 300 mm columns: 1-guard column,
Phenogel 5µ, SN 100309g; 2-500 Å columns, Phenogel 5 µ, SN's 79072 and
84346; and 1-100 Å column, Phenogel 5 µ SN 79073.  Column temperature is 40
deg C and toluene flow rate is 1.0 mL/min.  Sample size is ~24 mg.
```

```
=====================================================================
                        Area Percent Report
=====================================================================

Sorted by Signal
Multiplier                  :     1.000000
Dilution                    :     1.000000

Signal 1: ADC1 A, ADC CHANNEL A

Peak   RT      Type  Width      Area         Height      Area
 #   [min]           [min]                                %
|----|----------|------|-------|------------|------------|----------|
  1   15.939   PV    0.722   1041.22205     24.02048      4.2891
  2   17.294   VV    2.010   4386.91357     30.46459     18.0712
  3   22.366   VV    3.842   8234.79004     30.60847     33.9219
  4   25.331   VV    4.683  10612.83496     32.23018     43.7178

Totals :                    24275.75977    117.32373

HP 1090 Win system 6/6/97 7:37:19 AM JJD                       Page 1 of 2
```

Figure 2-1. HPLC/SEC DRID chromatogram of asphalt AAA-1, normal system integration, actual system report.

```
Data File C:\HPCHEM\1\DATA\946-24\009-1005.D        Sample Name: AAA-1, untreated


===================================================================
Injection Date   : 5/5/96 4:54:36 PM                Seq. Line :  10
Sample Name      : AAA-1, untreated                      Vial :   9
Acq. Operator    : JJD                                    Inj :   5
                                                  Inj Volume : 220 µl

Acq. Method      : C:\HPCHEM\1\METHODS\78N3CL.M
Last changed     : 5/5/96 4:52:10 PM by JJD
                   (modified after loading)
Analysis Method : C:\HPCHEM\1\METHODS\3CL195.M
Last changed     : 6/6/97 8:36:56 AM by JJD
                   (modified after loading)
This method is for the following 7.8 by 300 mm columns: 1-guard column,
Phenogel 5µ, SN 100309g; 2-500 Å columns, Phenogel 5 µ, SN's 79072 and
84346; and 1-100 Å column, Phenogel 5 µ SN 79073.  Column temperature is 40
deg C and toluene flow rate is 1.0 mL/min.  Sample size is ~24 mg.
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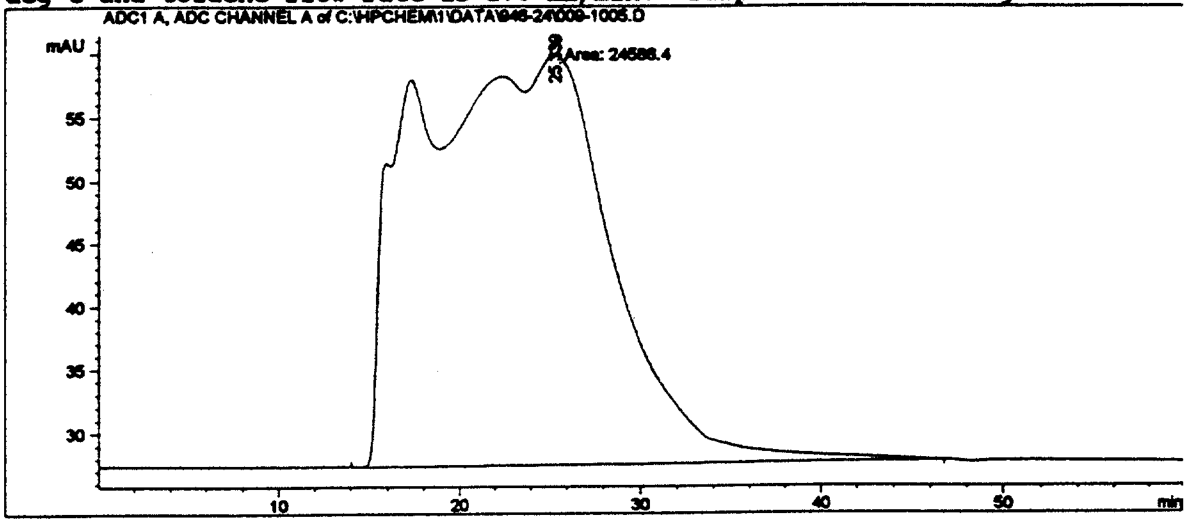

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===================================================================
                      Area Percent Report
===================================================================

Sorted by Signal
Multiplier                :        1.000000
Dilution                  :        1.000000

Signal 1: ADC1 A, ADC CHANNEL A

 Peak    RT      Type   Width      Area          Height        Area
  #     [min]          [min]                                    %
|----|---------|------|-------|-------------|------------|-----------|
  1    25.339   MM    12.662  24588.35742     32.36563     100.0000

Totals :                      24588.35742     32.36563

===================================================================

HP 1090 Win system 6/6/97 8:37:01 AM JJD                    Page 1 of 1
```
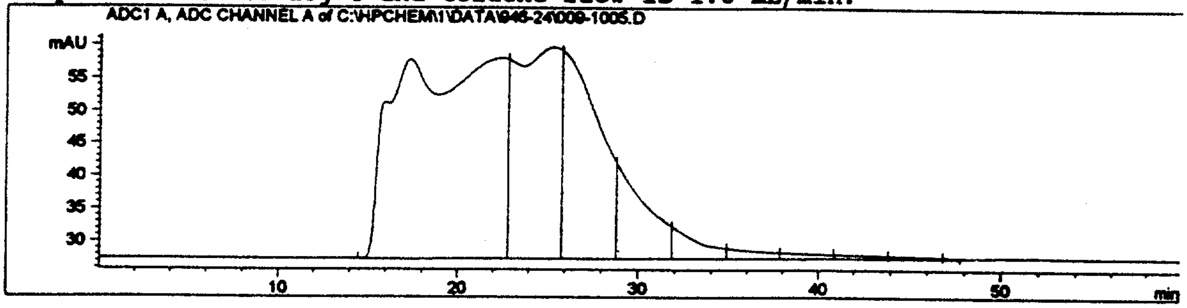

Figure 2-2. HPLC/SEC DRID chromatogram of asphalt AAA-1, integration using manual draw baseline option, actual system report.

```
Data File C:\HPCHEM\1\DATA\946-24\009-1005.D          Sample Name: AAA-1, untreated

=====================================================================
Injection Date  : 5/5/96 4:54:36 PM                 Seq. Line :  10
Sample Name     : AAA-1, untreated                       Vial :   9
Acq. Operator   : JJD                                     Inj :   5
                                                   Inj Volume : 220 µl

Acq. Method     : C:\HPCHEM\1\METHODS\78N3CL.M
Last changed    : 5/5/96 4:52:10 PM by JJD
                  (modified after loading)
Analysis Method : C:\HPCHEM\1\METHODS\GRVAAA.M
Last changed    : 6/6/97 8:55:13 AM by JJD
                  (modified after loading)
This method is for three new 7.8 by 300 mm columns, 2-500 Angstom columns,
Phenogel, 5 micron, SN's 79072 and 84346 and 1-100 Angstrom column,
Phenogel, 5 micron SN 79073 plus one guard column, SN 100309G.  Column
temperature is 40 deg C and toluene flow is 1.0 mL/min.
```



```
=====================================================================
                        Area Percent Report
=====================================================================

Sorted by Signal
Multiplier               :      1.000000
Dilution                 :      1.000000

Signal 1: ADC1 A, ADC CHANNEL A

Peak   RT     Type  Width      Area         Height       Area
 #   [min]          [min]                                  %
|----|--------|-----|-------|------------|------------|-----------|
  1  22.366   FF    6.669  12325.14453    30.79992     49.2836
  2  25.332   MF    2.863   5576.92188    32.46802     22.3000
  3  25.840   MF    2.248   4301.77637    31.89700     17.2012
  4  28.850   FF    1.425   1702.29163    14.66297      6.8068
  5  31.850   FF    1.307    536.88361     4.95777      2.1468
  6  34.860   FF    1.692    227.75970     1.62747      0.9107
  7  38.018   FF    2.629    148.83713  9.43479e-1      0.5951
  8  42.370   FF    2.633    106.15769  6.72008e-1      0.4245
  9  44.160   FF    2.505     69.98814  4.65699e-1      0.2799
 10  46.870   FM    0.707     12.84330  3.02873e-1      0.0514

Totals :                    25008.60352   118.79720

=====================================================================
HP 1090 Win system 6/6/97 8:55:18 AM JJD                  Page 1 of 1
```

Figure 2-3. HPLC/SEC DRID chromatogram of asphalt AAA-1, integration using manually entered cutpoints, actual system report.

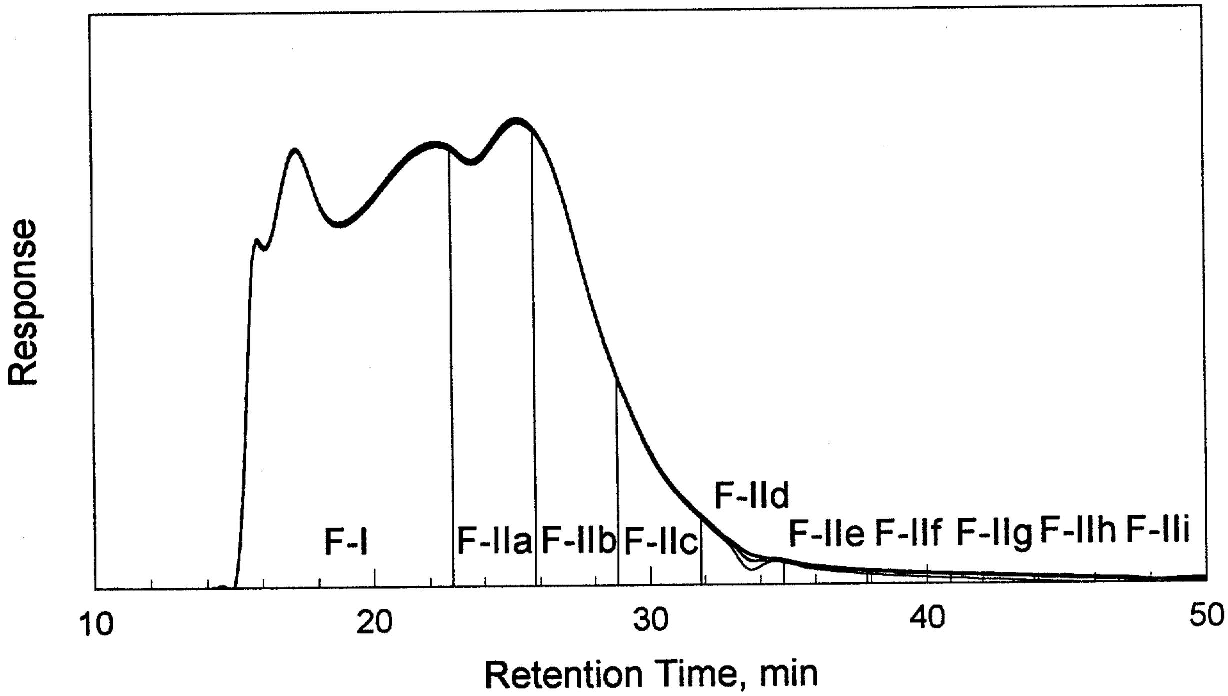


Figure 2-4. HPLC/SEC DRID chromatograms of five consecutive runs of asphalt AAA-1 including timed fractions.

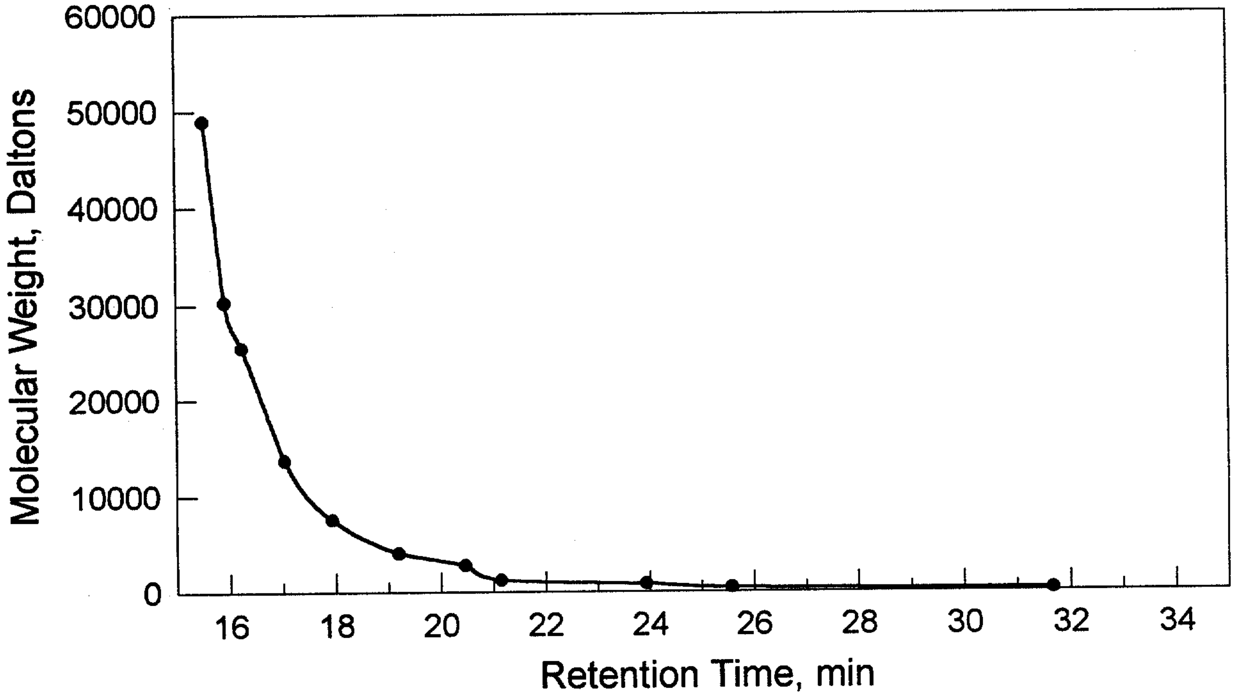


Figure 2-5. Calibration curve for HPLC/SEC system; 2-500Å and 1-100Å columns (7.8 by 300 mm) in series, toluene carrier, 40°C.

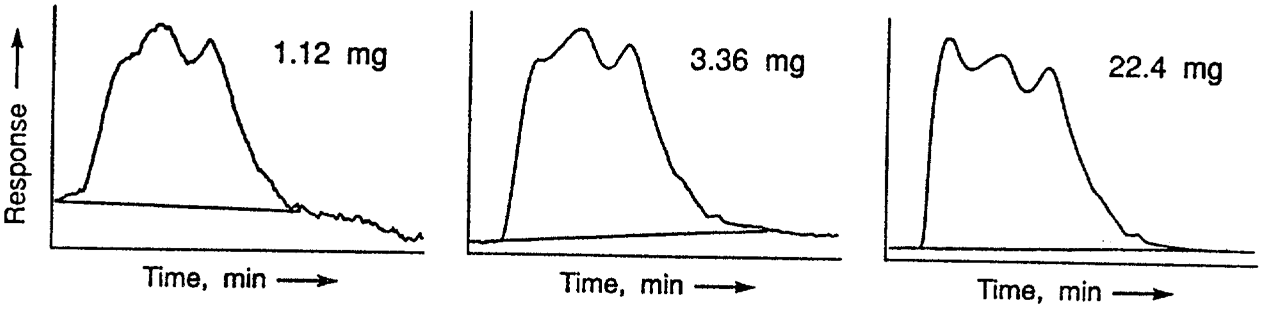


Figure 2-6. HPLC/SEC chromatograms of asphalt AAD-1 at three sample sizes.

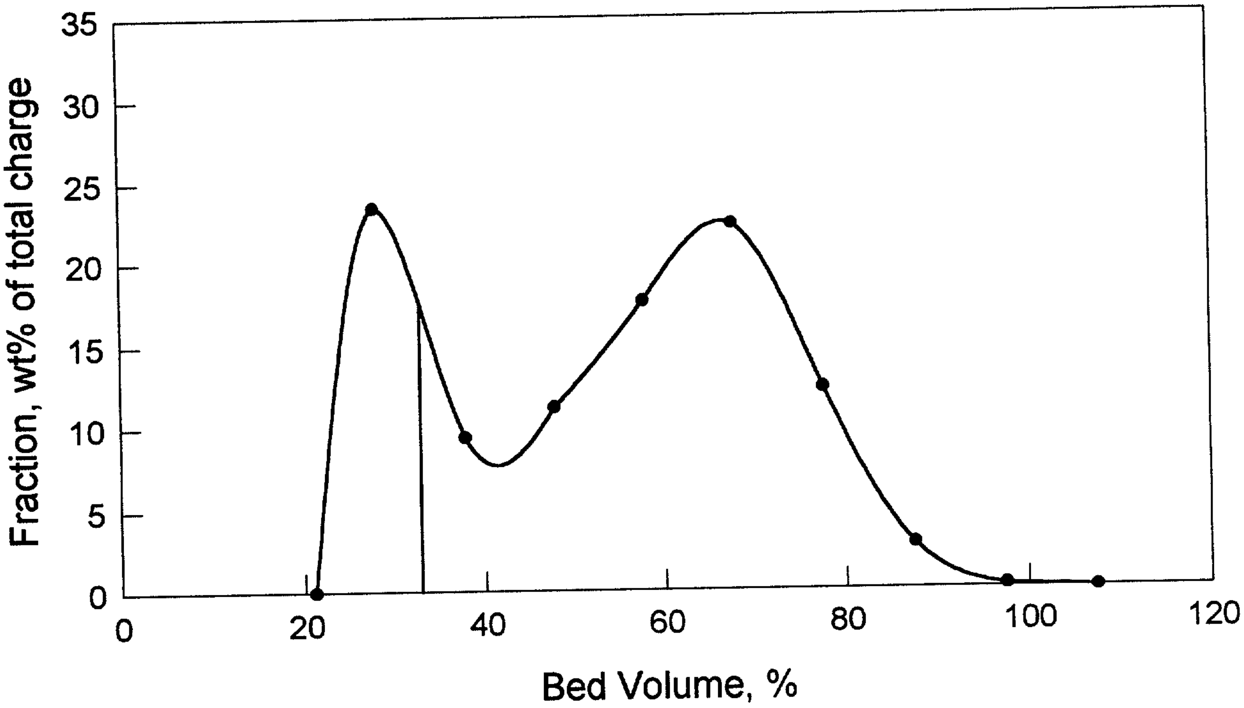


Figure 2-7a. Preparative SEC chromatogram of asphalt AAD-1, F-I cutpoint at 32.8% of bed volume.

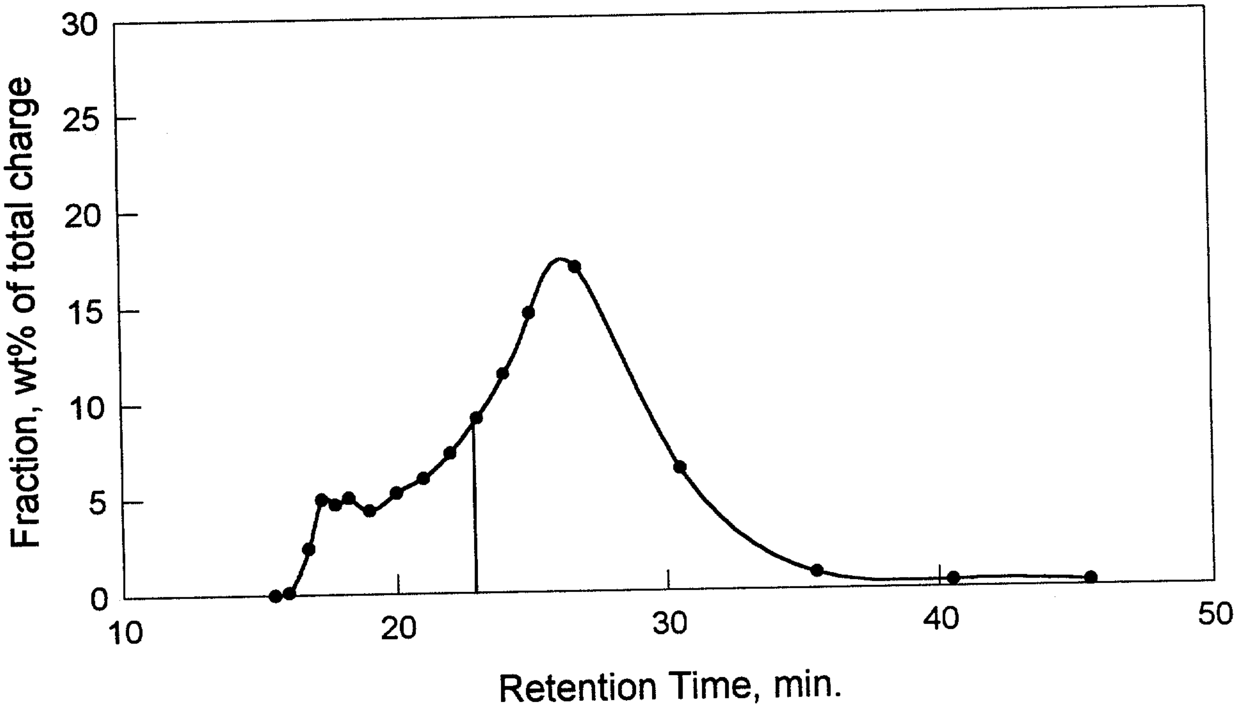


Figure 2-7b. Gravimetric HPLC/SEC of asphalt AAD-1; F-I cutpoint of 22.87 min.

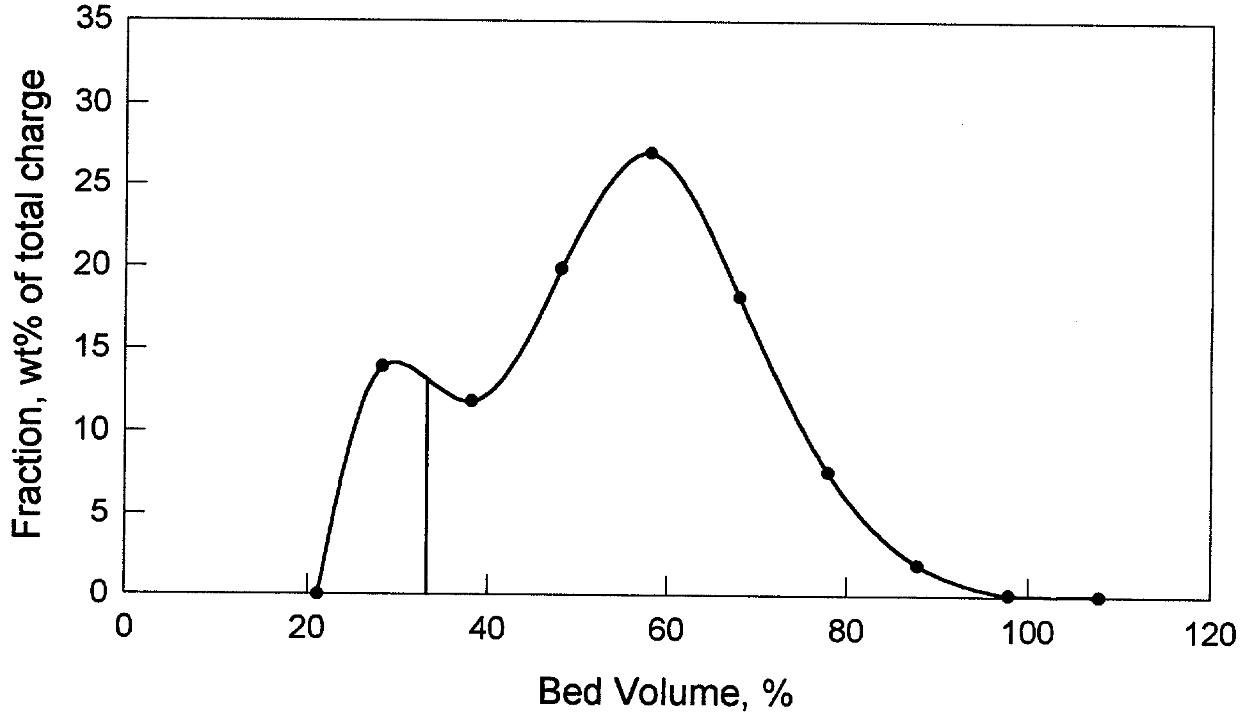


Figure 2-8a. Preparative SEC chromatogram of asphalt AAF-1, F-I cutpoint at 34.4% of bed volume.

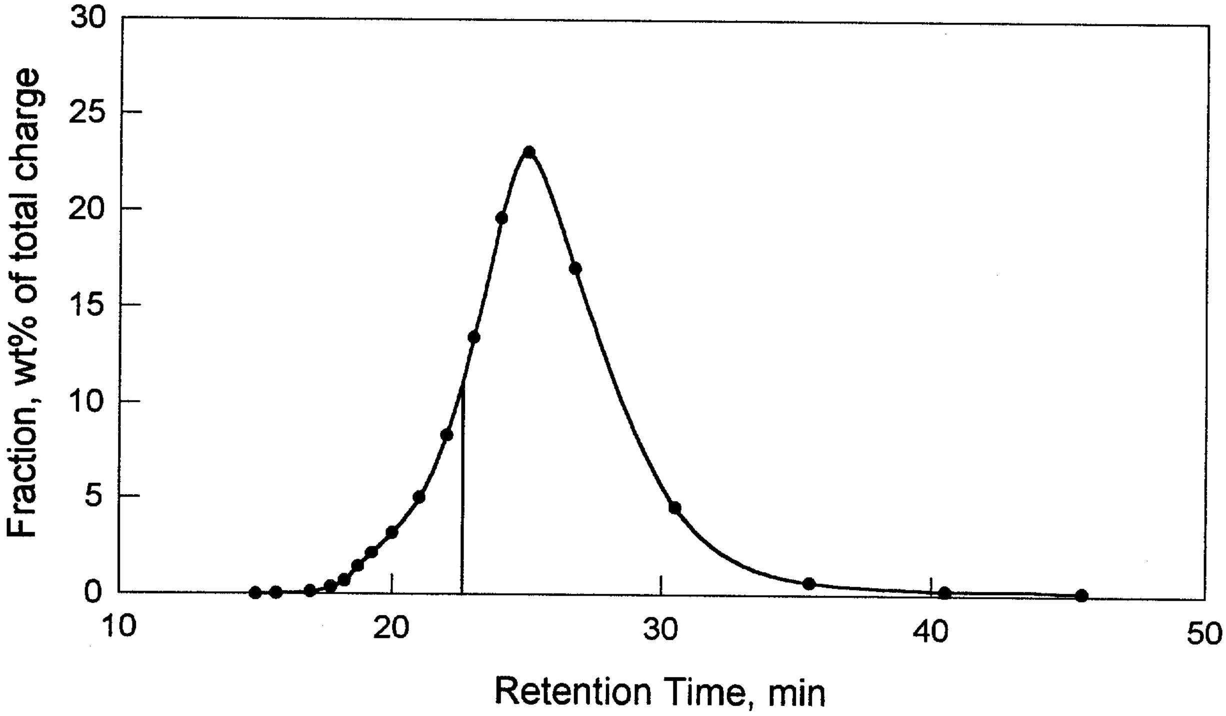


Figure 2-8b. Gravimetric HPLC/SEC of asphalt AAF-1; F-I cutpoint of 22.59 min.

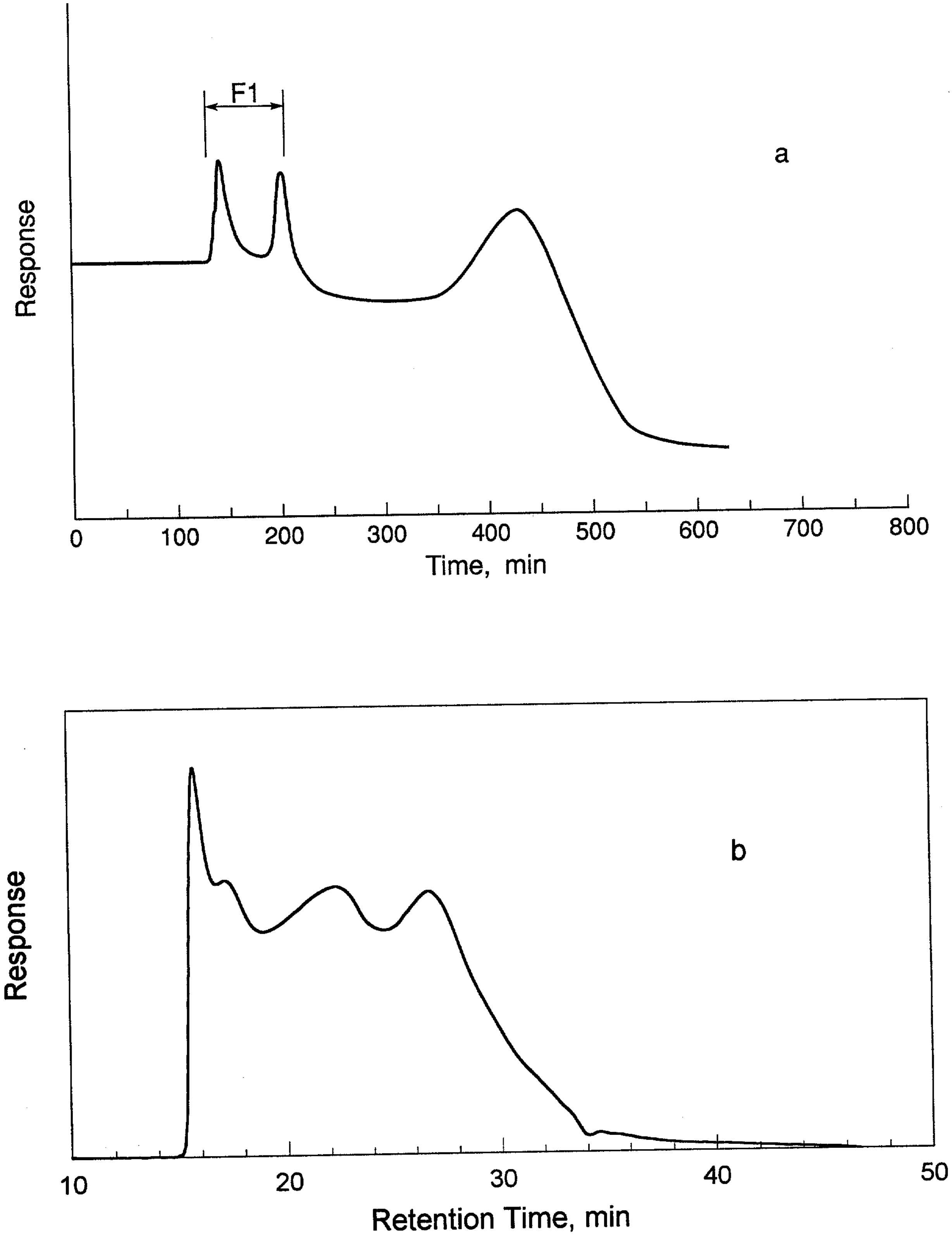


Figure 2-9. Preparative SEC DRID chromatogram (a) and HPLC/SEC DRID chromatogram (b) of unmodified core asphalt AAD-1.

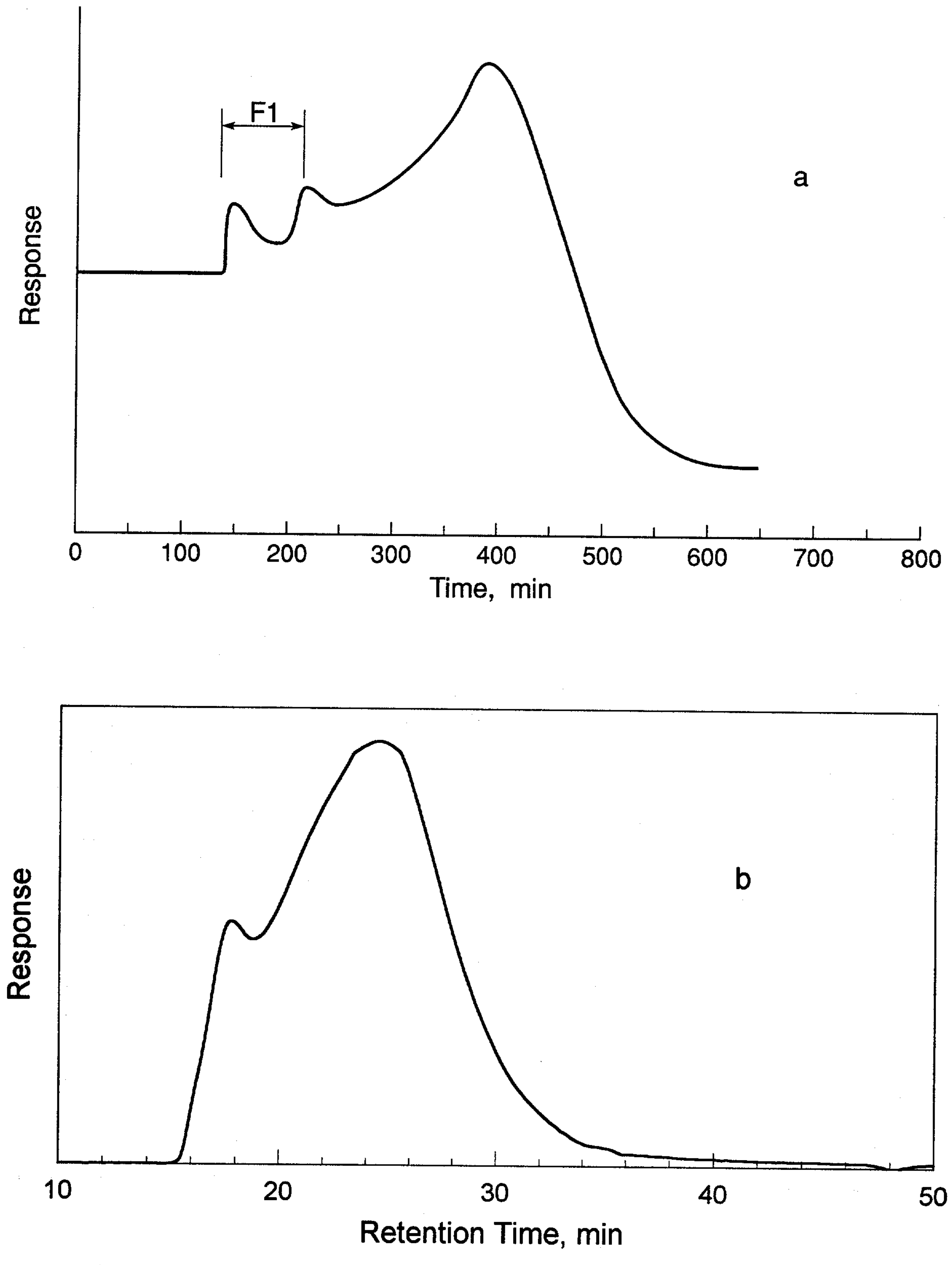


Figure 2-10. Preparative SEC DRID chromatogram (a) and HPLC/SEC DRID chromatogram (b) of unmodified core asphalt AAF-1.

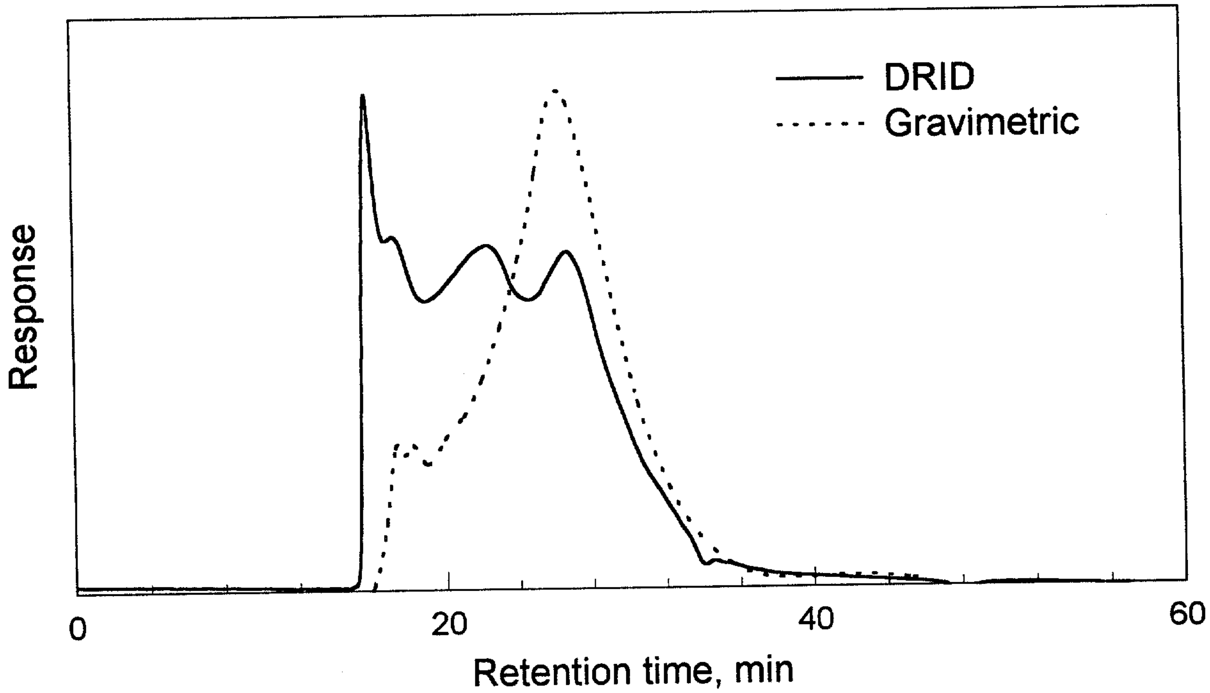


Figure 2-11. Comparison of HPLC/SEC chromatograms of core asphalt AAD-1 obtained gravimetrically and by differential refractive index detector.

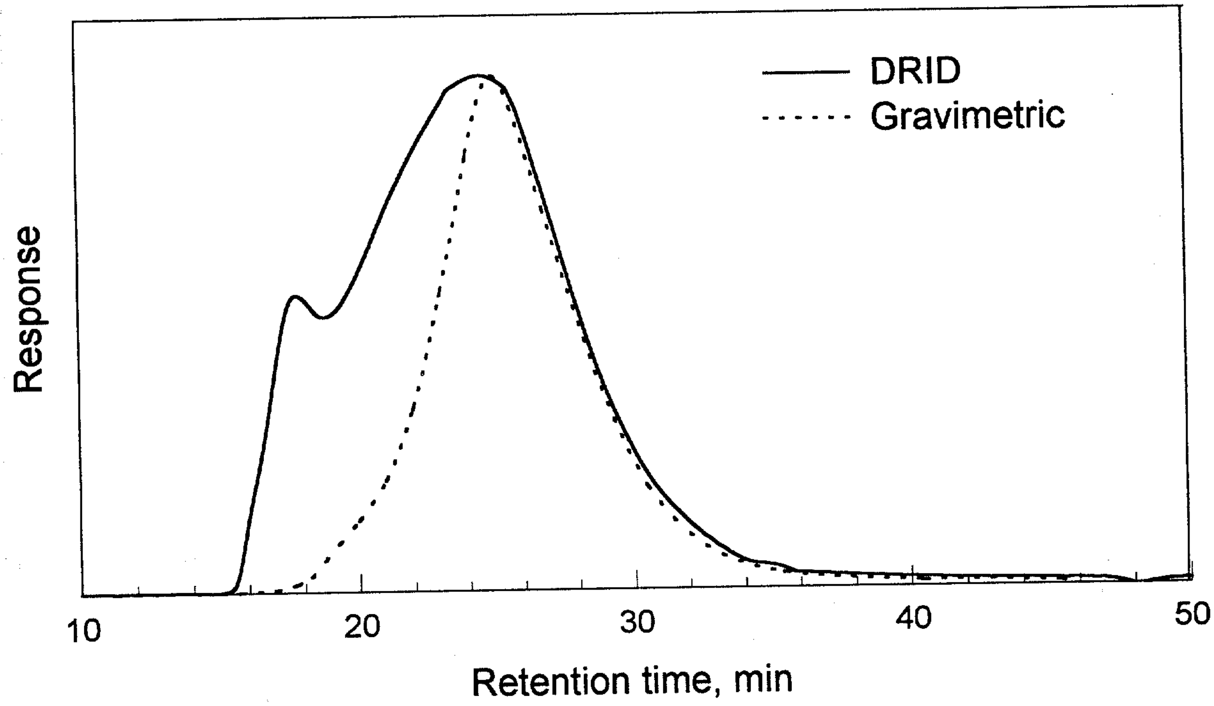


Figure 2-12. Comparison of HPLC/SEC chromatograms of core asphalt AAF-1 obtained gravimetrically and by differential refractive index detector.

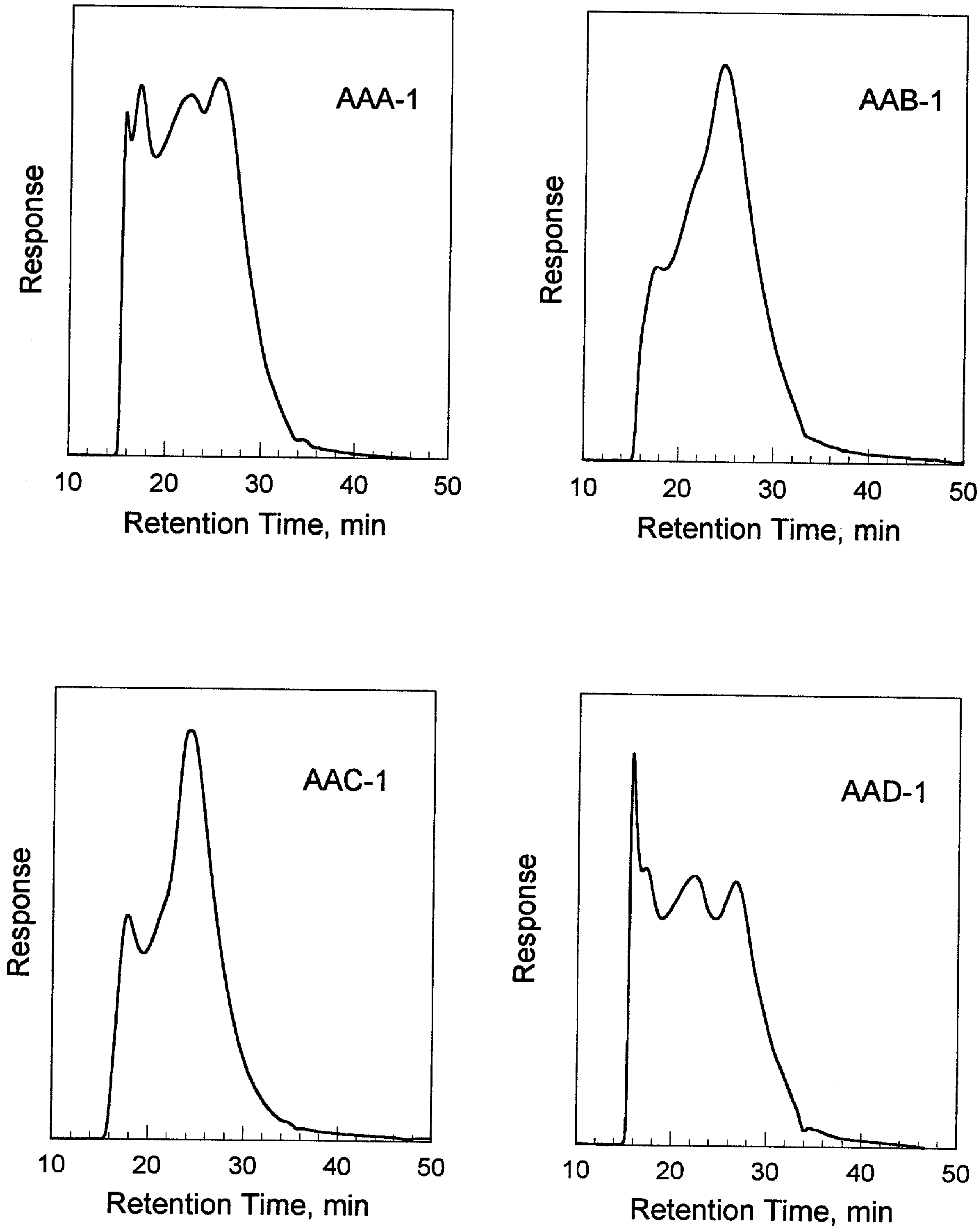


Figure 2-13. HPLC/SEC DRID chromatograms of core asphalts AAA-1, AAB-1, AAC-1, and AAD-1; toluene carrier, 40°C (104°F), two 500Å and one 100Å columns in series.

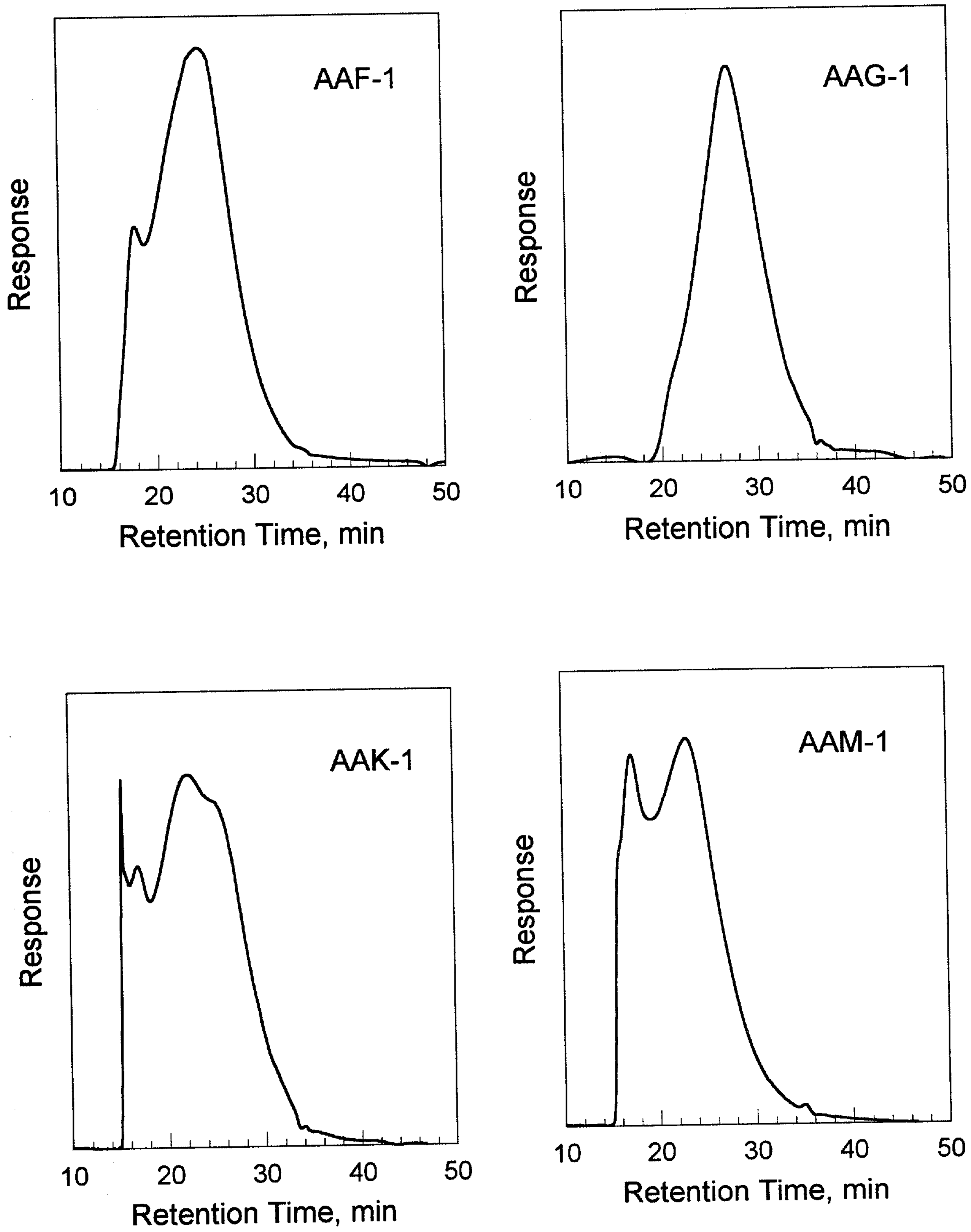


Figure 2-14. HPLC/SEC DRID chromatograms of core asphalts AAF-1, AAG-1, AAK-1, and AAM-1; toluene carrier, 40°C (104°F), two 500 Å and one 100 Å columns in series.

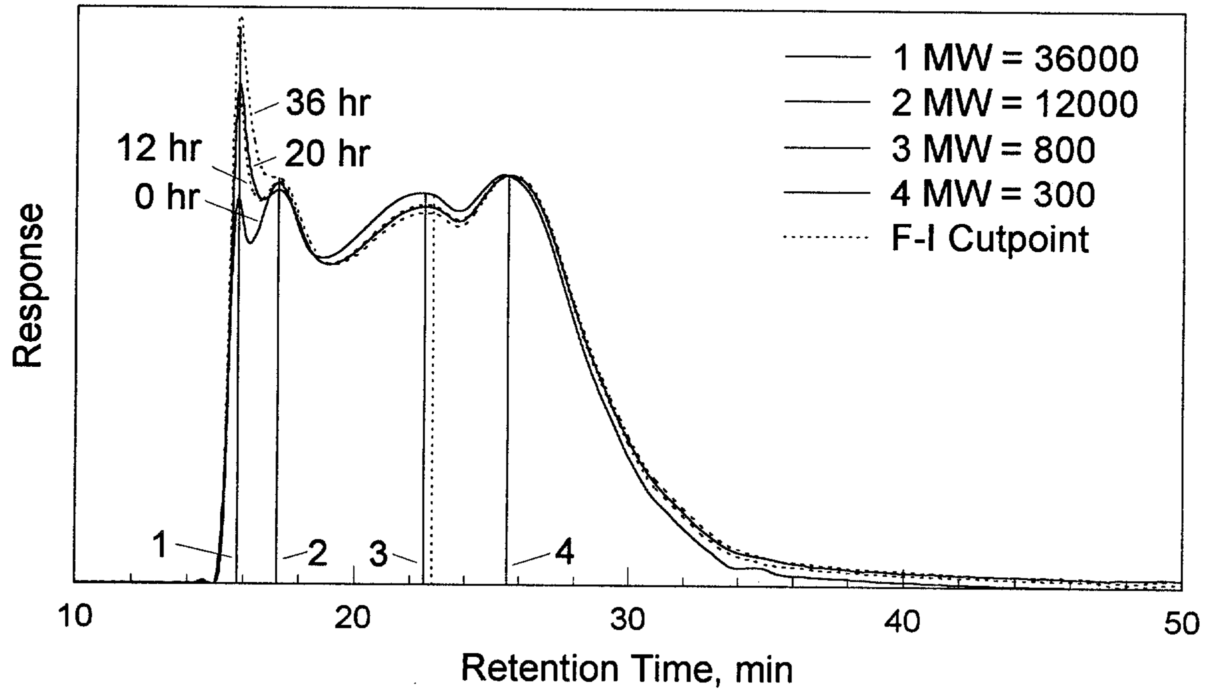


Figure 2-15. HPLC/SEC DRID chromatograms of asphalt AAA-1 TFO/PAV aged for 0, 12, 20, or 36 hours with molecular weights estimated from the calibration curve; F-I cutpoint = 22.84 min.

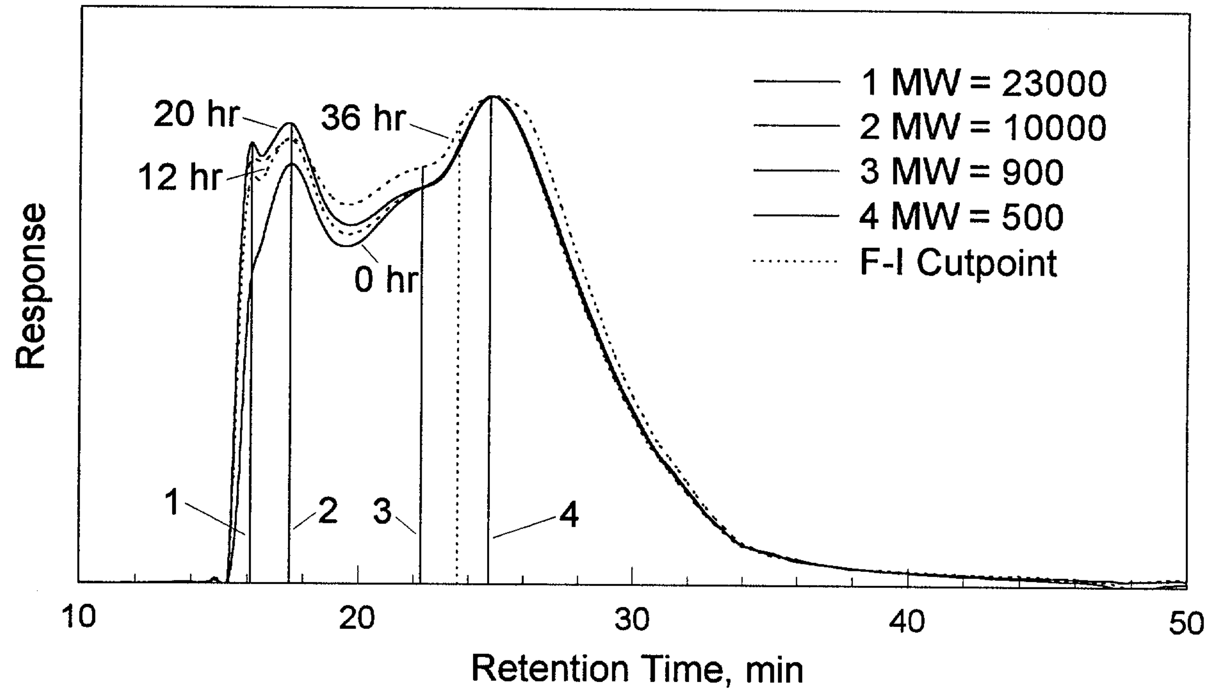


Figure 2-16. HPLC/SEC DRID chromatograms of asphalt AAB-1 TFO/PAV aged for 0, 12, 20, or 36 hours with molecular weights estimated from the calibration curve; F-I cutpoint = 23.61 min.

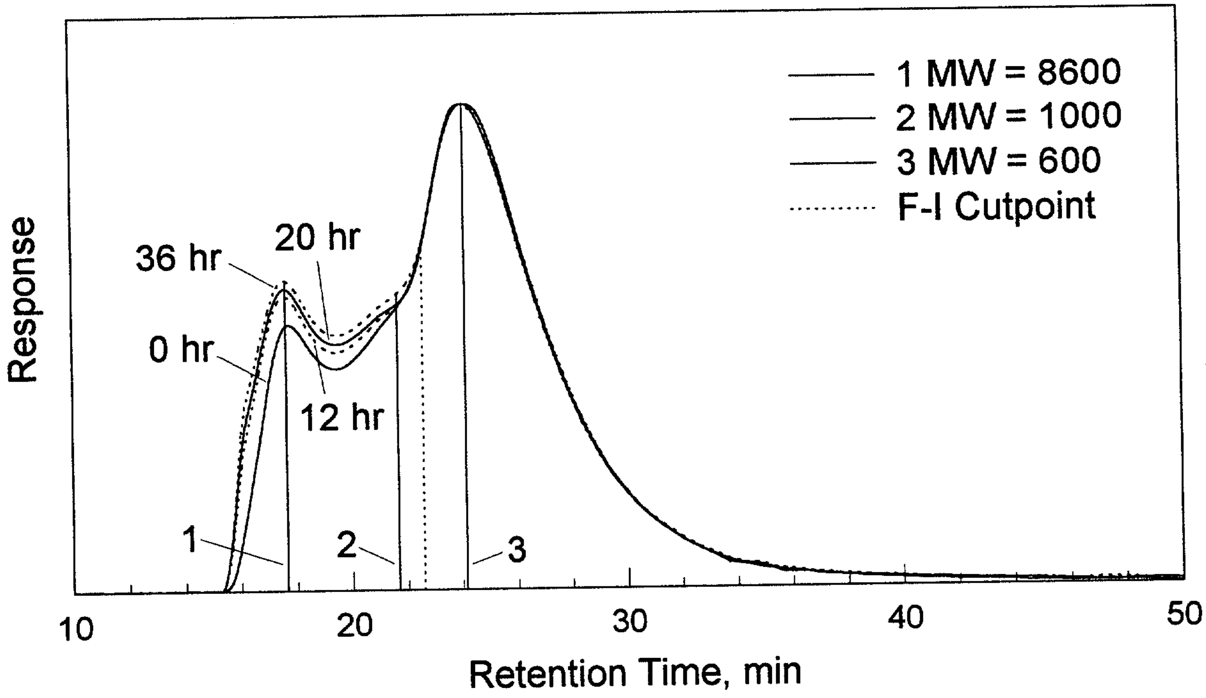


Figure 2-17. HPLC/SEC DRID chromatograms of asphalt AAC-1 TFO/PAV aged for 0, 12, 20, or 36 hours with molecular weights estimated from the calibration curve; F-I cutpoint = 22.60 min.

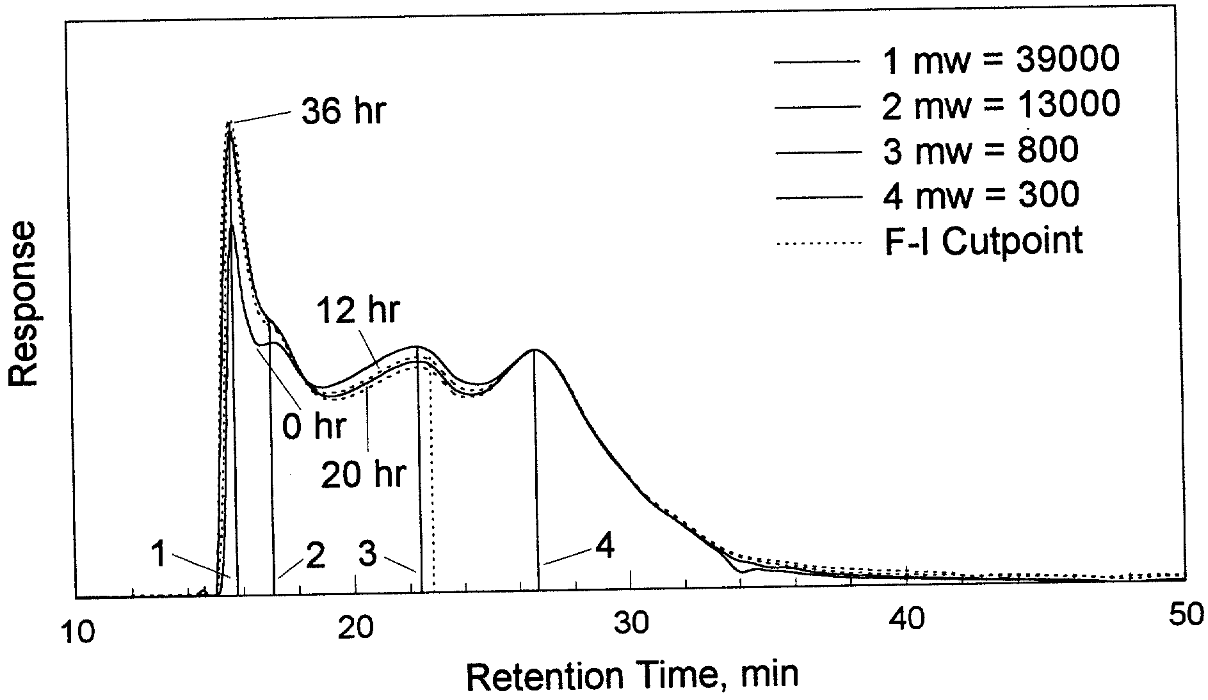


Figure 2-18. HPLC/SEC DRID chromatograms of asphalt AAD-1 TFO/PAV aged for 0, 12, 20, or 36 hours with molecular weights estimated from the calibration curve; F-I cutoint = 22.87 min.

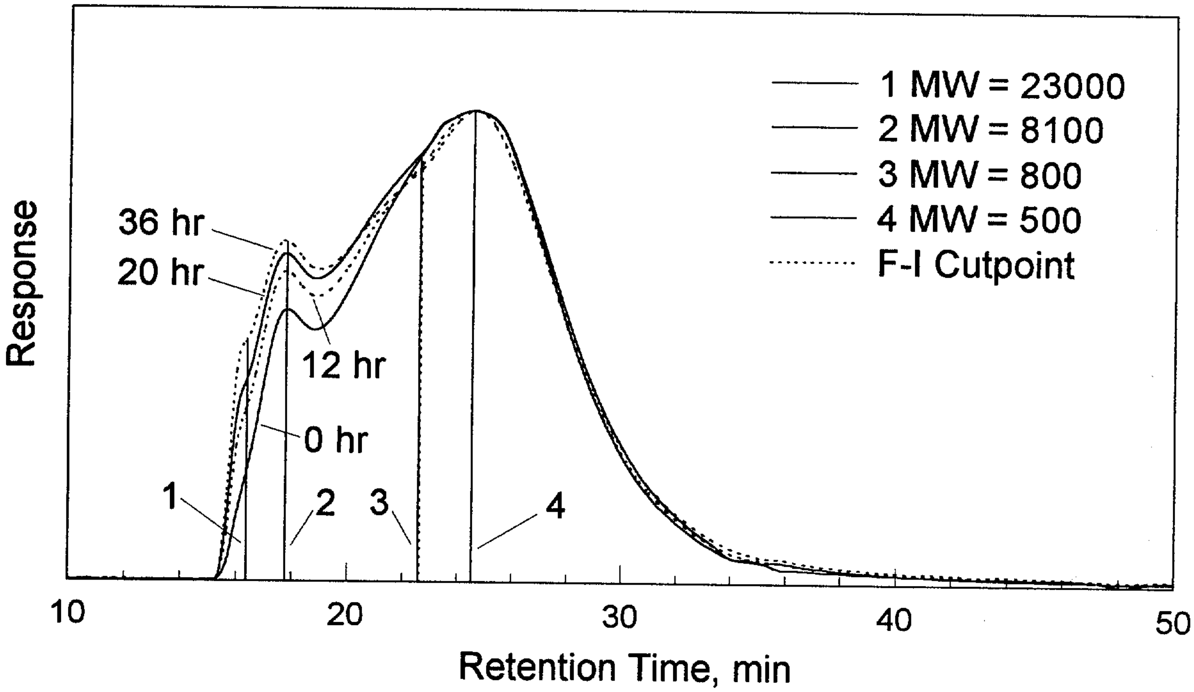


Figure 2-19. HPLC/SEC DRID chromatograms of asphalt AAF-1 TFO/PAV aged for 0, 12, 20, or 36 hours with molecular weights estimated from the calibration curve; F-I cutpoint = 22.59 min.

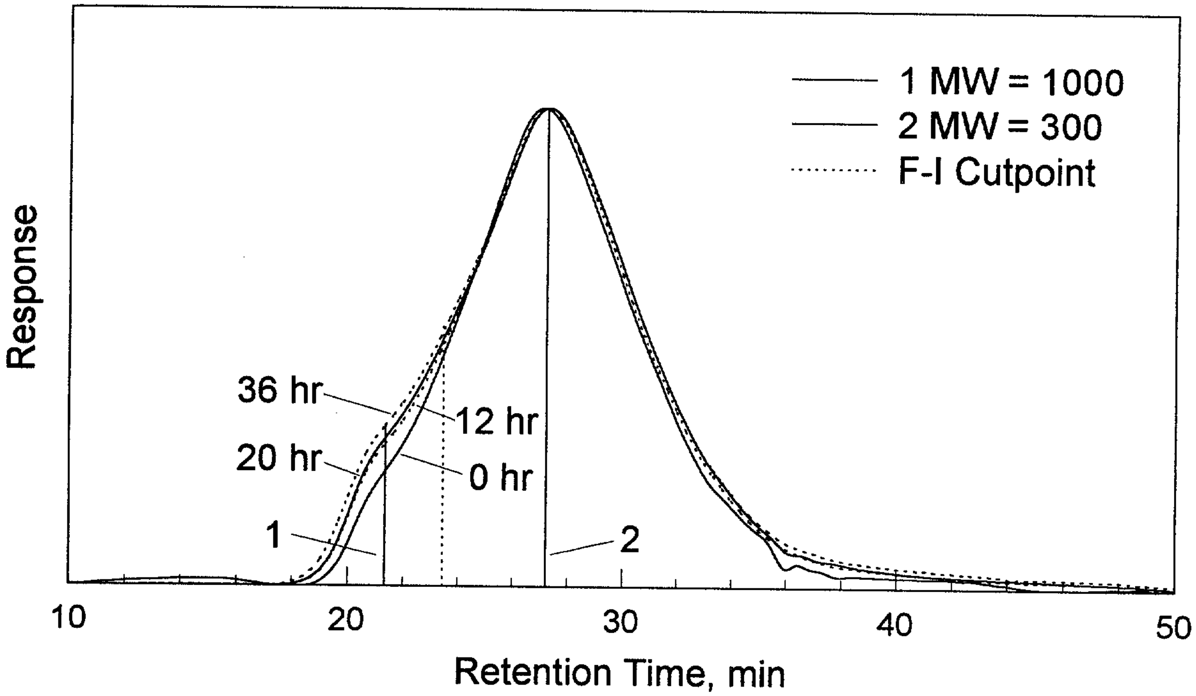


Figure 2-20. HPLC/SEC DRID chromatograms of asphalt AAG-1 TFO/PAV aged for 0, 12, 20, or 36 hours with molecular weights estimated from the calibration curve; F-I cutpoint = 23.47 min.

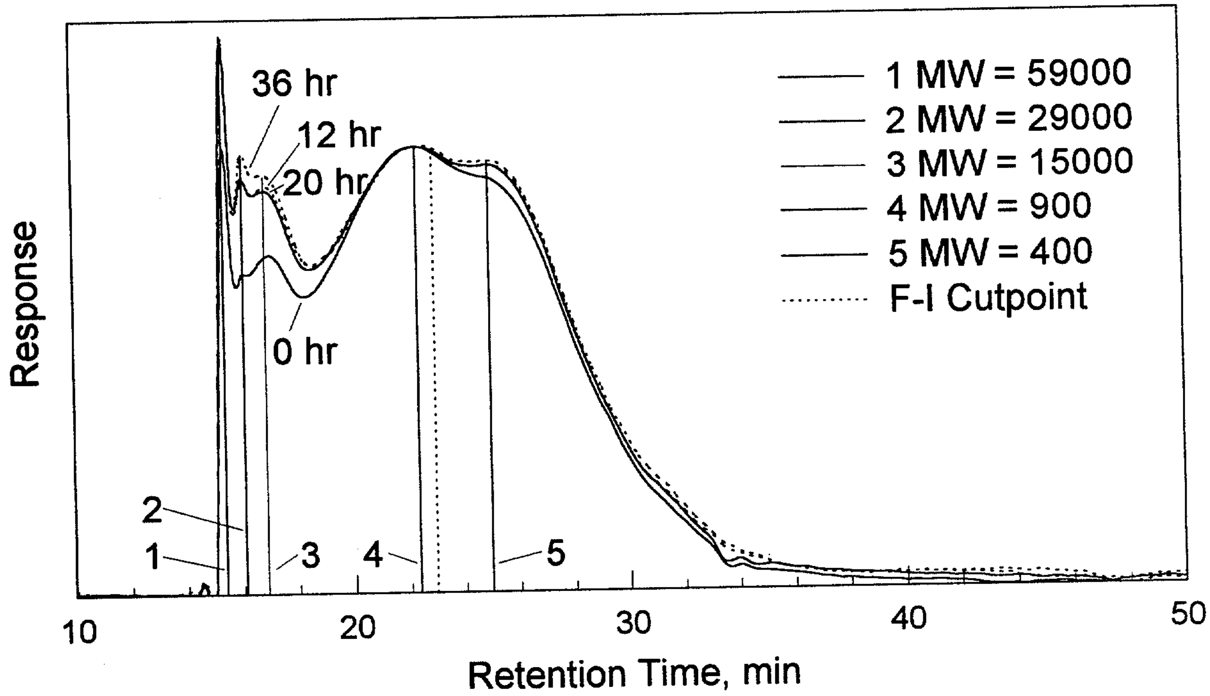


Figure 2-21. HPLC/SEC DRID chromatograms of asphalt AAK-1 TFO/PAV aged for 0, 12, 20, or 36 hours with molecular weights estimated from the calibration curve; F-I cutpoint = 22.95 min.

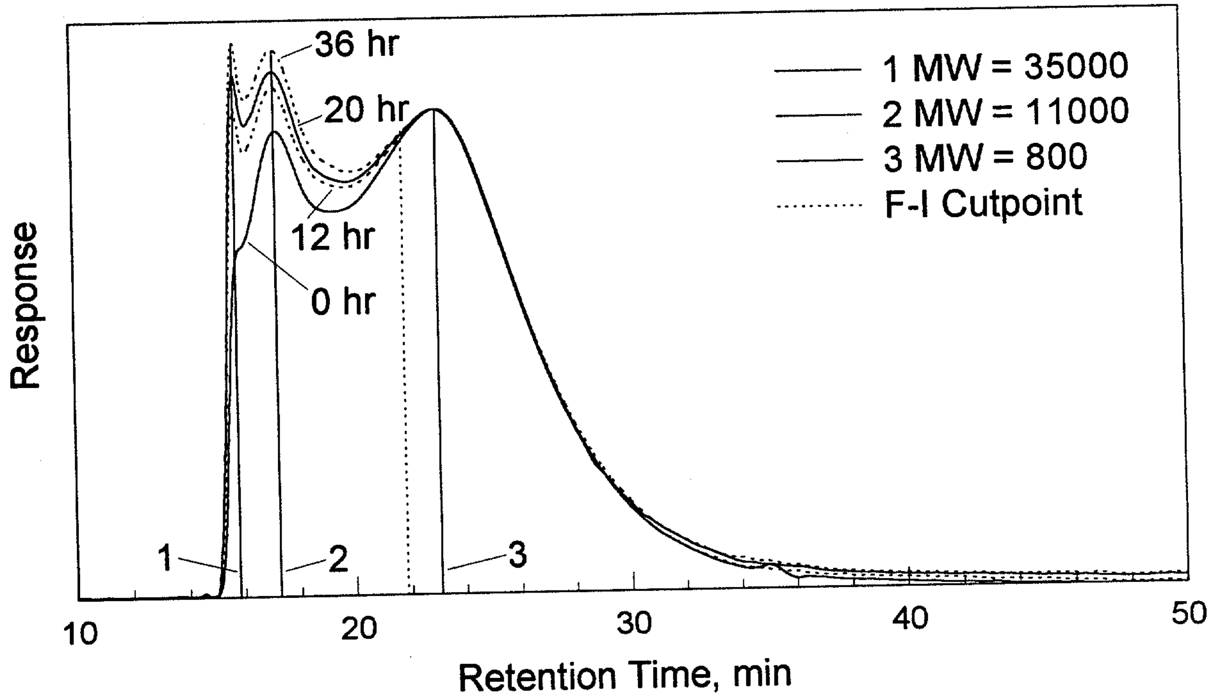


Figure 2-22. HPLC/SEC DRID chromatograms of asphalt AAM-1 TFO/PAV aged for 0, 12, 20, or 36 hours with molecular weights estimated from the calibration curve; F-I cutpoint = 21.85 min.

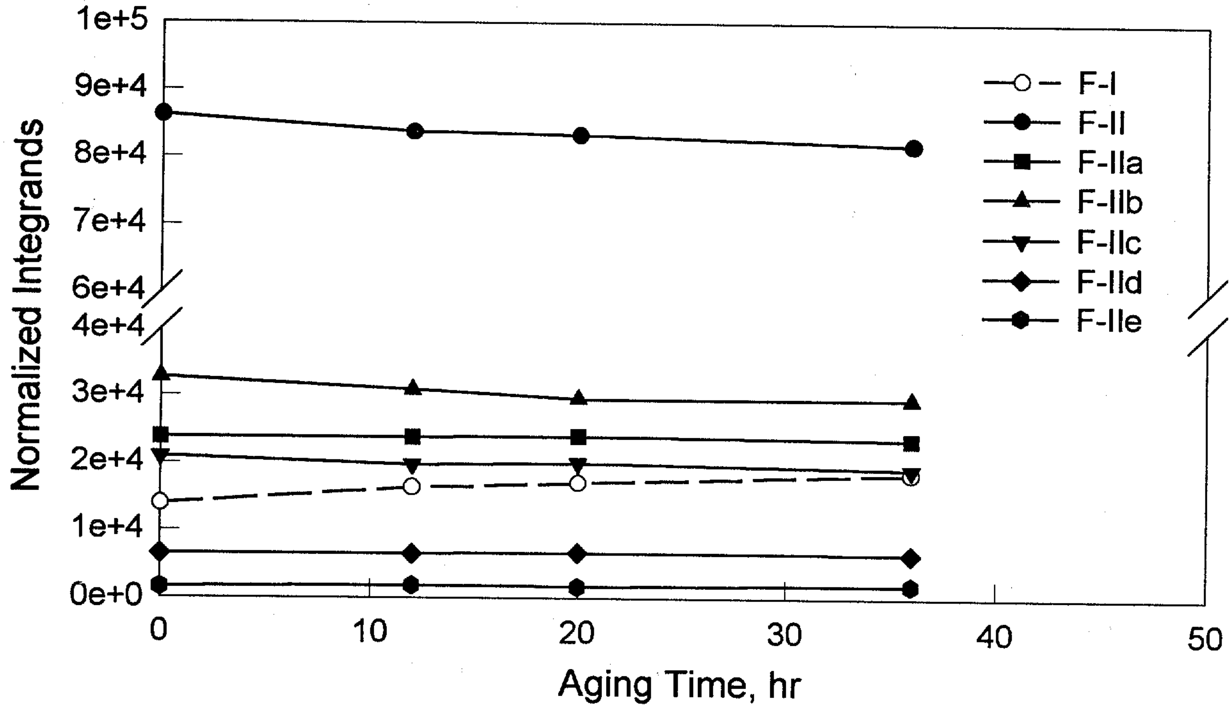


Figure 2-23. Normalized integrands versus aging time for asphalt AAF-1 HPLC/SEC fractions; F-I cutpoint used is from DRID area % equal to preparative SEC weight % F-I.

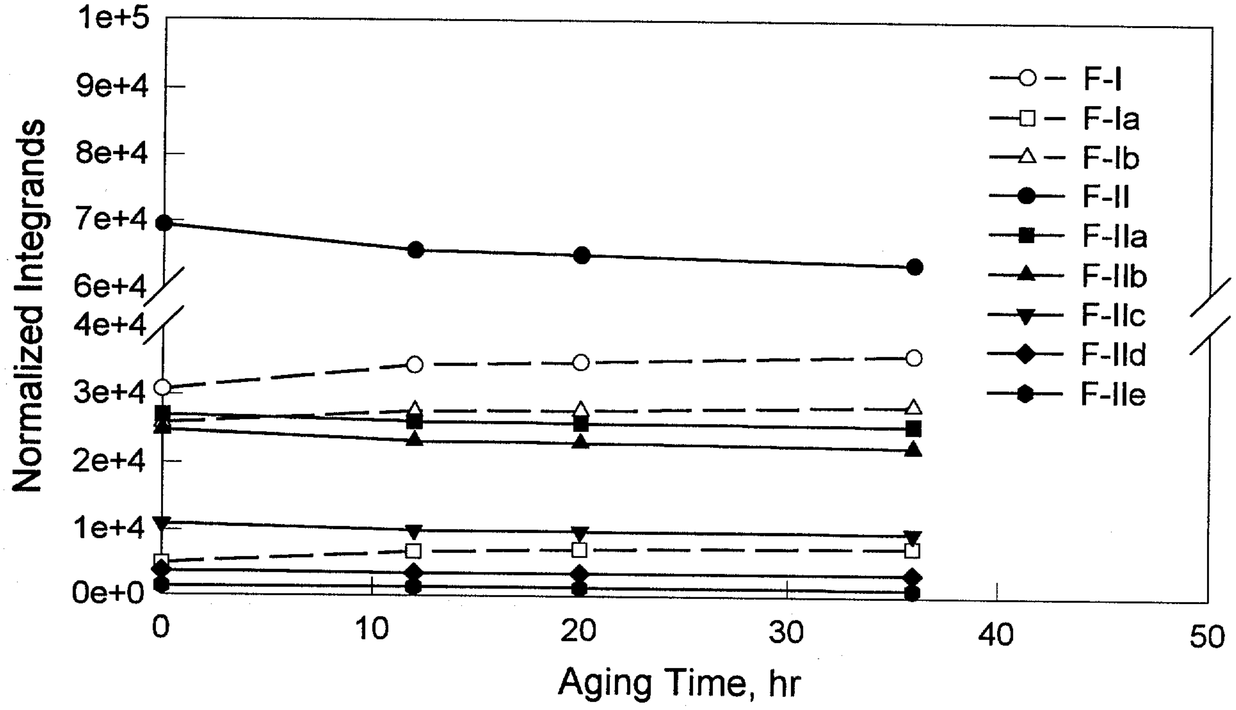


Figure 2-24. Normalized integrands versus aging time for asphalt AAM-1 HPLC/SEC fractions; F-I cutpoint used is from DRID area % equal to preparative SEC weight % F-I.

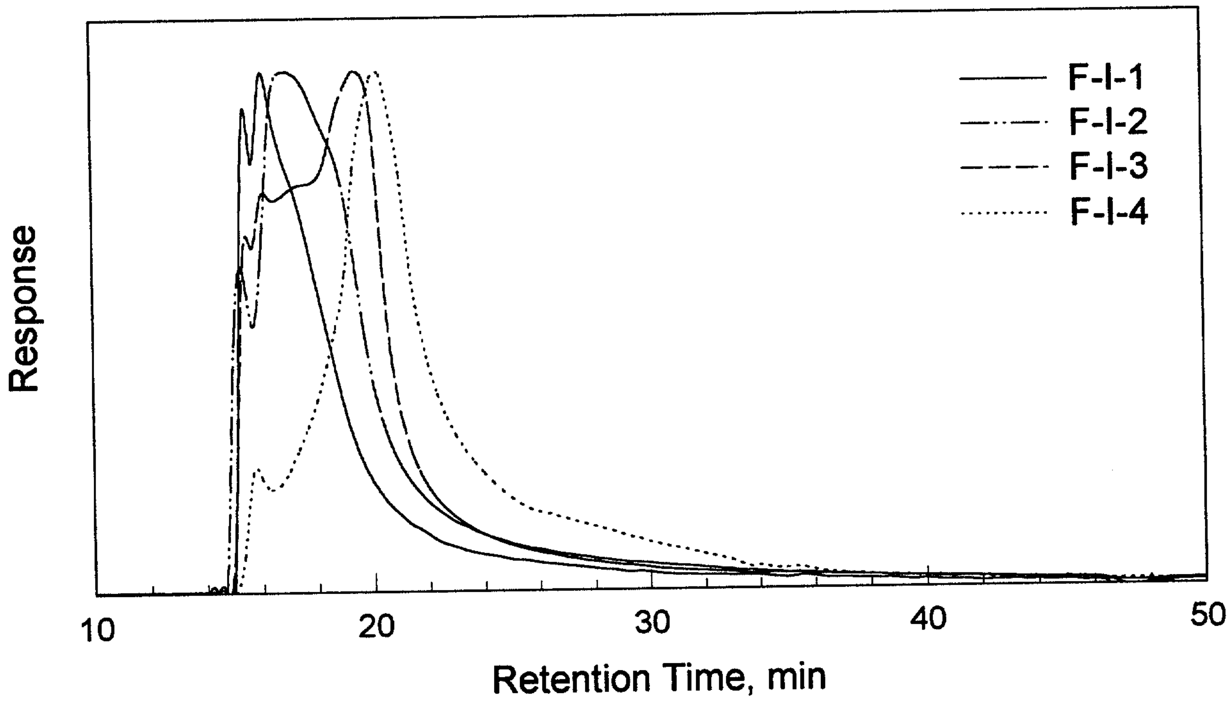


Figure 2-25. HPLC/SEC DRID chromatograms of core asphalt AAD-1 and its preparative SEC F-I subfractions in the same concentration.

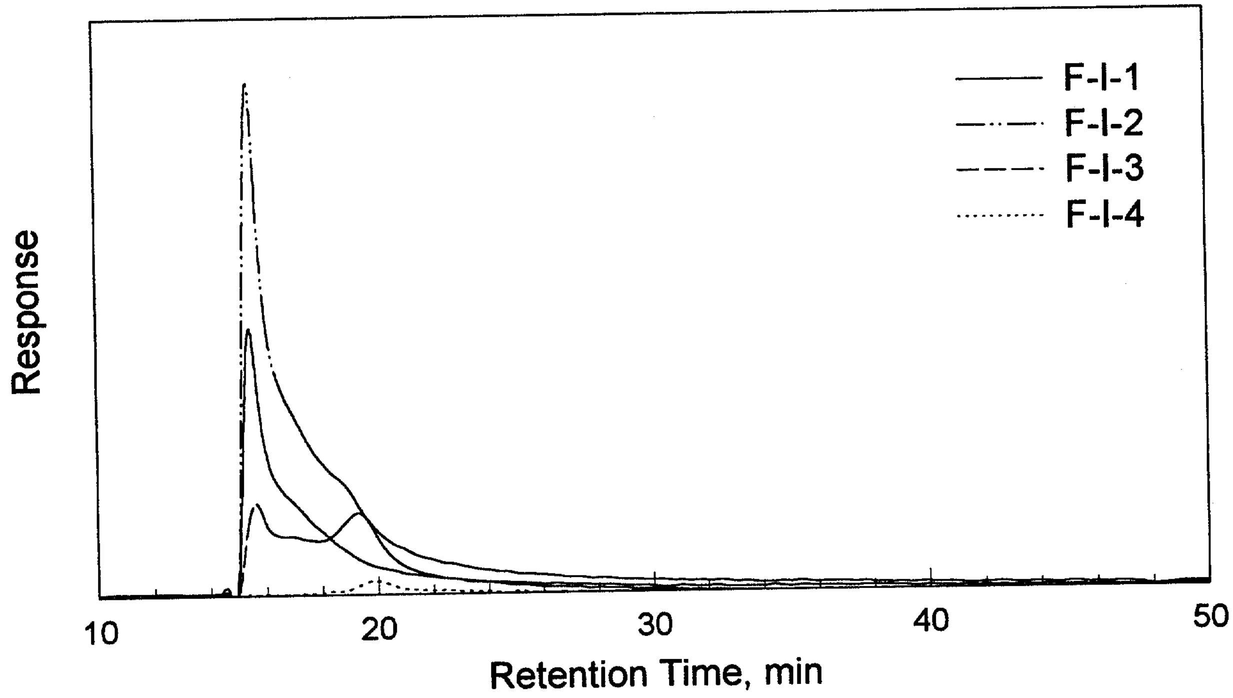


Figure 2-26. HPLC/SEC DRID chromatograms of core asphalt AAD-1 and its preparative SEC F-I subfractions in natural concentration.

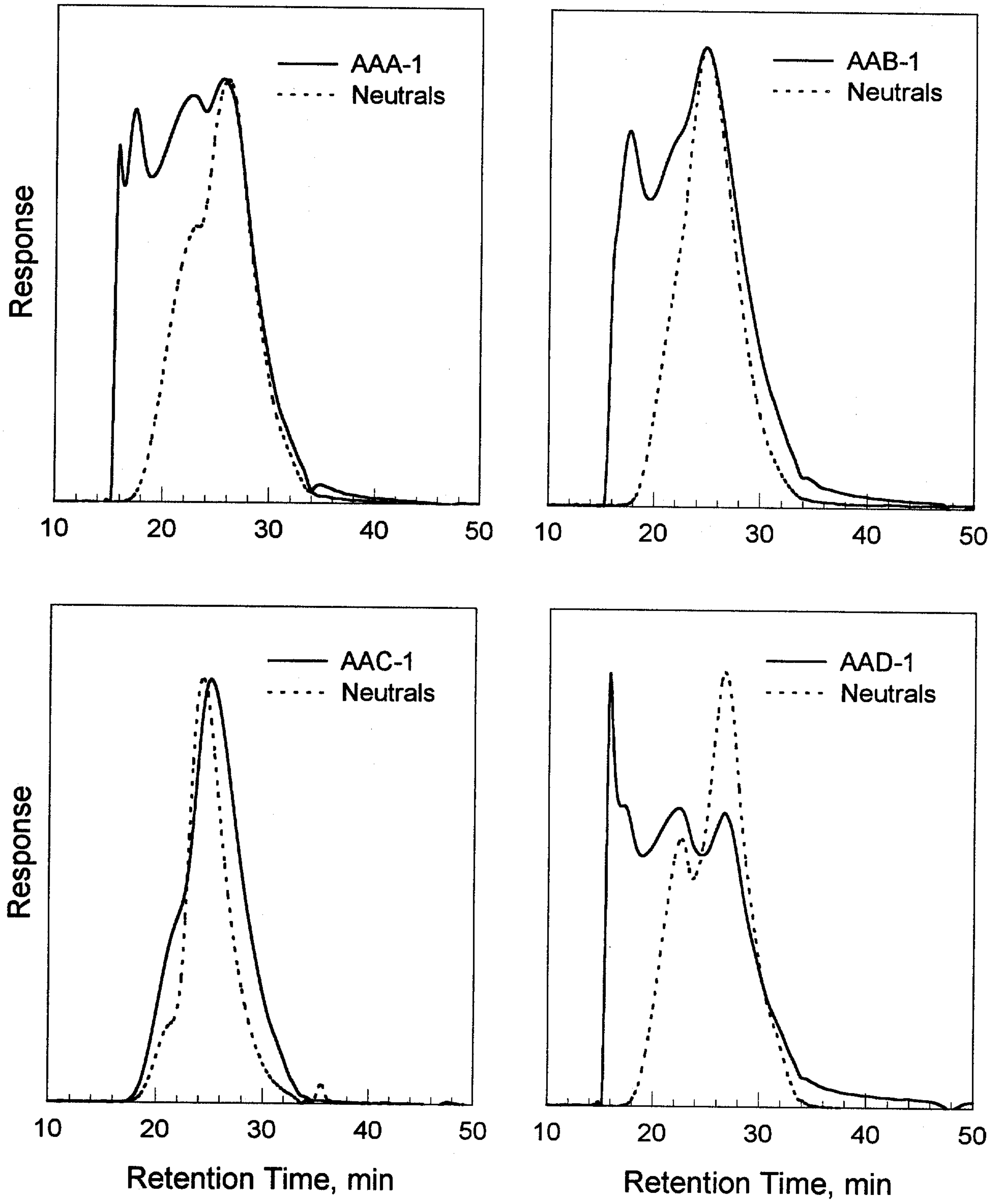


Figure 2-27. HPLC/SEC DRID chromatograms of unmodified core asphalts AAA-1, AAB-1, AAC-1, and AAD-1 and their IEC neutral fractions.

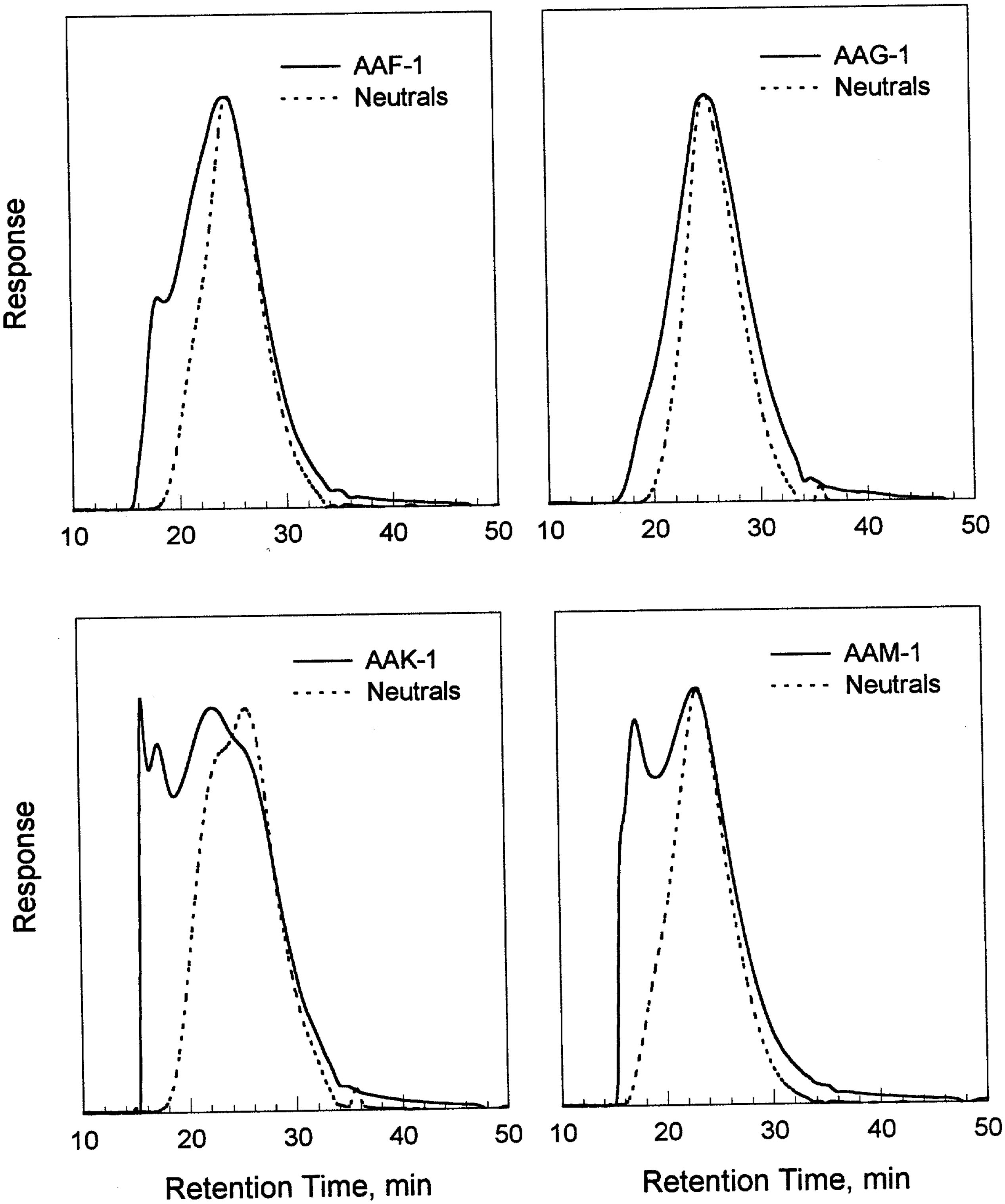


Figure 2-28. HPLC/SEC DRID chromatograms of unmodified core asphalts AAF-1, AAG-1, AAK-1. and AAM-1 and their IEC neutral fractions.

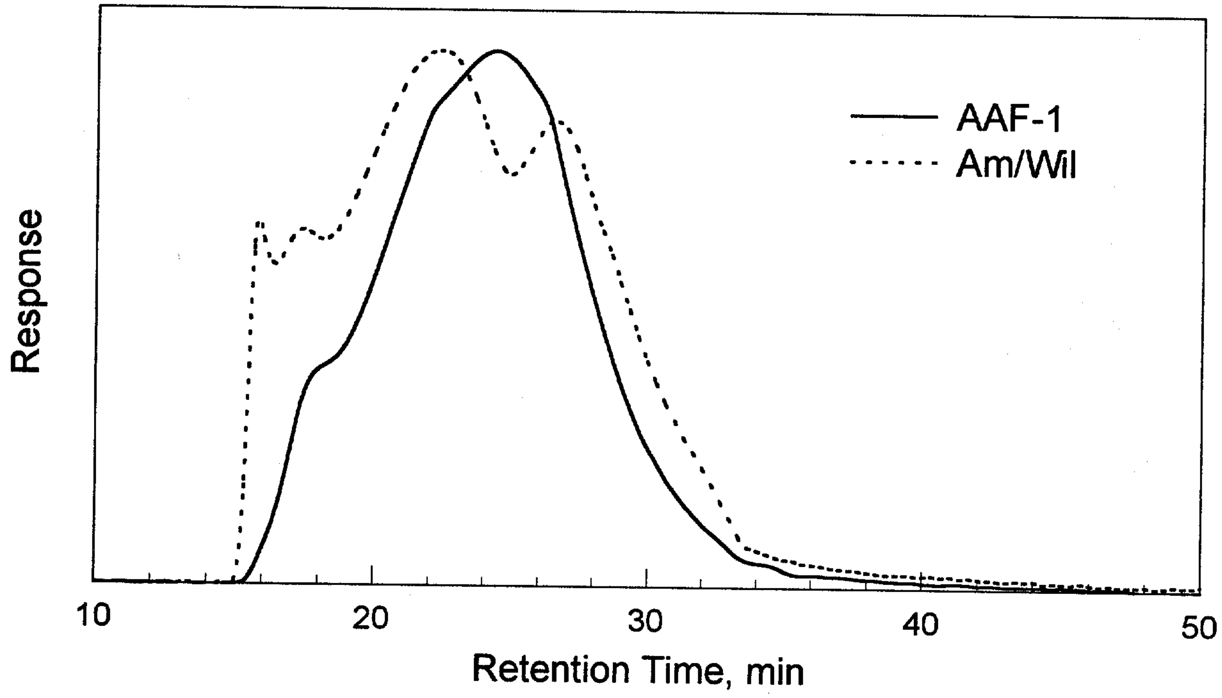


Figure 2-29. HPLC/SEC DRID chromatograms for asphalt AAF-1 and Amoco/Wilmington AC 2.5.

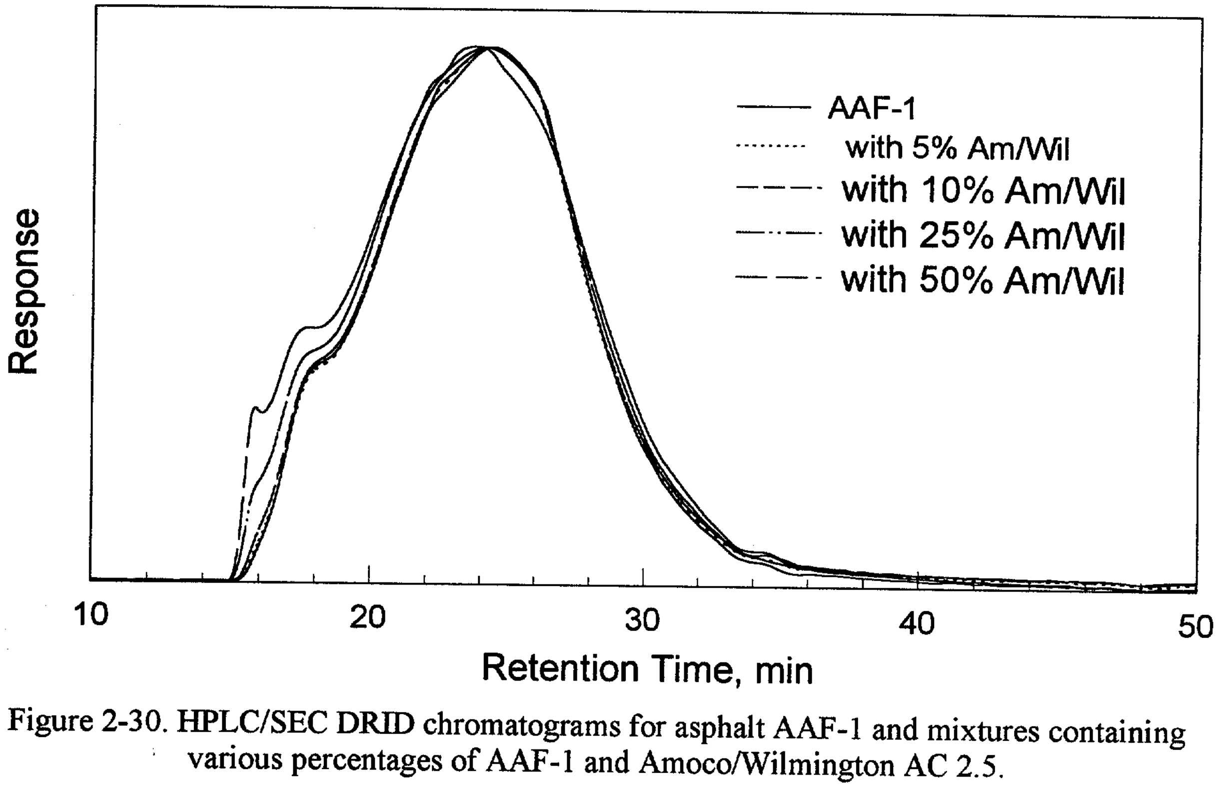


Figure 2-30. HPLC/SEC DRID chromatograms for asphalt AAF-1 and mixtures containing various percentages of AAF-1 and Amoco/Wilmington AC 2.5.

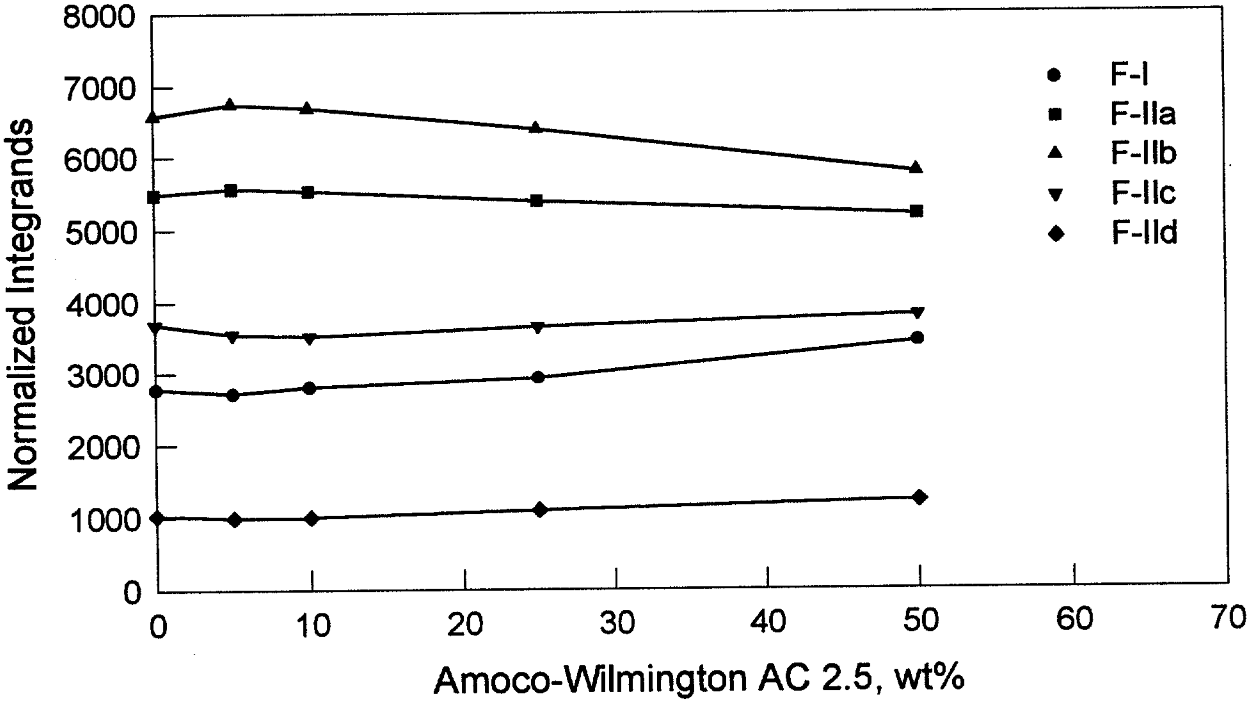


Figure 2-31. Normalized DRID integrands versus wt% Amoco/Wilmington AC 2.5 in asphalt AAF-1 for various HPLC/SEC fractions.

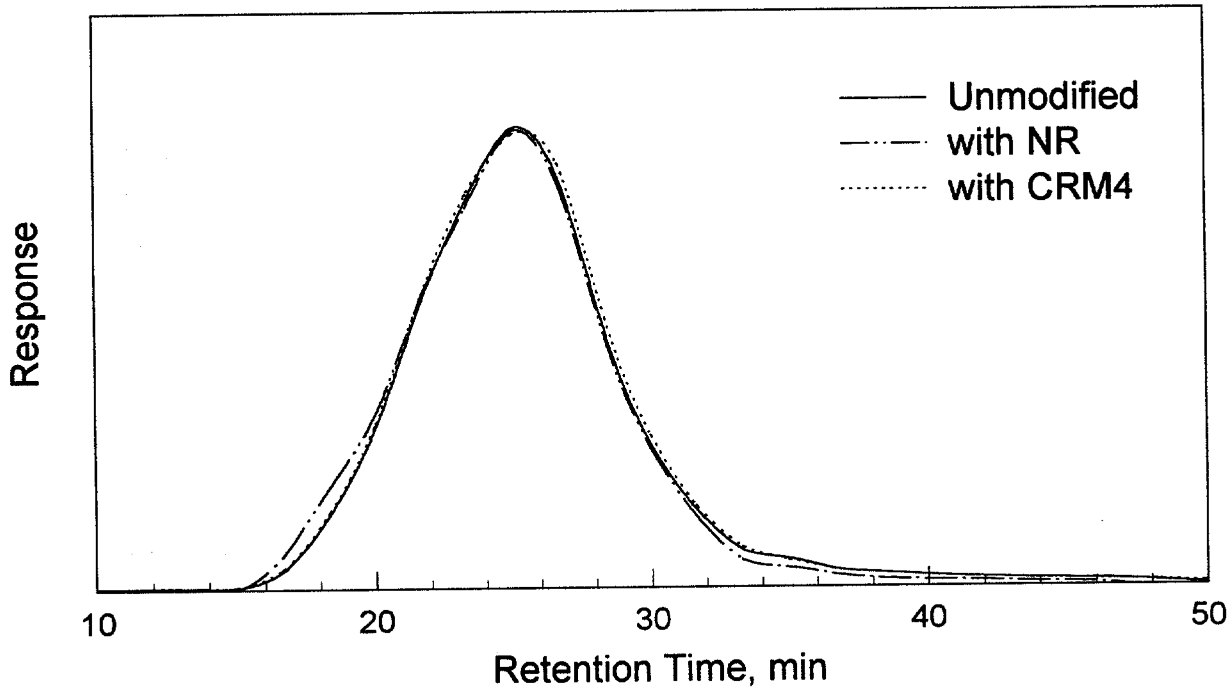


Figure 2-32. HPLC/SEC DRID chromatograms of asphalt ABD unmodified and with NR or CRM4, 0 hours heating.

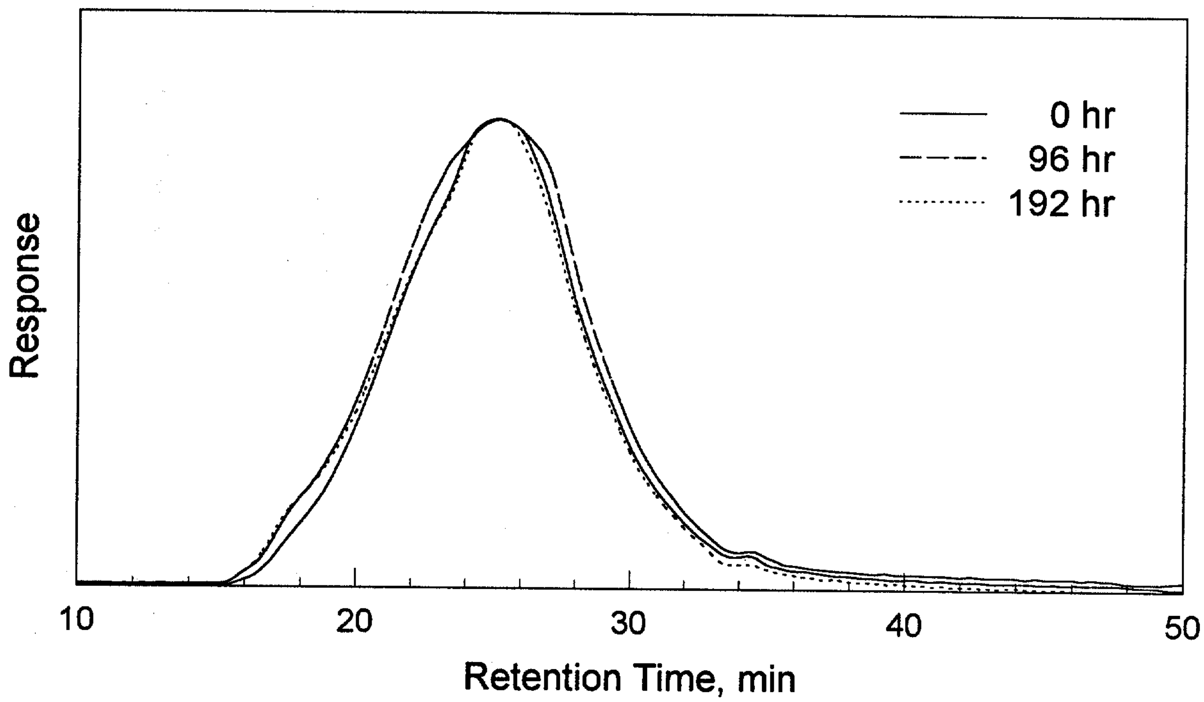


Figure 2-33. HPLC/SEC DRID chromatograms of asphalt ABD unmodified, heated for various times.

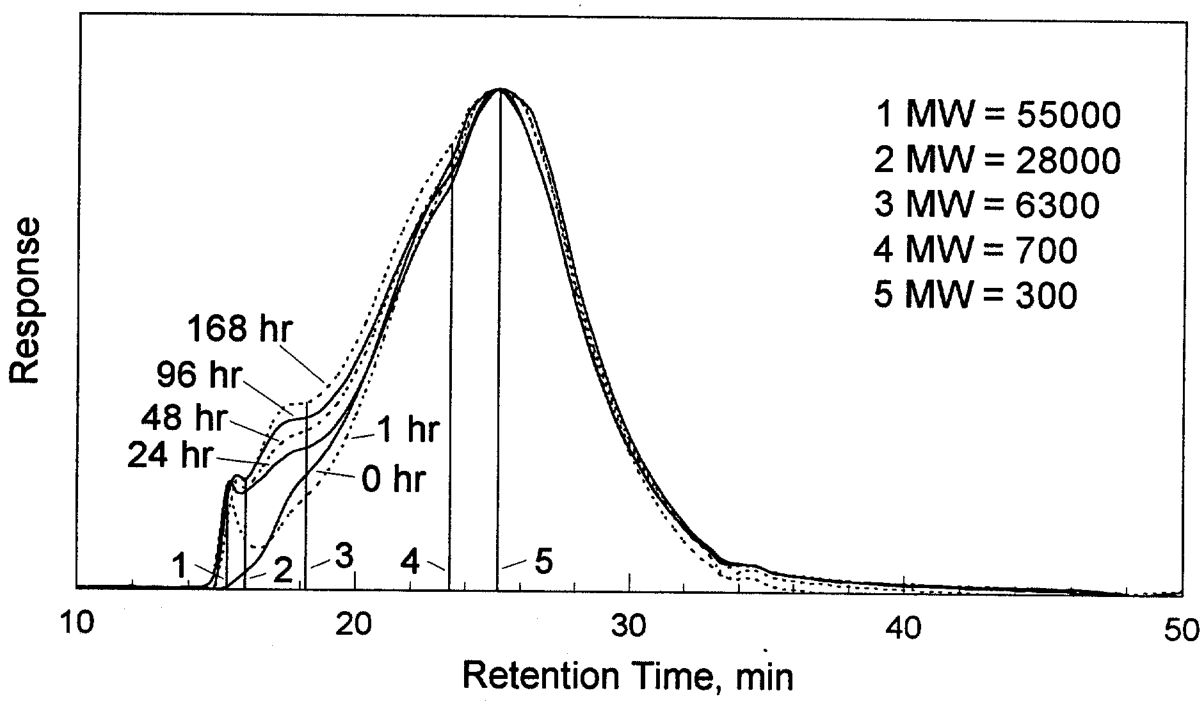


Figure 2-34. HPLC/SEC DRID chromatograms of asphalt ABD with NR, heated for various times.

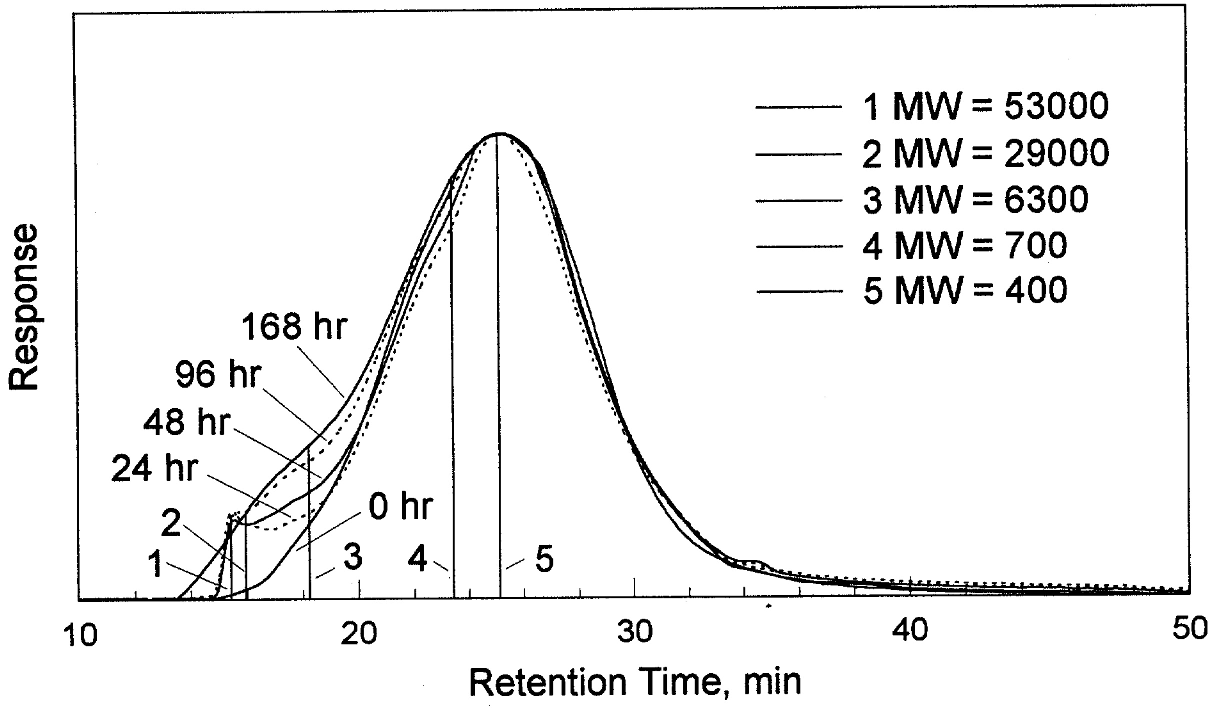


Figure 2-35. HPLC/SEC DRID chromatograms of asphalt ABD with CRM4, heated for various times.

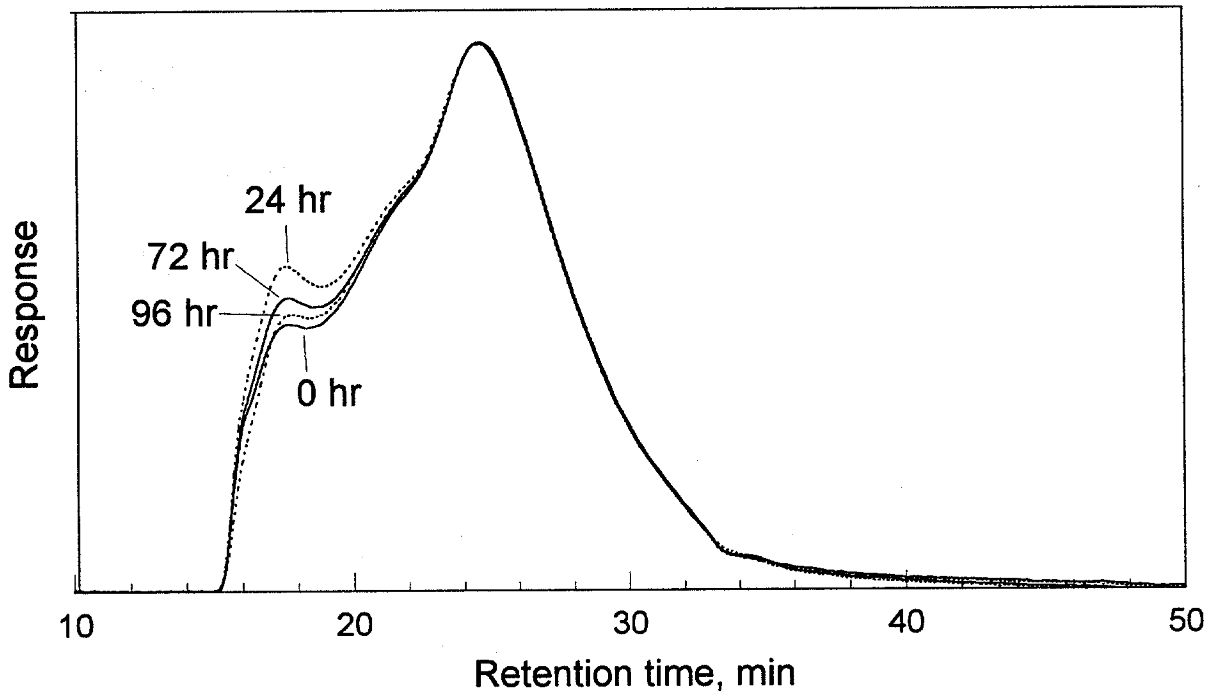


Figure 2-36. HPLC/SEC DRID chromatograms of unmodified core asphalt AAB-1, heated for various times.

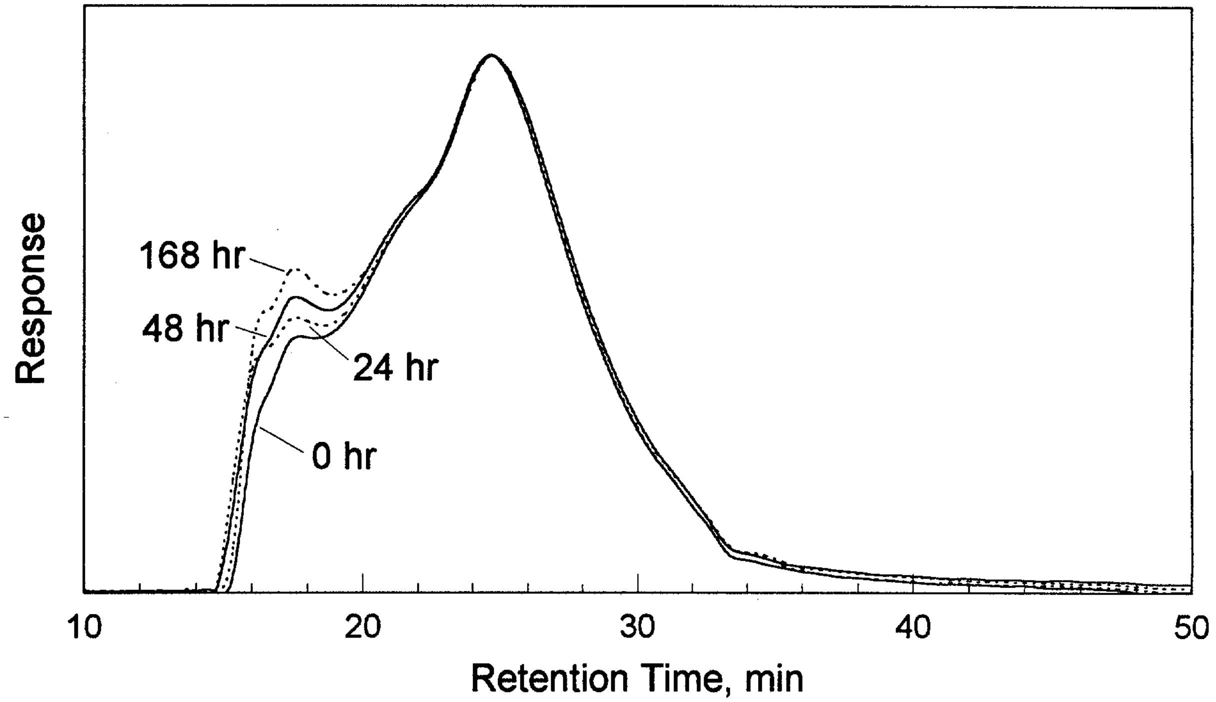


Figure 2-37. HPLC/SEC DRID chromatograms of asphalt AAB-1 with NR, heated for various times.

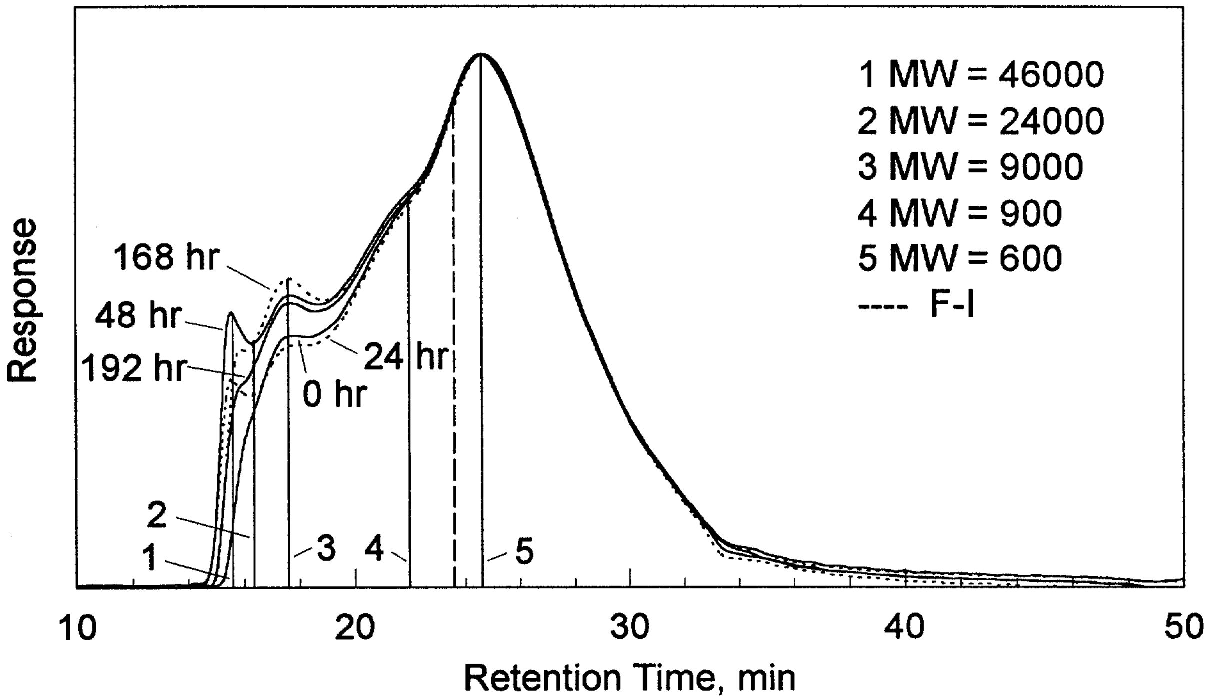


Figure 2-38. HPLC/SEC DRID chromatograms of core asphalt AAB-1 with CRM4, heated for various times.

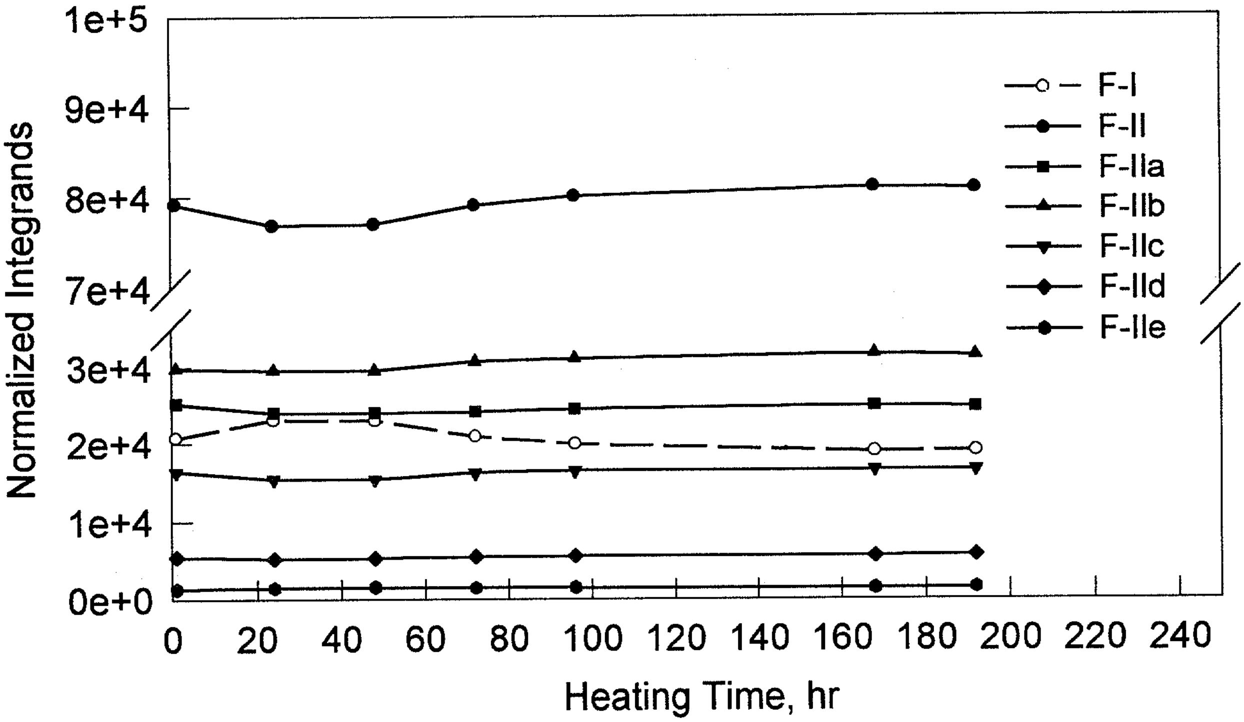


Figure 2-39. Normalized integrands versus heating time for unmodified core asphalt AAB-1 HPLC/SEC DRID chromatographic fractions.

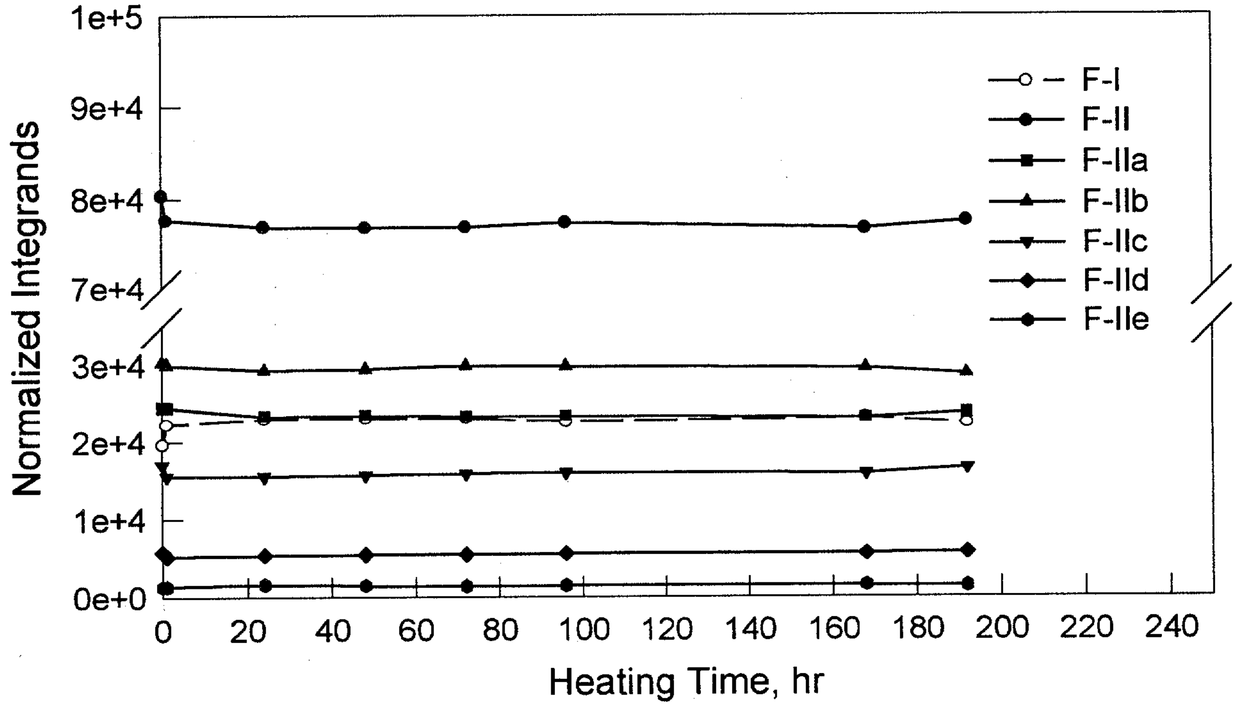


Figure 2-40. Normalized integrands versus heating time for core asphalt AAB-1, containing NR, HPLC/SEC DRID chromatographic fractions.

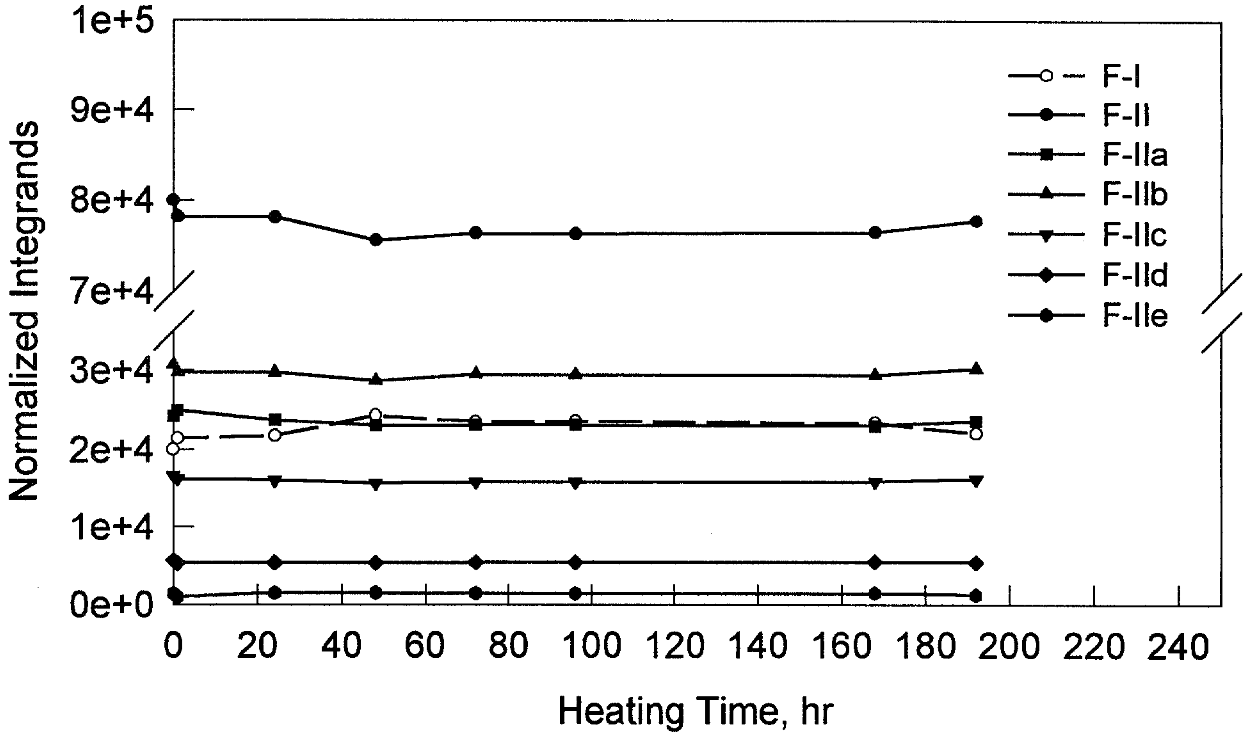


Figure 2-41. Normalized integrands versus heating time for core asphalt AAB-1 containing CRM4, HPLC/SEC DRID chromatographic fractions.

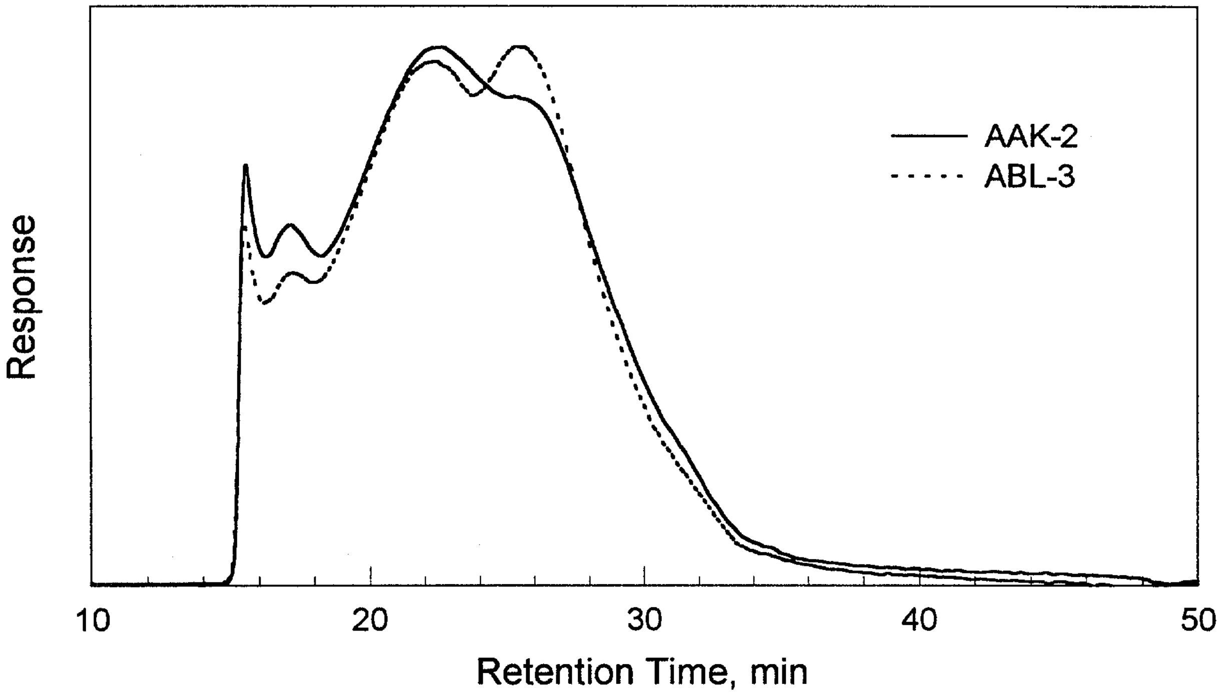


Figure 2-42. HPLC/SEC DRID chromatograms of unmodified asphalts AAK-2 and ABL-3.

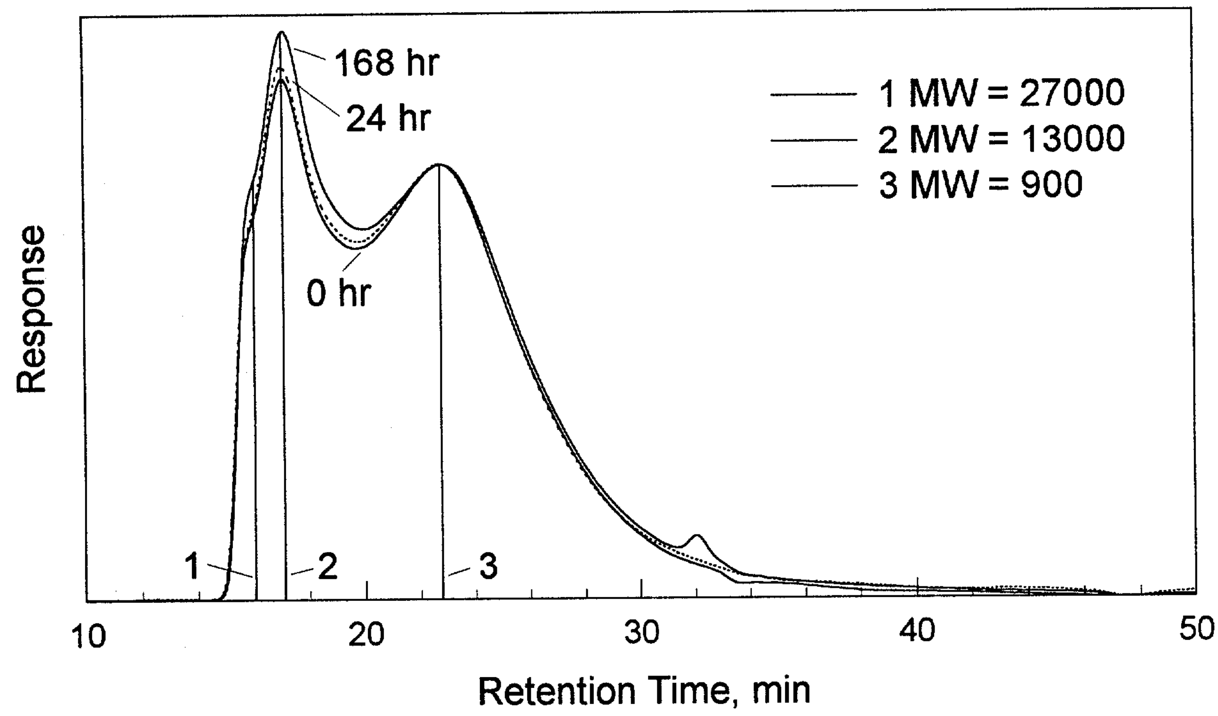


Figure 2-43. HPLC/SEC DRID chromatograms of unmodified core asphalt AAM-1, heated for various times.

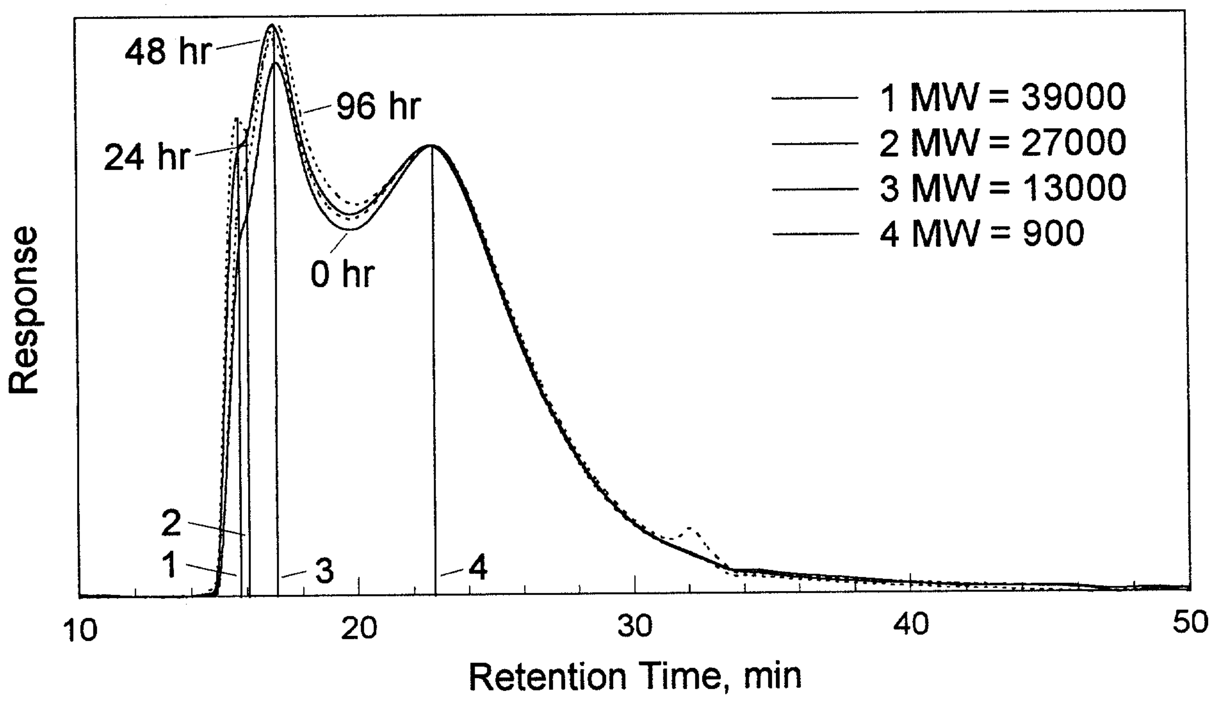


Figure 2-44. HPLC/SEC DRID chromatograms of asphalt AAM-1 with NR, heated for various times.

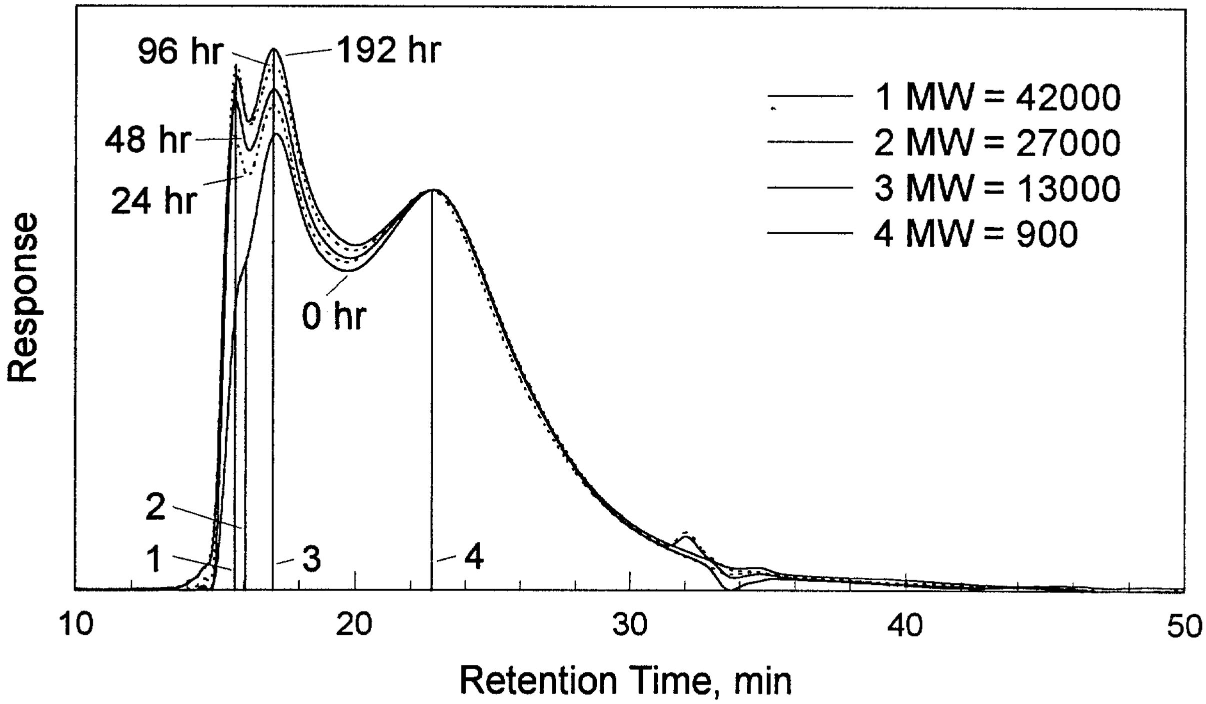


Figure 2-45. HPLC/SEC DRID chromatograms of asphalt AAM-1 with CRM4, heated for various times.

APPENDIX – DETAILED OPERATIONAL INSTRUCTIONS

SEQUENCE - MHSULFDE.S

Sequence Parameters:	Data entered	Notes
Operator:	JJD	
Data File Naming:	Auto	File names will be assigned by the computer system according to vial number, sequence line number, and injection number.
Data Subdirectory:	946-35	Assigned by the operator; in this case the lab book number and page number.
Wait Time after Loading Method:	0 min	This is the time assigned to the system to wait after the method to be used for the current sample is loaded and before beginning the injection procedure.
Barcode Reader:	not used	Can be used if a bar code label is on the sample vial.
Sequence Timeout:	60 min	The time allowed for a system component to get ready before the system shuts down.
Shutdown Cmd/Macro:	STANDBY	What the system should do at the end of a sequence, i.e., when all of the samples have been run.
Sequence Comment:		Comment entered at the discretion of the operator.

This sequence is for running asphalt in toluene solutions. Done in Notebook 946, subdirectory 946-35.

Sequence Table:

Data entered by the operator.

Method and Injection Info Part:

Line	Vial	Sample Name	Method	Injections
1	1	AAB-1 w bnzlslfd	78N3CL	3
2	0	AAB-1 untreated	78N3CL	2
3	2	AAM-1 untreated	78N3CL	2
4	3	AAM-1 w bnzlslfd	78N3CL	3
5	2	AAM-1 untreated	78N3CL	2

Sample Info for Vial 0:

Information entered at the discretion of the operator.

----

untreated AAB-1

Sample Info for Vial 1:

AAB-1 containing 1% benzylsulfide.

Sample Info for Vial 2:

----

untreated AAM-1

Sample Info for Vial 3:

AAM-1 containing 1% benzylsulfide.

A "Method" is prepared by setting up the run conditions (carrier flow rate, column temperature, run time, solvent source and mix, injection volume, injector draw and eject speeds, start and stop data collection times, number of data points collected per second, etc.), the data analysis parameters to be used (which detector signals to be analyzed, integration on and off times, minimum area reject, signal threshold to be recognized, etc.), and the type of report wanted, i.e., the specific results wanted. An example of a "Method" is illustrated by the following method for analysis of core asphalt AAB-1.

METHOD - GRVAAB.M

	Notes
Method Information	Information entered at the discretion and for the benefit of the operator.

This method is for one 7.8 by 50 mm guard column, SN 100309G, followed by three analytical columns in series, two 500 Å columns, SN's 79072 and 84346, and one 100 Å column, SN 79073, all 7.8 by 300 mm. All columns are packed with 5 µm Phenogel. Column temperature is 40° C (104°F) and toluene flow rate is 1.00 mL/min. Data analysis includes manual integration events for 10 equal time fractions.

Run Time Checklist	Those parts of the method the operator wants run.

Pre-Run CMD/Macro:	off
Data Acquisition:	on
Standard Data Analysis:	on
Customized Data Analysis:	off
Save GLP Data:	off
Post-Run Cmd/Macro:	off
Save Method with Data:	on

LC 1090

Pump (DR5):	Allows the operator to set pump parameters such as the time to stop data gathering, the time between the end of data gathering and the next sample injection, flow rate, minimum and maximum system pressures, column oven temperature, solvent source (bottle) and mix, and whether or not to store curves that show variability of certain parameters during the run.

Stop Time	60.00 min
Post Time	120.00 min
Flow	1.00 mL/min
Store Flow Curve	Yes
Minimum Pressure	0 bar
Maximum Pressure	150 bar

Store Pressure Curve	Yes
Oven Temperature	40.0° C (104° F)
Store Temperature Curve	Yes
Solvent A	100.0 % (Bottle A)
Store Solvent A Curve	Yes
Solvent B	0.0 % (Bottle B)
Store Solvent B Curve	Yes

Injector:

Injection volume to be used and the syringe draw speed.

Injection Volume	223.0 μL
Draw Speed	119.0 μL/min

Whether contacts should be closed that will operate outside equipment such as starting a fraction collector and their times for starting and stopping.

Contacts:

Contact 1	Off
Contact 2	Off
Contact 3	Off
Contact 4	Off

Time Table:

Time (min)	Contact 1	Contact 2	Contact 3	Contact 4
0.01		On		
0.02		Off		

DIODE ARRAY DETECTOR

Here the operator sets the time, from sample injection until the end of data gathering, the time between the end of data gathering and the time to be prepared to start gathering data again, peakwidth, sampling interval, and automatic balancing of the detector.

Settings:

Stop time	Same as Pump: 60.00 min
Post Time	100.00 min
Peakwidth	0.170 min
Sampling Interval	0.960 sec
Autobalance	On

Signals:

The operator sets the wavelength(s) for which data are to be gathered. There are eight possible wavelengths to be set. Bandwidth(s) are also to be set.

	Sample, Bw		Reference, Bw	(nm)
A:	525	4	Off	
B:	575	4	Off	
C:	Off			
D:	Off			
E:	Off			
F:	Off			
G:	Off			
H:	Off			

Spectrum:

The operator sets whether or not to have spectra stored and if so for what wavelength span, the sensitivity, and the minimum signal to be recognized.

Store	Peak controlled
From	300 nm
To	600 nm
Step	4 nm
Threshold	10.0 mAU

ANALOG DIGITAL CONVERTER

This is the instrument that takes the analog signal from the differential refractive index detector (DRID) and converts it to a digital signal and feeds it to the computer.

Signal 1

The operator sets peakwidth (which controls frequency of data sampling) and data sampling interval.

Description:	ADC CHANNEL A
Source:	Signal
Unit:	mAU
Units/Volt:	1000.000
Peakwidth (Data Rate):	0.532 Min (0.50 Hz)
Stop Time:	No Limit
Data Storage:	Partial
Start Data:	0.01 Min
Stop Data:	60.01 Min

Integration Event Table "Event"

The default settings where the operator sets minimum peak size to be recognized, minimum signal to be recognized, a peakwidth setting that helps filter noise from real signals, and the time span, from sample injection, for the system integrator to be operable.

Event	Value	Time
Initial Area Reject	10.000	
Initial Threshold	-7.000	
Initial Peakwidth 0.750		
Initial Shoulders	OFF	
Integrator ON		14.000
Integrator OFF		48.000

Integration Event Table "Event_DAD1A"

The same as above for DAD signal A.

Event	Value	Time
Initial Area Reject	10.000	
Initial Threshold	-7.000	
Initial Peakwidth 0.750		

Initial Shoulders	OFF	
Integrator ON		14.000
Integrator OFF		48.00

Integration Event Table "Event_DAD1B"

The same as above for DAD signal B.

Event	Value	Time
Initial Area Reject	10.000	
Initial Threshold	-7.000	
Initial Peakwidth	0.750	
Initial Shoulders	OFF	
Integrator ON		14.000
Integrator OFF		48.000

Integration Event Table "Event_ADC1A"

The same as above for ADC signal A.

Event	Value	Time
Initial Area Reject	10.000	
Initial Threshold	-7.000	
Initial Peakwidth	0.750	
Initial Shoulders	OFF	
Integrator ON		14.000
Integrator OFF		48.000

Manual Integration Event Table "ManInt_ADC1A"

Table showing the manually set times for starting and stopping data gathering for operator set chromatography fractions. The times shown here are set using the split peak feature of the system, which draws a vertical line from the curve to the baseline. This table allows the operator to divide the chromatogram into time intervals desired such as F-I and succeeding fractions.

Manual Integ. Event	Time1

Draw Baseline	13.863
Split Peak	14.502
Split Peak	23.610
Split Peak	26.530
Split Peak	29.450
Split Peak	32.370
Split Peak	35.280
Split Peak	38.200
Split Peak	41.120
Split Peak	44.040
Split Peak	48.000

Apply Manual Integration Events: Yes

Specify Report

This section allows the operator to specify the information to be included in a report on a chromatographic run and the style of report (from a selection offered by the system or a customized report generated by the operator). Included in the details selected by the operator is the physical size of the chromatogram in the report.

Destination: Printer
Quantitative Results Sorted by: Signal
Report Style: Short
Sample Info on Each Page: No
Add Chromatogram Output: Yes
Chromatogram Output: Portrait
Size in Time Direction: 100 % of Page
Size in Response Direction: 40 % of Page

Signal Options

Include: Axes, Retention Times, Baselines, Tick Marks
Font: Arial, Size: 8
Ranges: Full
Multi Chromatograms: Overlaid, All the same Scale

METHOD 3. LARGE SCALE PLANT MIX SIMULATION

ABSTRACT

The rolling thin film oven test (RTFOT) is the standard plant mix simulation being used as part of the Superpave® binder specification. The RTFOT produces small amounts of "plant-aged" asphalts divided among many bottles. A modification of the German Rolling Flask (MGRF) method designed to produce a single 200 g batch of "plant-aged" asphalt has been developed. The results indicate that there is generally less than 1°C (1.8°F) of difference in all subsequent Superpave® binder specification values if the MGRF is used in place of RTFOT.

INTRODUCTION

The classical rolling thin film oven test (RTFOT), AASHTO method T-240 [AASHTO 1995], is the method currently used in the Superpave® binder specification to simulate asphalt mix plant conditions. However, this method produces small amounts of "plant-aged" asphalts among many bottles, and it is a tedious effort to recover and consolidate these samples for the oxidative aging step that follows. Further, polymer-modified asphalts tend to crawl out of RTFOT bottles when they are being rotated in an RTFOT oven. The FHWA Superpave® Expert Task Group (ETG) requested that an attempt be made to scale up and simplify plant mix simulation using the German Rolling Flask method [Deutsche Norm DIN 52016, 1988] and further adjustments of this method as reported by Höppel et al. [1991] as guidelines.

The German Rolling Flask method requires that 100 g of asphalt be placed in a 500 mL round-bottom flask (RBF). This is connected to a rotating evaporation apparatus, which is operated at 20 rpm with the flask immersed into an oil bath at 165°C (329°F) for 2.5 hr with a 500 mL/min air flow over the asphalt. Höppel devised a similar method using 100 g of asphalt in a 1-liter RBF and heated the sample to 165°C (329°F) for 3.5 hr while exposing the asphalt sample to 500 mL/min air flow. The asphalts produced by Höppel had very similar properties to RTFOT-aged asphalts as measured by ring-and-ball softening points (AASHTO T53) and by penetration (AASHTO T49) [AASHTO 1995].

APPLICABILITY

The objective in this effort is to develop a method to produce 200 g of "plant-aged" asphalt that match RTFOT-aged material as measured by the Superpave® binder specification methods. This work was conducted under contract by Advanced Asphalt Technologies, Inc. (AAT) in Sterling, Virginia.

STANDARDIZATION OF THE PROCEDURE

The AAT, Inc., conducted many trial runs to determine the best experimental conditions, but all were based on the procedure reported by Höppel et al. [1991]. The first data set was acquired on the eight SHRP core asphalts (except that asphalt ABM was used in place of AAG-1) aged in a 2-L RBF at 165°C (329°F) for 3.5 hr with 500 mL/min air flow. The materials produced by the Modified German Rolling Flask (MGRF) and by RTFOT were then subjected to all subsequent Superpave® binder tests and continuous (to 0.1°C) grading was performed on both sets of materials. The volatile loss for the 500 mL/min air flow was consistently much lower for the MGRF method, but the high, intermediate, and low temperature specification values for MGRF and RTFOT materials were somewhat similar. The method was adjusted to employ 1000 mL/min air flow into the RBF with all other conditions kept the same. Tables 3-1 and 3-2 give the data for materials recovered from the 1000 mL/min experiment. Note that volatile losses from the MGRF (table 3-1) are still quite low compared with RTFOT samples, but the high, intermediate, and the two low temperature specification values agree rather closely for seven asphalts. The difference in grade (to 0.1°C) between the RTFOT and MGRF methods is given in the right hand column of table 3-2. Only the high and intermediate temperature Superpave® values for asphalt AAD-1 and the m-value for asphalt AAK-1 are significantly more than 1°C (1.8°F) off for the MGRF method.

The next step was to employ a 2-L Morton flask in place of the standard RBF. A Morton flask is an RBF with four indentations in the sides. This promotes faster evaporation, especially for atmospheric crude tower-produced asphalts, and hence more closely matches the MGRF to the RTFOT. Finally, the air flow rate was adjusted to 2000 mL/min to increase the severity of aging further. These experimental conditions were applied to the same eight conventional asphalts and to three polymer-modified asphalts. The results of these experiments, showing replicates R_1 and R_2, are given in tables 3-3 and 3-4. It is particularly important to note that the polymer-modified asphalts showed no tendency to crawl out of the flask during MGRF aging.

The results were presented to the Superpave® binder ETG, which then requested a standardized procedure for conducting MGRF aging. This procedure is shown herein as Exhibit A.

The results given in tables 3-3 and 3-4 indicate that the MGRF is a usable, large-scale preparative method that simulates RTFOT aging, but the method is probably not useful to simulate RTFOT volatile loss.

Table 3-1. Percent mass change for RTFOT and Modified GRF repetitions.

Asphalt	RTFOT			200 g modified GRF		
	Run 1	Run 2	Ave.	Run 1	Run 2	Ave.
AAA-1	-0.382	-0.360	**-0.371**	0.00	-0.03	**-0.01**
AAB-1	-0.043	-0.061	**-0.052**	0.05	0.00	**0.02**
AAC-1	-0.238	-0.242	**-0.240**	-0.14	-0.13	**-0.14**
AAD-1	-1.030	-1.040	**-1.035**	-0.18	-0.16	**-0.17**
AAF-1	-0.150	-0.146	**-0.148**	-0.08	-0.08	**-0.08**
ABM	-0.295	-0.250	**-0.273**	-0.02	-0.01	**-0.02**
AAK-1	-0.640	-0.610	**-0.625**	-0.10	-0.19	**-0.15**
AAM-1	0.058	0.070	**0.064**	0.03	0.01	**0.02**

Table 3-2. Pass/fail temperatures for RTFOT and GRF repetitions.

Asphalt	RTFOT			Modified GRF			RTFOT-MGRF (°C)
	Run 1	Run 2	Ave.	Run 1	Run 2	Ave.	
AAA-1							
Temp. at 2.2 kPa	59.0	59.3	**59.2**	58.8	58.2	**58.5**	**0.7**
Temp. at 5000 kPa	14.1	13.5	**13.8**	14.4	13.4	**13.9**	**-0.1**
Temp. at 300 MPa	-22.6	-22.8	**-22.7**	-23.2	-23.1	**-23.1**	**0.4**
Temp. at 0.300 slope	-24.1	-25.7	**-24.9**	-24.4	-25.6	**-25.0**	**0.1**
AAB-1							
Temp. at 2.2 kPa	62.2	62.1	**62.2**	62.4	62.0	**62.2**	**0.0**
Temp. at 5000 kPa	18.8	17.7	**18.3**	18.9	18.7	**18.8**	**-0.5**
Temp. at 300 MPa	-18.7	-18.6	**-18.6**	-18.8	-19.0	**-18.9**	**0.3**
Temp. at 0.300 slope	-19.1	-19.1	**-19.1**	-17.9	-18.2	**-18.0**	**-1.1**
AAC-1							
Temp. at 2.2 kPa	56.3	55.8	**56.0**	54.9	56.5	**55.7**	**0.3**
Temp. at 5000 kPa	18.7	17.3	**18.0**	18.6	17.2	**17.9**	**0.1**
Temp. at 300 MPa	-18.0	-18.3	**-18.1**	-19.1	-18.4	**-18.8**	**0.7**
Temp. at 0.300 slope	-16.8	-16.0	**-16.4**	-17.0	-16.6	**-16.8**	**0.4**
AAD-1							
Temp. at 2.2 kPa	63.7	64.1	**63.9**	61.3	62.1	**61.7**	**2.2**
Temp. at 5000 kPa	16.4	15.8	**16.1**	14.8	14.0	**14.4**	**1.7**
Temp. at 300 MPa	-20.9	-20.7	**-20.8**	-21.7	-21.8	**-21.7**	**0.9**
Temp. at 0.300 slope	-22.7	-21.9	**-22.3**	-23.2	-22.9	**-23.1**	**0.8**
AAF-1							
Temp. at 2.2 kPa	65.4	65.0	**65.2**	64.3	64.6	**64.5**	**0.7**
Temp. at 5000 kPa	26.9	27.0	**26.9**	26.9	26.8	**26.8**	**0.1**
Temp. at 300 MPa	-13.3	-12.8	**-13.0**	-12.9	-12.9	**-12.9**	**-0.1**
Temp. at 0.300 slope	-11.3	-10.7	**-11.0**	-11.2	-11.3	**-11.2**	**0.2**
ABM							
Temp. at 2.2 kPa	64.2	63.5	**63.9**	63.8	63.4	**63.6**	**0.3**
Temp. at 5000 kPa	29.3	28.8	**29.0**	28.9	28.3	**28.6**	**0.4**
Temp. at 300 MPa	-3.0	-3.5	**-3.3**	-4.4	-2.9	**-3.7**	**0.4**
Temp. at 0.300 slope	-8.9	-7.6	**-8.3**	-8.7	-8.9	**-8.8**	**0.5**
AAK-1							
Temp. at 2.2 kPa	70.6	70.9	**70.7**	69.9	69.8	**69.8**	**0.9**
Temp. at 5000 kPa	20.4	21.3	**20.9**	20.6	20.7	**20.6**	**0.3**
Temp. at 300 MPa	-16.9	-16.7	**-16.8**	-17.7	-17.1	**-17.4**	**0.6**
Temp. at 0.300 slope	-19.6	-18.9	**-19.2**	-21.1	-21.1	**-21.1**	**1.9**
AAM-1							
Temp. at 2.2 kPa	65.9	65.8	**65.9**	65.6	65.4	**65.5**	**0.4**
Temp. at 5000 kPa	18.5	18.2	**18.3**	18.4	19.2	**18.8**	**-0.5**
Temp. at 300 MPa	-17.0	-16.6	**-16.8**	-16.4	-17.1	**-16.7**	**-0.1**
Temp. at 0.300 slope	-10.6	-12.0	**-11.3**	-11.9	-12.2	**-12.0**	**0.7**

Table 3-3. Percent mass change for RTFOT and GRF repetitions.

Asphalt	RTFOT			200 g Morton GRF			Wt loss or gain ratio, RTFOT/ Morton GRF
	R1	R2	Ave.	R1	R2	Ave.	
AAA-1	-0.382	-0.360	**-0.371**	-0.19	-0.19	**-0.19**	**1.95**
AAB-1	-0.043	-0.061	**-0.052**	-0.02	0.00	**-0.01**	**5.20**
AAC-1	-0.238	-0.242	**-0.240**	-0.24	-0.21	**-0.23**	**1.04**
AAD-1	-1.030	-1.040	**-1.035**	-0.44	-0.45	**-0.44**	**2.35**
AAF-1	-0.150	-0.146	**-0.148**	-0.12	-0.11	**-0.12**	**1.23**
ABM	-0.295	-0.250	**-0.273**	-0.13	-0.10	**-0.12**	**2.28**
AAK-1	-0.640	-0.610	**-0.625**	-0.35	-0.34	**-0.34**	**1.84**
AAM-1	0.058	0.070	**0.064**	0.05	0.08	**0.07**	**0.91**
Styrelf	-0.060	-0.077	**-0.069**	-0.03	-0.03	**-0.03**	**2.30**
SBR	-0.316	-0.328	**-0.322**	-0.20	-0.18	**-0.19**	**1.69**
Novaphalt	-0.078	-0.067	**-0.073**	+0.05	+0.04	**+0.05**	**0.88**

Table 3-4. Pass/fail temperatures for RTFOT and GRF repetitions.

Asphalt	RTFOT			Morton GRF			RTFOT-GRF (°C)
	R1	R2	Ave.	R1	R2	Ave.	
AAA-1							
Temp. @ 2.2 kPa	59.0	59.3	**59.2**	59.4	59.0	**59.2**	**0.0**
Temp. @ 5000 kPa	14.1	13.5	**13.8**	13.7	13.7	**13.7**	**0.1**
Temp. @ 300 MPa	-22.6	-22.8	**-22.7**	-23.0	-23.2	**-23.1**	**0.4**
Temp. @ 0.300 slope	-24.1	-25.7	**-24.9**	-26.1	-25.1	**-25.6**	**0.7**
AAB-1							
Temp. @ 2.2 kPa	62.2	62.1	**62.2**	62.5	62.3	**62.4**	**-0.2**
Temp. @ 5000 kPa	18.8	17.7	**18.3**	19.4	18.2	**18.8**	**-0.6**
Temp. @ 300 MPa	-18.7	-18.6	**-18.7**	-19.2	-19.0	**-19.1**	**0.4**
Temp. @ 0.300 slope	-19.1	-19.1	**-19.1**	-18.9	-19.0	**-19.0**	**-0.1**
AAC-1							
Temp. @ 2.2 kPa	56.3	55.8	**56.1**	55.5	55.6	**55.6**	**0.5**
Temp. @ 5000 kPa	18.7	17.3	**18.0**	17.8	16.7	**17.3**	**0.7**
Temp. @ 300 MPa	-18.0	-18.3	**-18.2**	-18.5	-18.4	**-18.5**	**0.3**
Temp. @ 0.300 slope	-16.8	-16.0	**-16.4**	-16.6	-17.5	**-17.1**	**0.7**
AAD-1							
Temp. @ 2.2 kPa	63.7	64.1	**63.9**	64.2	63.5	**63.9**	**0.0**
Temp. @ 5000 kPa	16.4	15.8	**16.1**	16.3	15.8	**16.1**	**0.0**
Temp. @ 300 MPa	-20.9	-20.7	**-20.8**	-21.4	-21.9	**-21.6**	**0.8**
Temp. @ 0.300 slope	-22.7	-21.9	**-22.3**	-22.8	-24.3	**-23.6**	**1.3**
AAF-1							
Temp. @ 2.2 kPa	65.4	65.0	**65.2**	65.2	64.9	**65.1**	**0.1**
Temp. @ 5000 kPa	26.9	27.0	**26.9**	26.9	27.4	**27.2**	**-0.3**
Temp. @ 300 MPa	-13.3	-12.8	**-13.0**	-13.0	-13.0	**-13.0**	**0.0**
Temp. @ 0.300 slope	-11.3	-10.7	**-11.0**	-11.1	-10.9	**-11.0**	**0.0**
ABM							
Temp. @ 2.2 kPa	64.2	63.5	**63.9**	63.8	63.8	**63.8**	**0.1**
Temp. @ 5000 kPa	29.3	28.8	**29.0**	29.2	29.7	**29.4**	**-0.4**
Temp. @ 300 MPa	-3.0	-3.5	**-3.3**	-3.7	-3.2	**-3.5**	**0.2**
Temp. @ 0.300 slope	-8.9	-7.6	**-8.3**	-7.7	-9.3	**-8.5**	**0.2**
AAK-1							
Temp. @ 2.2 kPa	70.6	70.9	**70.7**	70.2	70.0	**70.1**	**0.6**
Temp. @ 5000 kPa	20.4	21.3	**20.9**	20.3	19.8	**20.1**	**0.8**
Temp. @ 300 MPa	-16.9	-16.7	**-16.8**	-17.4	-17.5	**-17.5**	**0.7**
Temp. @ 0.300 slope	-19.6	-18.9	**-19.2**	-20.0	-20.9	**-20.4**	**1.2**

Table 3-4. Pass/fail temperatures for RTFOT and GRF repetitions (continued).

Asphalt	RTFOT			Morton GRF			RTFOT-GRF (°C)
	R1	R2	Ave.	R1	R2	Ave.	
AAM-1							
Temp. @ 2.2 kPa	65.9	65.8	**65.9**	65.8	65.8	**65.8**	**0.1**
Temp. @ 5000 kPa	18.5	18.2	**18.3**	19.6	19.4	**19.5**	**-1.2**
Temp. @ 300 MPa	-17.0	-16.6	**-16.8**	-16.6	-16.4	**-16.5**	**-0.3**
Temp. @ 0.300 slope	-10.6	-12.0	**-11.3**	-11.7	-12.6	**-12.1**	**0.8**
STYRELF							
Temp. @ 2.2 kPa	73.6	73.5	**73.6**	73.4	73.4	**73.4**	**0.2**
Temp. @ 5000 kPa	22.3	21.9	**22.1**	21.7	21.8	**21.7**	**0.4**
Temp. @ 300 MPa	-17.3	-17.5	**-17.4**	-17.3	-17.3	**-17.3**	**-0.1**
Temp. @ 0.300 slope	-16.1	-17.0	**-16.5**	-16.6	-17.0	**-16.8**	**0.3**
SBR							
Temp. @ 2.2 kPa	59.9	60.4	**60.2**	60.2	60.2	**60.2**	**0.0**
Temp. @ 5000 kPa	16.9	16.3	**16.6**	15.6	15.8	**15.7**	**0.9**
Temp. @ 300 MPa	-21.4	-21.7	**-21.6**	-21.5	-21.9	**-21.7**	**0.2**
Temp. @ 0.300 slope	-21.1	-21.1	**-21.1**	-22.5	-22.8	**-22.7**	**1.6**
NOVAPHALT							
Temp. @ 2.2 kPa	74.5	74.4	**74.5**	75.3	75.4	**75.4**	**-0.9**
Temp. @ 5000 kPa	23.0	23.1	**23.1**	22.8	22.1	**22.5**	**0.6**
Temp. @ 300 MPa	-15.6	-15.5	**-15.6**	-16.0	-15.9	**-16.0**	**0.4**
Temp. @ 0.300 slope	-13.1	-12.0	**-12.6**	-14.1	-13.1	**-13.6**	**1.1**

EXHIBIT A

Draft Procedure for Modified German Rolling Flask Method Developed for FHWA

Standard Method of Test for FHWA-Modified German Rotating Flask Equivalent of Rolling Thin Film Oven Test for Conventional and Polymer-Modified Asphalts

1. Scope

1.1 This standard serves to simulate the changes in rheological properties in a conventional or a polymer-modified asphalt sample due to exposure to heat and a simultaneous supply of air. It is a large scale version of the Rolling Thin Film Oven Test (AASHTO T-240).

1.2 This method is applicable to conventional and polymer-modified asphalts.

1.3 *This standard may involve hazardous materials, operations and equipment. This standard does not purport to address all of the safety problems associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.*

2. Reference Documents

2.1 AASHTO and DIN Standards

T-240,	Effects of Heat and Air on a Moving Thin Film of Asphalt (Rolling Thin Film Oven Test).
T-179,	Effects of Heat and Air on Asphalt Materials (Thin Film Oven Test).
DIN 52016,	Testing the Thermal Stability of Bitumen in a Rotating Flask.

3. Summary

3.1 A 200 gram conventional or polymer-modified asphalt sample is placed in a Morton flask attached to a rotary evaporator with a spring clip for 210 minutes at 165°C, with 2000 mL/min air being supplied continuously. The flask is continuously rotated at 20 revolutions per minute (rpm) to prevent a hard skin forming on the asphalt sample surface.

3.2 The mass loss is determined and the asphalt sample is then tested to determine the effects of heat and air.

4. Apparatus

The following apparatus shall be used:

(a) rotary evaporator (without condenser and receiver) fitted with an adapter for a 45/50₷joint, capable of being adjusted to a speed of (20 ± 5) rpm;
(b) 2000 mL Morton flask with a 45/50₷ joint;
(c) glass air supply tube, minimum of 550 mm long with an inside diameter of 7 mm, to be inserted into the flask;
(d) compressor equipped with filter and air drier or bottled compressed air of Industrial or Breathing Grade quality;
(e) gas flow control device, capable of adjusting the flow rate to 2000 ± 40 mL/min corrected to standard barometric pressure;
(f) gas flow meter with a limit of error of ± 40 mL/min at a flow rate of 2000 mL/min;

(g) thermostatically controlled bath capable of maintaining a temperature of 165 ± 1.5°C while a 2000 mL Morton Flask is immersed to a depth where the sample, while rotating, is below the level of the bath fluid (see figure 1);
(h) 8 oz ointment tin;
(i) bath wax or oil heat transfer liquid with a flash point greater than 300°C, capable of being safely maintained at operating temperatures;
(j) ASTM Loss on Heat Thermometer 13C, immersed in the bath up to the 163°C mark in a vertical position;
(k) balance with a capacity of 1000 grams and accurate to 0.01 g;
(l) oven capable of being adjusted to 165 ± 1.5°C and large enough to accommodate the Morton flask and an 8 oz ointment tin.

NOTE: See figures 1 and 2 for assembly of apparatus

5. Procedure

5.1 Exposure of asphalt to heat including determination of change in mass

Weigh 200 ± 1 g of the sample (i.e., the specimen) into the tared flask and, after the specimen has cooled to ambient temperature (18 to 28°C), determine the initial mass (m_e) and report it to the nearest 0.01 g.

Place the Morton flask containing the specimen in the bath, with its axis at 45° to the horizontal and its bulbous part immersed so that the sample, while rotating, is below the level of the bath fluid maintained at a temperature of 165 ± 1.5°C (see figure 1). The 13C thermometer should be immersed in the bath up to the 163°C mark in a vertical position. *Use caution during this step to avoid splashing of the hot bath wax.*

Fix the air supply tube so that its axis coincides with that of the flask, with a clearance of 50 ± 2 mm between tube and flask bottom.

Heat the specimen for 10 ± 1 minutes while rotating the flask at 20 ± 5 rpm. Then, introduce air at ambient temperature, at a rate of 2000 ± 40 mL/min. During the test, maintain the bath temperature at 165 ± 1.5°C and rotate the flask at 20 ± 5 rpm.

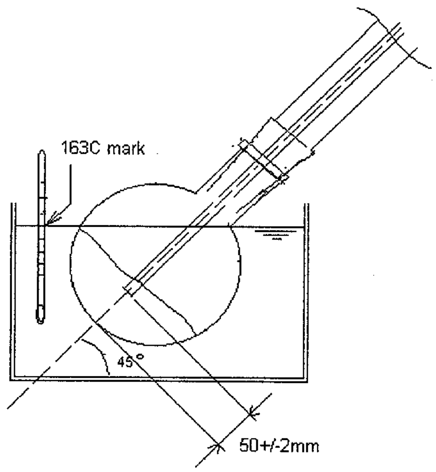


Figure 1. Test Arrangement

After 210 ± 1 minutes, measured from the time when flask was first immersed, stop both the air flow and the flask rotation, and immediately remove the flask from the bath. When the flask has cooled slightly, carefully remove all bath wax (or oil) residue adhering to its surface for proper mass determination. *Caution: The surface will still be hot.*

Cool the flask to ambient temperature (18 to 28°C), determine the final mass of the specimen (m_a) and report it to the nearest 0.01g.

Heat the contents of the flask in an inverted position with an 8 oz ointment tin placed under the mouth of the flask in an oven at 160 ± 5°C for approximately 15 to 20 minutes, or until the sample has stopped dripping out of the flask. Following that, transfer the specimen to the vessels or molds required for subsequent testing.

5.2 Exposure of bitumen to heat without determining the change in mass

Proceed as specified in subclause 5.1 using a bitumen specimen of 200 ± 1 g, determination of the initial mass (m_e) to an accuracy of 0.01 g not being required here.

Following exposure to heat, carefully remove all bath wax residue adhering to its surface. *Caution: The surface will still be hot.* Place the flask in an inverted position with an 8 oz. ointment tin placed under the mouth of the flask in an oven at 160 ± 5°C for approximately 15 to 20 minutes, or until the sample has stopped dripping out of the flask. Following that, transfer the specimen to the vessels or molds required for subsequent testing.

6. Evaluation and expression of results

The change in mass, Δm, shall be calculated as a percentage by mass, expressed to the nearest 0.01%, using the following equation:

$$\Delta m\% = \frac{m_a - m_e}{m_e} \times 100$$

where:

m_e is the specimen mass prior to heat exposure;

m_a is the specimen mass after heat exposure.

7. Precision and Bias

Precision - The research required to develop precision estimates for this test method has not been conducted.

Bias - The research required to develop precision estimates for this test method has not been conducted.

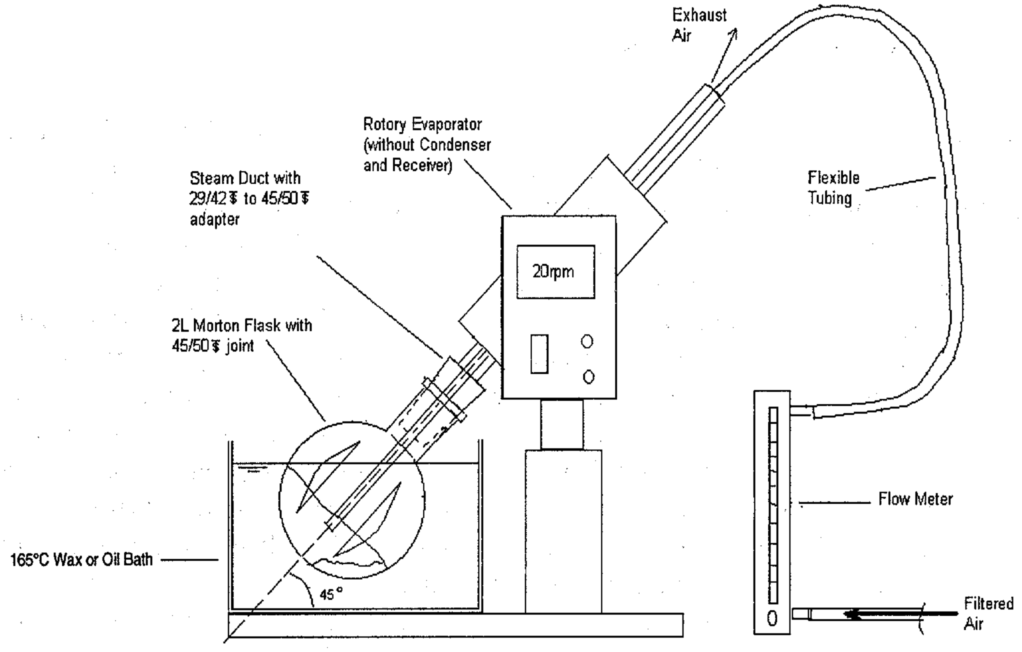


Figure 2. Modified German Rotating Flask Apparatus

METHOD 4. DIFFERENTIAL SCANNING CALORIMETRY/MODULATED DIFFERENTIAL SCANNING CALORIMETRY (DSC/MDSC) ANALYSIS METHODS

ABSTRACT

Differential scanning calorimetry (DSC) and modulated differential scanning calorimetry (MDSC) are shown to provide complementary information about the thermal processes occurring in asphalts and asphalt components. MDSC is especially suited for examination of the glass transition regions of materials because it separates cold crystallization from the glass transition profile. Conventional DSC at relatively high heating rates provides good sensitivity to melting and crystallization enthalpies.

INTRODUCTION AND APPLICABILITY

Thermal analyses by differential scanning calorimetry (DSC) and modulated differential scanning calorimetry (MDSC) provide information on those phenomena that release energy to the surroundings (exothermic) and take energy from the surroundings (endothermic). In asphalts and asphalt components three phenomena that can be measured by DSC and MDSC are of interest. The first and most important of these is the glass transition, a fundamental property of amorphous (i.e., non-crystalline or semi-crystalline) materials, including asphalt binders. An important glass transition parameter is the temperature at which it occurs, the glass transition temperature, T_g. Below the glass transition temperature there is insufficient thermal energy in a material to allow large amplitude molecular motion. Without this motion and the viscous flow it allows, the approach to a thermodynamic equilibrium is slow (this slow approach to equilibrium is called physical hardening). The transition is manifested by changes in slope of primary thermodynamic quantities such as specific volume and enthalpy and by discontinuities or jumps in secondary quantities such as thermal expansion coefficient and specific heat capacity. Secondary quantities are proportional to the derivatives of primary quantities with respect to temperature. The change in specific heat capacity is seen as a step change in heat flow during a temperature scan by a DSC. This step change is endothermic on heating and exothermic on cooling.

The other two phenomena observed by DSC and MDSC are crystallization (or association) and melting (or dissolution) of waxy components of the asphalts and asphalt components. Crystallization of waxy materials is an exothermic process and can occur during cooling or during heating. Melting is endothermic and occurs only during heating.

The methods discussed in this section are applicable to asphalts and to the lower molecular weight components of asphalts. High molecular weight materials and highly polar associated species often do not have glass transitions or have glass transitions so broad as to be essentially meaningless.

PROCEDURES

Apparatus

Early thermal analysis tests were performed on a TA Instruments model 2910 MDSC. This was upgraded during this project to a model 2920. Cryogenic cooling was supplied by either the liquid nitrogen cooling accessory (LNCA, low-temperature limit: -140°C [-220°F]) or the refrigerated cooling system (RCS, low-temperature limit: -70°C [-94°F]) depending on the phenomena of interest. The RCS provides a better baseline.

Setup

Temperature calibration of the DSC follows the manufacturer's procedures using the melting points of indium (156.6°C [313.9°F]), water (0.01°C [32.02°F]), and n-octane (-56.76°C [-70.17°F]). (See TA Instruments Thermal Applications Note TN-11 for these and other reference values.) Indium is also used for enthalpy calibration (20.57 J/g). Heat capacity calibration for MDSC uses high-density polyethylene (HDPE: 2.565 J/g·°C at 140°C [284°F]) or sapphire (Al_2O_3: 0.9545 J/g·°C at 137°C [279°F]).

Sample Preparation

Approximately 15 mg of sample is spread evenly across the bottom of a crimped or hermetic aluminum DSC pan. A heat lamp or hot plate is sometimes used to promote uniform spreading of the sample. Hermetic pans are used for low molecular weight samples where volatility and low viscosity might cause DSC cell contamination. The sample-filled pan and an empty reference pan are placed in the DSC. A temperature program is then selected and started (see methods below).

Testing, Calculation, and Discussion

Thermal analyses performed in this program represent the first large-scale application of MDSC to asphalts and asphalt components. Commercial introduction of the first MDSC instruments coincided roughly with the start of this asphalt research program. The initial instrumentation was developmentally mature, the adaptation from standard DSC instrumentation being minor. However, appropriate application and interpretation of MDSC have improved dramatically since instrument introduction. Our procedures for examining asphalts and asphalt components have also improved during this period, resulting in a reasonable compromise among resolution, sensitivity, and experiment time.

Standard DSC and MDSC differ in temperature programming and data analysis, but do not necessarily require different hardware. Both techniques measure heat flow compared to a reference. The relevant heat flow equation is [Reading 1993]:

$$dQ/dt = Cp\ dT/dt + f(t,T) \qquad (4\text{-}1)$$

where: dQ/dt = total heat flow (W/g)
Cp = heat capacity (J/g·°C)
dT/dt = heating rate (°C/s)
f(t,T) = kinetic component (W/g)

The first term on the right side of equation 4-1 is the heat-flow contribution due to the sample heat capacity and the heating or cooling rate. Because there is a shift in heat capacity at the glass transition, this term contains the information about the glass transition. The second term on the right is the kinetic component, which comes from the time dependency of crystallization, melting, or chemical reactions. The sensitivity of conventional DSC is proportional to the heating rate as can be seen from equation 4-1. The resolution is inversely proportional to heating rate. Important experimental variables for conventional DSC are: sample size, heating rate, sample environment, sample pan type, and sample thermal history.

MDSC is an adaptation in which the temperature (and, therefore, the heating rate) is modulated about an underlying heating or cooling program. The average temperature follows that of the conventional DSC; however, a periodic sine wave perturbation of the temperature is superimposed. This provides a slow underlying heating rate for good resolution, yet still provides short-duration high heating rates for good sensitivity to heat capacity-related transitions. MDSC dramatically improves the ease of glass transition measurement in complex systems where cold crystallization (crystallization on heating) and melting interfere with baseline determination. Important experimental variables for MDSC are the same as for conventional DSC with two additions: modulation amplitude and modulation period. MDSC requires an additional calibration procedure for heat capacity measurements.

Through signal processing of the MDSC heat-flow signal five thermograms are produced: modulated heat flow, total heat flow, heat capacity, reversing heat flow, and non-reversing heat flow. The modulated heat flow signal is the measured heat flow to the sample. The total heat flow is calculated as the average of the modulated heat flow signal and is equivalent to the signal from a conventional DSC. The heat capacity signal is calculated from the ratio of the modulated heat flow amplitude divided by the modulated heating rate amplitude. It contains the sample heat capacity plus generally minor influences from changes in heat capacity caused by crystallization or other time-dependent phenomena. The reversing heat flow signal is the heat capacity component of the total heat flow calculated as the negative product of the heat capacity and the average heating rate. The non-reversing signal is the difference between the total heat flow and the reversing heat flow. This signal contains time-dependent phenomena and any baseline irregularities in the total heat flow signal.

Two thermal methods are currently used to characterize asphalts and asphalt components. In the first method, two modulated heating scans on a single sample are used to examine the sample as received and after annealing (figure 4-1). During the cooling and isothermal steps of the thermal program no modulation is used. A heating rate of 2°C/minute (3.6°F/min) in the modulated heating steps provides good resolution for the glass transition. A modulation amplitude of 0.25°C (0.45°F) and a modulation period of 80 seconds are conservative values, minimizing heat transfer perturbations of the results. Heat transfer in the sample during modulation limits the maximum acceptable frequency, minimum period, and the maximum amplitude of modulation. A series of quasi-isothermal (modulated about a constant temperature) experiments with different modulation periods show the dependency of the apparent heat capacity of a sample on the modulation period. At higher modulation frequencies (short periods) there is insufficient time for heat transfer through the sample, and the apparent heat capacity is lower than the true heat capacity of the sample. As the period is increased, the apparent heat capacity approaches the true heat capacity. For asphalt samples, a modulation period of 80 seconds ensures adequate heat transfer time. The underlying heating rate should be adjusted to ensure that at least four to five modulation cycles occur in a transition of interest. The annealing temperature for both methods discussed here is selected based on the type of material being examined. For a neat asphalt, a temperature of 160°C (320°F) is usually acceptable; for some SEC fractions, IEC neutrals, and waxes, sample volatility is a problem and a lower annealing temperature of 100°C (212°F) is selected.

A second thermal method is used to measure the total endothermic and exothermic heat flow during cooling and heating (figure 4-2). These time-dependent processes are better examined at high heating rates that increase sensitivity. Since modulation is not recommended at underlying heating rates above 5°C (41°F), a conventional, unmodulated DSC method is applied. After annealing, the sample is cooled at 10°C/minute (18°F/min) to below -60°C (-76°F), held isothermal for 15 minutes, and then heated at 10°C/minute (18°F/min) to the annealing temperature. The minimum temperature selected in each of the methods depends on the events of interest and the type of material being examined. The RCS system, with a minimum temperature capability of -70°C (-94°F), is the preferred cooling system because it provides more uniform temperature control. However, some of the SEC fractions, IEC neutrals, and supercritical fluid extracts have thermal events near -70°C (-94°F) and, thus, require the use of the liquid nitrogen cooling accessory (LNCA) with its low-temperature limit of -140°C (-220°F). This simple thermal method provides reasonable sensitivity to melting and crystallization phenomena in asphalts. It is often helpful to refer to thermograms from the modulated experiment to aid in selection of integration end points in these unmodulated thermograms.

Examples of cooling and heating thermal profiles obtained using the first method discussed above are shown in figures 4-3 and 4-4. A 15 mg sample of asphalt AAM-1 doped with 3 mass percent pentacosane (n-C25) was cooled from 160°C (320°F) to -140°C (-220°F) at a programmed 10°C/minute (18°F/min). Initially, there is a large increase in heat flow because of the difference in mass between the sample and reference. This perturbation has a relatively short duration and the heat-flow signal assumes an almost linear decrease with temperature as the sample heat capacity decreases. At 50°C (122°F) the exothermic crystallization of pentacosane (plus some AAM-1 waxes) starts. Crystallization continues until just above the glass transition region. At 0°C (32°F), heat flow begins to drop as the sample heat capacity decreases in the glass transition region. Near the low temperature end of the glass transition region there is a sharp exothermic spike that is believed to be caused by either pan deformation or a sample adhesion break with the pan as stresses in the sample are relieved. The asphalt has a larger coefficient of thermal expansion than do the aluminum pans. Spikes like this occur below the glass transition temperature where stress relaxation through cooperative molecular motion is slow. Occasionally, the exothermic excursion does not return to the local baseline. Absolute heat capacity measured after such an excursion is suspect, although changes in heat capacity and glass transition parameters appear to be unaffected. Around -100°C (-148°F), the system is no longer able to maintain a cooling rate of 10°C/minute (18°F/minute), and the heat flow is sharply reduced.

The AAM-1 asphalt with 3 mass percent pentacosane was held at -140°C (-220°F) for 15 minutes and was then heated at 2°C/minute (3.6°F/min) while modulating with a period of 80 seconds and amplitude of 0.25°C (0.45°F). Resulting total, reversing, and non-reversing heat flow thermograms are shown in figure 4-4. The total heat flow signal is the sum of the reversing and non-reversing signal components and is equivalent to a conventional DSC thermogram. Overlapping glass transition, cold crystallization, and melting regions complicate interpretation of the signal. The reversing signal, which contains heat capacity information, has a much simpler, more easily interpreted profile. The cold crystallization exotherm is removed and, even though there is some endothermic interference from melting, selection of the glass transition parameters is relatively simple. The analyst must be certain to scan to a high enough temperature to ensure accurate baseline extrapolation when melting interference is present. The non-reversing signal contains virtually all of the cold crystallization information, some of the melting signal, and non-linearities in the baseline.

SUMMARY

MDSC has proved to be a valuable tool for deciphering complex thermograms. It is especially useful for determining the glass transition temperatures of waxy asphalts and their lighter components. Conventional DSC, at higher heating rates, is used to determine melting and crystallization enthalpies.

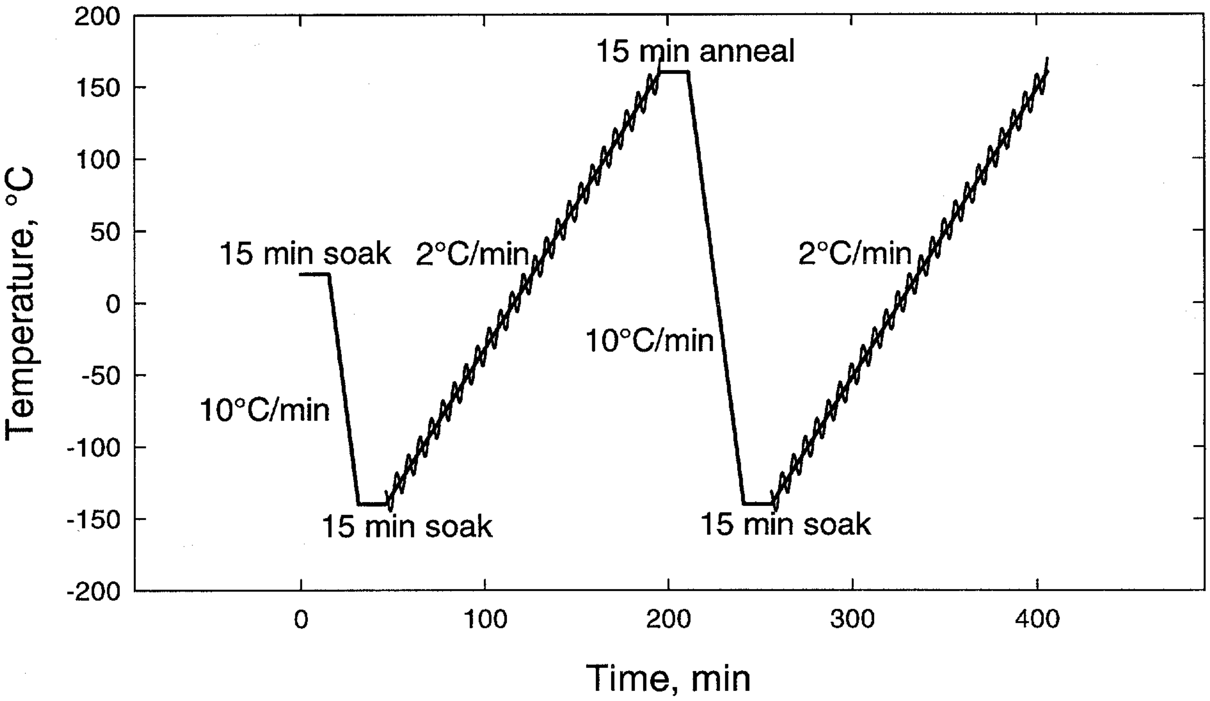


Figure 4-1. Underlying temperature program for determination of glass transition by MDSC showing unmodulated and modulated segments (modulation amplitude and period are not to scale).

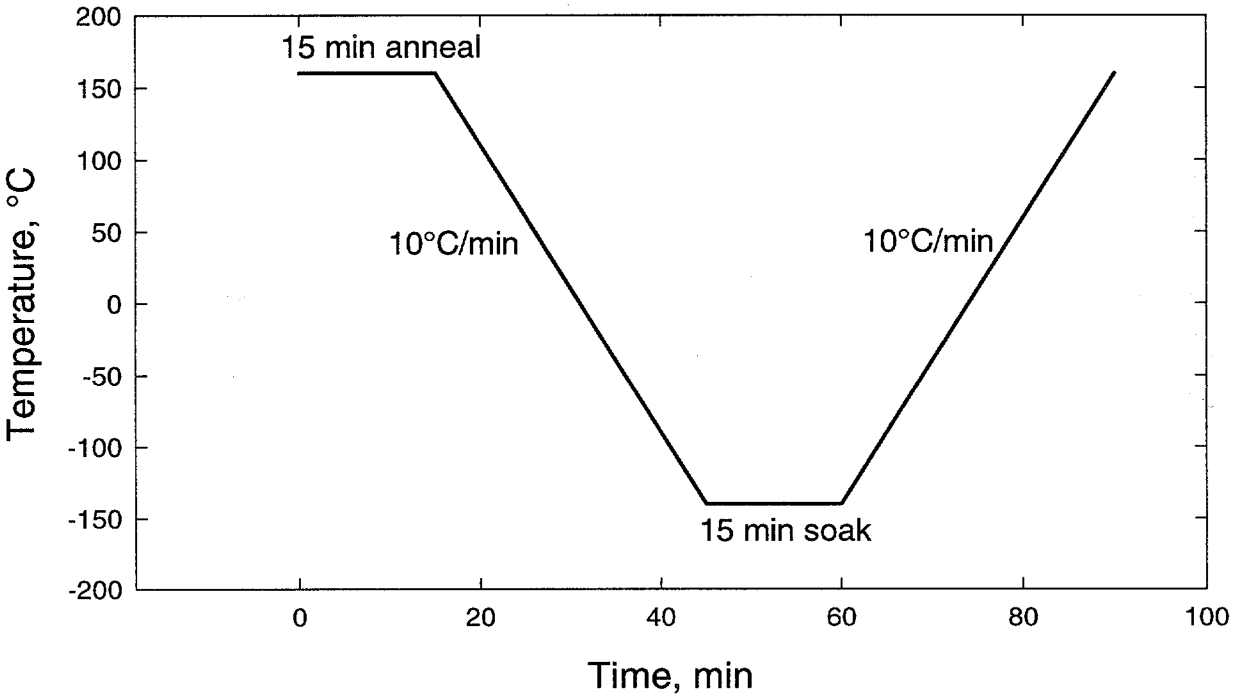


Figure 4-2. Temperature program for determination of crystallizable material by DSC.

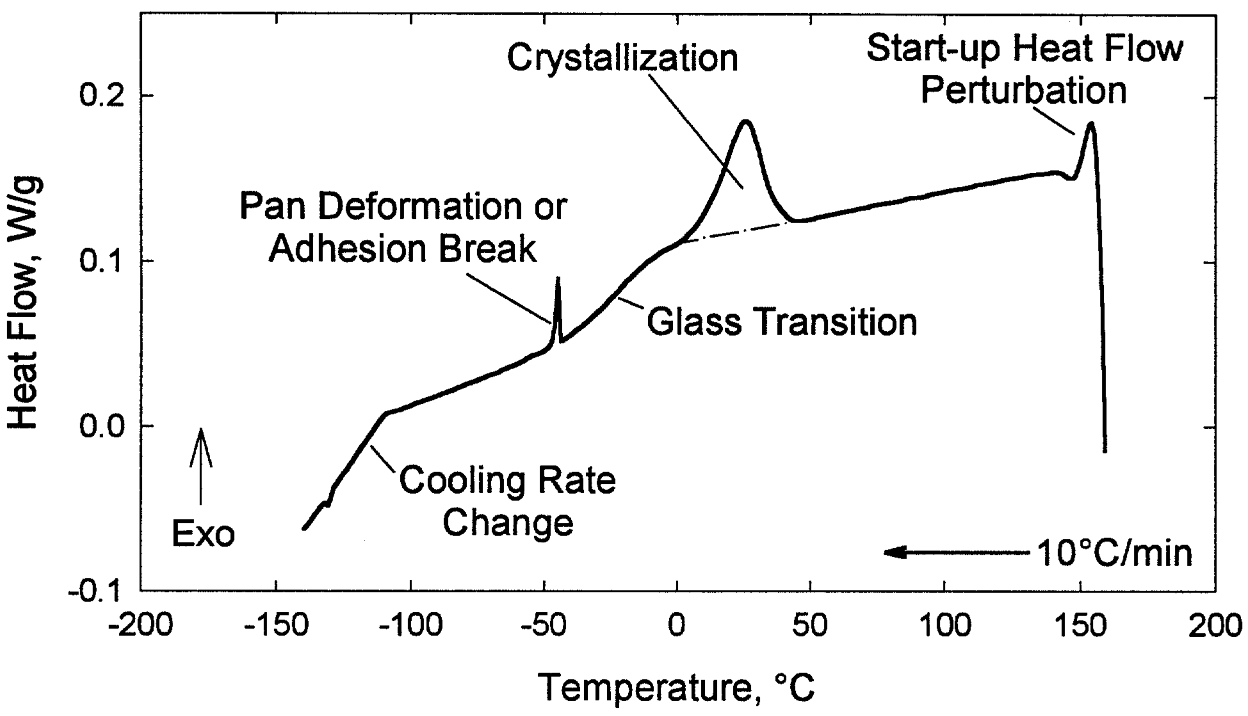


Figure 4-3. DSC cooling thermogram for AAM-1 with 3 mass % pentacosane, $C_{25}H_{27}$.

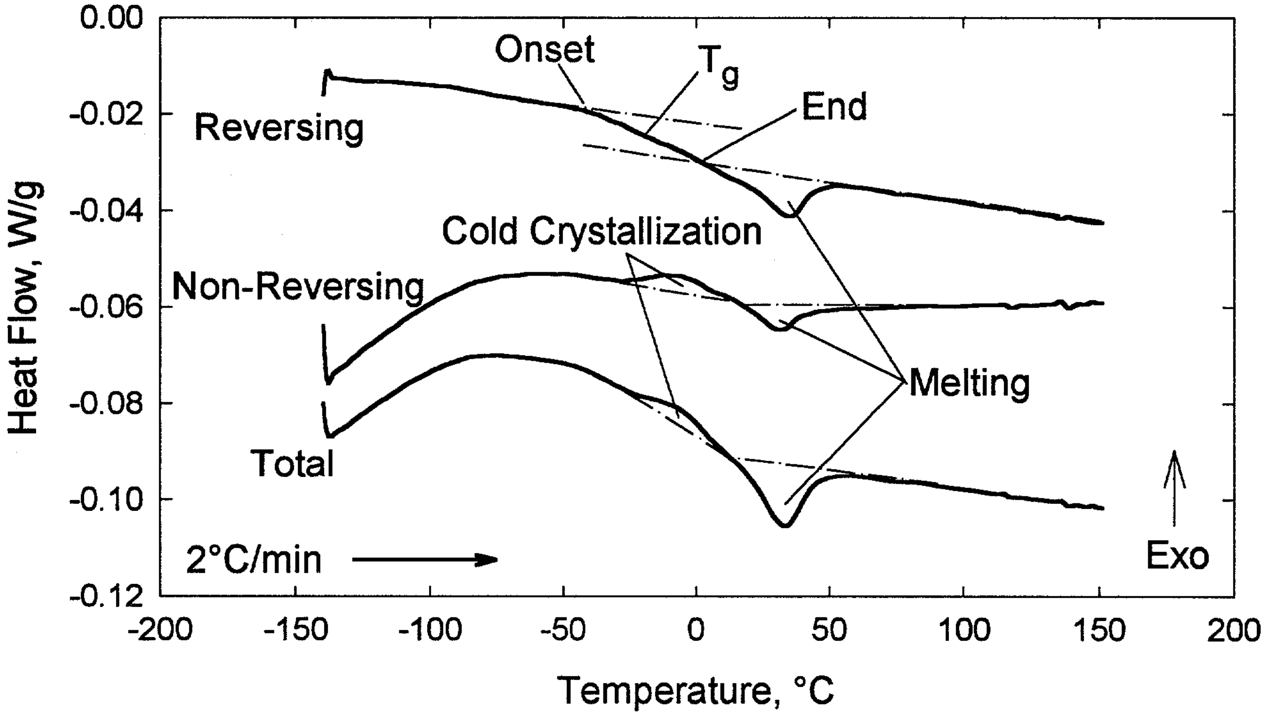


Figure 4-4. MDSC heating thermogram for AAM-1 with 3 mass % pentacosane, $C_{25}H_{27}$.

METHOD 5. FAST ION EXCHANGE CHROMATOGRAPHY (IEC) SEPARATION OF ASPHALTS

ABSTRACT

A preparative ion exchange chromatography separation method used to separate asphalts into four chemically distinct fractions was scaled down. The scaled down, or "Fast ion exchange chromatography," method provides results comparable to those obtained by using the preparative method with respect to relative masses of the four fractions. The "Fast" method thus can be used to "fingerprint" asphalts and to generate sufficient amounts of fractions for some analytical determinations. The "Fast" method saves much time and expense in resin preparation and in desorption of fractions from resins. Hood space is conserved and toluene replaced benzene in all operations.

INTRODUCTION AND APPLICABILITY OF METHOD

Ion exchange chromatography (IEC) is a useful technique for the separation of petroleum and petroleum fractions into defined chemical components [Green et al. 1984]. The method also has been used to separate shale oils [McKay et al. 1975] and tar sand bitumens [Selucky et al. 1981]. In the separation of fossil fuels, IEC works as a form of affinity chromatography, as few ionic materials are found in these substrates.

Most IEC separations of petroleum-derived materials involve passing solutions of substrate through columns filled with an activated anion resin or an activated cation resin. Resins obtained from manufacturers arrive in inactive form. Immediately prior to use, the resins are activated by means of a prescribed chemical treatment [SHRP 1994b]. Only activated resins are used in the separations. Molecules containing acidic functional groups are adsorbed on the cation resins, and molecules containing basic functional groups are adsorbed on the anion resins. Molecules with no polar functional groups are not adsorbed by either of the activated resins. Acidic and basic petroleum fractions are desorbed from the resins by stronger acids or bases. The petroleum fractions then are separated from the desorbing agents and solvents by evaporation.

The IEC separations of fossil fuels and derived materials depend on the method of activation of the resins, the solvent used to dissolve the substrate, flow rate, and the temperature at which the separations are performed. These variables are discussed at length by Green et al. [1984]. Other factors are sample-to-resin ratios and column configurations, which would influence IEC separations of any kind of materials.

Boduszynski et al. [1977] reported the first separation of an asphalt by IEC. In the recently concluded Strategic Highway Research Program SHRP A-002A Project, Binder Characterization and Evaluation, preparative IEC separations were used to accumulate chemically defined fractions of eight asphalts [SHRP 1993a]. These fractions were subjects of physical property studies [SHRP 1993a], and chemical composition-physical property correlations were developed. It was found that the chemical composition of the various IEC fractions of an asphalt differed markedly and that relative amounts of the fractions varied among the asphalts studied. This observation suggested that IEC could be used to characterize or "fingerprint" asphalts. If this were the sole objective of an IEC separation, much less material would be required compared with a preparative separation. Thus the preparative separation reported in SHRP [1993a; 1994b] could be scaled down. Such a modified procedure would consume less resin (which is expensive) and require less time to be invested in the tedious activation process. The same amount of resin is activated at any given time in a batch process. A scaled-down procedure would permit many more runs for each batch of resin activated.

Two different preparative IEC separation methods were utilized during the course of the SHRP Binder Characterization and Evaluation A-002A Project. One method is very similar to that described by Green et al. [1984], and separates asphalts into neutral, strong acid, weak acid, strong base, and weak base fractions. Asphalts are dissolved in a mixed solvent consisting of benzene, tetrahydrofuran, and ethanol and are pumped successively through two columns, the first filled with activated anion resin (AG MP-1, 100-200 mesh, obtained from Bio-Rad Laboratories), and the second filled with activated cation resin (AG MP-50, 100-200 mesh, obtained from Bio-Rad Laboratories). Strong acids are adsorbed on the anion resin, and strong bases are adsorbed on the cation resin. Because the solvent is highly polar, weak acids and weak bases are not adsorbed by either resin and pass through both columns, along with neutral materials. This mixture is dried, redissolved in cyclohexane, and pumped through another pair of columns, the first containing activated anion resin (AG MP-1), and the second containing activated cation resin (AG MP-50). Weak acids are adsorbed on the anion resin and weak bases are adsorbed on the cation resin. Neutrals are not adsorbed on either column. The individual fractions are desorbed from the columns. They are isolated by removing solvents. Green et al. [1993] separated some of the SHRP core asphalts using columns of different dimensions and reported results similar to those reported in the SHRP Binder Characterization and Evaluation Project [SHRP 1993a]. Including resin activation, about 2½ weeks are required for a complete separation using this preparative IEC method. This method is referred to as the "conventional" method for purposes of reference.

A variant on the above described procedure, using the same activated cation and anion resins, was developed during the SHRP Binder Characterization and Evaluation Project. Interest developed in polyfunctional molecules having both acidic and basic functional groups. It was theorized that such compounds would tend to form extensive associations in asphalts and thus be the principal viscosity builders and major contributors to elastic properties. In the IEC method described above, amphoteric molecules become distributed among the two acid fractions and the strong base fraction. If amphoterics were to be isolated using this procedure, three more IEC separation steps would be required. Each of these three polar fractions would have to be separated into two fractions, one amphoteric and the other not amphoteric. Each of the three amphoteric fractions would be different in properties and would be combined to constitute a total amphoteric fraction.

The preparative IEC method developed for the isolation of amphoterics involves pumping a solution of asphalt in cyclohexane through two columns connected in series, the first filled with activated cation resin (AG MP-50, 100-200 mesh) and the second with activated anion resin (AG

MP-1, 100-200 mesh). In this procedure, the order in which the solution contacts the resins is reversed compared with the first method. Because cyclohexane is a non-polar solvent, essentially all polar materials are adsorbed on the two resin columns and neutrals are eluted. An acid fraction is recovered by desorbing the anion resin, and this fraction is not the same as either of the acid fractions in the first procedure. The polar materials adsorbed on the cation resin are desorbed, redissolved in cyclohexane, and pumped through a single column filled with activated anion resin. A base fraction is eluted, and amphoterics are adsorbed on the anion resin. Several asphalts were separated using this method, and distinctive fractionation patterns were observed. In the subsequent discussion, it should be borne in mind that two preparative IEC separation methods were used to fractionate asphalts in SHRP, and that with the exception of the neutral fraction, the fractions obtained are not the same. For the fast IEC method, the second preparative procedure, referred to as the "amphoterics" method, was scaled down.

The above preparative procedures are designed to process 16.0 g samples of asphalts and serve to isolate chemically defined fractions in amounts sufficient for subsequent study. More than 2 weeks are required, much of the time involved in resin preparation (activation). If only gravimetric finishes to obtain fractionation patterns of asphalts are required, then it should be possible to scale one of the procedures down significantly. One resin preparation exercise, which still takes up to 1 week, should provide enough resin for several scaled-down runs. Running the separation itself more rapidly might not be possible, as time might be required to break up asphalt associations in cyclohexane [Selucky et al. 1981]. Solvent evaporation and column stripping are inherently time-consuming and not so readily susceptible to economies of scale. The experiments described below describe efforts to develop a scaled-down version of the second IEC method for use in the current program.

EXPERIMENTAL

Apparatus

The apparatus used in the Fast IEC separations are listed here. Much of the equipment is standard laboratory ware and may be obtained from several vendors. Some of the more specialized equipment may not be available in the future from vendors listed below, but equivalent materials should be obtainable from alternate vendors.

Equipment

Two glass columns (0.9 cm I.D. x 50 cm), water jacketed, with plungers (Spectrum)
Packing Reservoir
Two pumps, Fluid Metering Inc., model RP-SY
Two pulse dampeners, Fluid Metering Inc., model PD-60-LF
Constant temperature bath
Rotary evaporator (Buchi) with pear-shaped flask (1 L)
Soxhlet extraction apparatus, with condenser and glass thimble with sintered glass frit (5.2 cm I.D. x 13.5 cm above frit)
Glass frit, 5.0 cm I.D., coarse porosity

Graduated cylinder, 100 mL
Erlenmeyer flask, 500 mL wide-mouth
Glass beaker, 250 mL
Teflon® tubing
Buchner funnels with sintered glass plates (m porosity), 350 mL
Suction flask
Round bottom flask, 2 neck, 1 L
Round bottom flask, 1 neck, 100 mL
Flat bottom flask, 1 neck, 500 mL
Glass vial, 20 mL
Heating mantles with variacs
Stirring plates with magnets (Sargent Welch)
Lab jack
Dropping funnel with pressure bypass
Syringe

Reagents

Activated AG MP-50, 100-200 mesh cation resin (Bio-Rad Laboratories, 2000 Alfred Nobel Drive, Hercules, CA 94547)
Activated AG MP-1, 100-200 mesh anion resin (Bio-Rad)
Toluene, spectrophotometric grade (EM Sciences, P. O. Box 70, Gibbstown, NJ 07080)
Cyclohexane, spectrophotometric grade (EM Sciences)
Formic Acid, reagent grade, 96% (Aldrich Chemical Co., 1001 W. St. Paul Avenue, Milwaukee, WI 53233)
Methylene Chloride, spectrophotometric grade (EM Sciences)
1-Propylamine, 98% (Aldrich Chemical Co.)
Argon
Nitrogen

Fast Ion Exchange Chromatography Separations

All operations should be performed in an area with proper ventilation by a chemist with experience in column chromatographic separations.

Activation of ion exchange resins was performed as described previously [SHRP 1994b]. The reagents and equipment required for this procedure are listed in this reference.

Column Packing

Activated resins are packed into columns in a cyclohexane slurry. The procedure can be completed in about 30 minutes.

A packing reservoir is attached to the top of a 0.9 cm I.D. by 50 cm Spectrum glass column with water jacket fitted with one lower Teflon® end plate (figure 5-1a). A Teflon® support grid, fine mesh cloth support, and retainer ring are placed on the resin bed side of the lower end plate. A Teflon® multifit tubing connector, ferrule, multifit nut, and 1/8 in (0.3175 cm) I.D. tubing are connected to the opposite end of the lower end plate. The packing reservoir is connected to the column with a column extender and then the whole assembly is mounted vertically.

Activated anion or cation resin (in cyclohexane slurry) is poured into a 100 mL graduated cylinder. Enough slurry is poured into the cylinder so that, after settling, the top of the resin bed is at the 30 mL mark. The resin-cyclohexane slurry is then poured into the top of the packing reservoir. Degassed (using argon) cyclohexane is added to rinse any resin remaining on the sides of the glass reservoir. Cyclohexane elution is by gravity and flows out of the column by means of the Teflon® tubing connected to the bed support at the bottom of the column. Gas pressure is not used to fill these small columns.

The resin should largely fill the column. Cyclohexane should cover the top of the resin bed no more than 2 cm. The packing reservoir is detached from the column and replaced with a Spectrum plunger. The components of the plunger are illustrated in figure 5-1b. Filled columns are allowed to stand approximately 15 hours before use to allow settling of the resin bed. Thus, columns may be filled late in one working day and separations performed the next morning.

Separation of Asphalts into Neutral, Acid, Base, and Amphoteric Fractions

The IEC separation of asphalts into neutral, acid, base, and amphoteric fractions differs from the procedure of Green et al. [1984]. Solutions of asphalts contact cation resins first instead of anion resins, as in the Green et al. [1984] procedure. A flow chart for this separation is illustrated in figure 5-2.

Chromatographic separation of asphalts into neutrals, acids, bases, and amphoterics is performed with cyclohexane as the solvent at 37°C (98.6°F). Use of cyclohexane allows basic and amphoteric molecules to adsorb on a cation resin while acids adsorb on an anion resin and the neutrals are not adsorbed. Amphoteric fractions and bases are desorbed and are then separated from each other using an anion column in a separate operation. The anion resin interacts with the acidic functional groups of amphoteric molecules, resulting in adsorption. Basic molecules do not interact with anion resins. The use of cyclohexane for IEC separation of asphalts is reported by Boduszynski et al. [1977]. The IEC separation can be performed in approximately 5 hours. Some highly polar materials become irreversibly adsorbed on the resins. Thus recoveries are never 100 percent in IEC separations, and resins cannot be used again.

Two grams of asphalt are weighed into a 500 mL wide-mouthed Erlenmeyer flask and are dissolved in 35 mL of degassed cyclohexane. Two columns with fitted water jackets, one filled with activated cation resin and the other filled with activated anion resin, are used. Two FMI Lab Pumps, model RP-SY, are connected to two FMI Pulse Dampeners, model PD-60-LF, which are then connected to the bottom of the columns. Approximately 200 mL of degassed cyclohexane is pumped through each column individually (they are not yet connected in series) at a flowrate of about 2 mL per minute to stabilize the resin beds and remove gas bubbles. The water jackets then are connected to a constant temperature bath maintained at 37°C (98.6°F). The columns then are arranged in series, side by side, with the top of the cation column connected to the bottom of the anion column. One pump and one pulse dampener are removed from service at this time. Degassed cyclohexane (50 mL) then is pumped through both columns. Removal of the remaining pulse dampener from the system is necessary before the asphalt solution is introduced. Otherwise some of the sample would be retained in the pulse dampener. The dissolved asphalt is introduced into the system at the bottom of the cation resin column using Teflon® tubing, followed by rinsing of the flask that contained the asphalt solution with approximately 5 mL of degassed cyclohexane. The pulse dampener is reconnected to the system and 300 mL of degassed cyclohexane is pumped through both columns. The pump is then connected directly to the anion resin column and another 50 mL of degassed cyclohexane is pumped through the anion column alone. This minimizes desorption of small amounts of weak bases from the cation column, which would appear in the neutral fraction. After pumping 300 mL solvent through both columns, most of the neutral fraction has been collected, with only a small amount remaining in the anion column. All eluates are collected as the neutral fraction. These eluates are filtered through a 350 mL Buchner funnel with a medium porosity sintered glass plate to remove resin particles. The filtrate then is divested of solvent on a rotary evaporator (Buchi). After the cyclohexane has been removed, the neutral fraction is transferred to a 20 mL vial with methylene chloride and again is divested of solvent on the rotary evaporator. The flask and contents are then rotated in a boiling water bath under reduced pressure until a constant weight is reached, in approximately 3 hours. The neutral fraction is blanketed with argon or nitrogen and the flask is stoppered and stored in a cool, dark cabinet.

Extraction of Asphalt Fractions Adsorbed on Resins

The combination of amphoteric and basic fractions is adsorbed on the cation resin, and these materials must be desorbed. This is done as follows. The plunger on the top of the column is detached from the column and rinsed with toluene in a 250 mL beaker. This and subsequent operations must be performed in a good fume hood to avoid exposure to vapors. The plunger is removed from the beaker and the column is then inverted over the beaker. A syringe containing about 25 mL toluene is inserted into the Teflon® tube that leads into the column. Hand pressure on the syringe should be sufficient to dislodge the resin into the beaker. Several rinses are required to fully remove the resin from the column. The end cap at the top of the column is unscrewed, and the bed support assembly is removed and rinsed into the beaker. Five mL of a mixture of 1-propylamine and toluene then is added to the beaker. This mixture, which desorbs asphaltic materials from the cation resin, had previously been prepared and consists of 7 mL 1-propylamine and 14 mL toluene. After adding the 5 mL of the mixture to the beaker, the remainder is reserved.

The cation resin in the beaker is poured into a Soxhlet thimble resting in another beaker. After the solvent has drained from the thimble, a glass frit is placed on top of the resin bed. The liquids drained from the resin are poured into a 1 L round bottom, two-necked flask with a vertical side arm containing a magnetic stirring bar. More toluene is added to the flask to allow for convenient flushing. The Soxhlet extraction apparatus is set-up similar to the one used in the resin activation, only on a smaller scale. A stirring plate is set under the heating mantle in place of the laboratory jack. A dropping funnel with a pressure by-pass is placed in the second neck of the flask to allow the remainder of the 1-propylamine-toluene mixture to be slowly added to the system, approximately 2 mL every 30 minutes. The amine-toluene mixture must be added cautiously, or "bumping" of the resin will result, causing resin to be ejected from the extractor. The solvent is allowed to reflux for approximately 8 hours (which need not be continuous), after which the resin should be clean of most adsorbed material. During the addition of the 1-propylamine and the extraction, dry argon is introduced into the top of the condenser. This is to minimize contact of the contents of the extractor with water and oxygen.

When the extraction is finished the thimble is carefully removed from the Soxhlet extraction apparatus and the resin is removed as a slurry into a beaker. The solution of desorbed IEC fraction in the round bottom flask is then filtered through a 350 mL medium porosity Buchner funnel by gravity filtration. Any resin in the flask (resulting from bumping) is washed with toluene until the filtrate is clean. The resin from the thimble is then poured into the Buchner funnel and rinsed with toluene until a clean filtrate appears.

After desorption is complete the solution containing the desorbed combined amphoteric and basic fractions is transferred to a 1 L pear-shaped flask and is <u>carefully</u> divested of solvent using a rotary evaporator. These fractions tend to form rigid foams, which enter the rotary evaporator from the flasks. After almost all solvent has been removed, the residue concentrated in the flask is treated three more times with small portions of toluene to remove the last traces of 1-propylamine. After each addition of toluene, the flask is returned to the rotary evaporator, and solvent again is removed. The desorbed materials are then dissolved in a small amount of methylene chloride and transferred to a 100 mL round bottom flask. This mixture of solvent, amphoteric, and basic fractions is dried to a constant weight, as for the neutral fraction. These desorbed materials comprise the combined base and amphoteric fractions. The flask is blanketed with an inert gas, is stoppered, and is stored in a dark place.

The desorption of the anion resin is similar to the procedure above with a few changes. The column is emptied of resin as described above, and the anion resin is desorbed with 7 mL of formic acid. Approximately 2 mL of formic acid is mixed with the anion resin slurry before the resin is transferred to the Soxhlet thimble and the remaining 5 mL is added to a 500 mL round bottom, single-necked flask. Enough toluene is then added to allow for convenient refluxing. The anion resin is placed in an extraction thimble. The thimble and contents are placed in a Soxhlet extractor, which is mounted on the round bottom flask. A condenser is mounted on top of the Soxhlet extractor. The toluene-formic acid mixture is refluxed for approximately 8 hours or until the resin is cleaned of adsorbed material. Dry argon is introduced into the mouth of the condenser during addition of formic acid and refluxing. The filtration and drying procedures after the extraction are the same as for the cation resin.

To separate the base from the amphoteric fraction, a second separation is required. The mixture of the two fractions is dissolved in 25 mL cyclohexane, and the solution is pumped through a column of activated anion resin, as described above. The base fraction is eluted, and the amphoteric fraction is adsorbed on the resin. Isolation of each fraction is the same as described above for the anion resin.

Data Calculation and Precision

Weights of the neutral, acid, base, and amphoteric fractions are recorded. As for any complex chemical separation, reproducibility requires a skilled operator. There are a large number of steps in the procedure. The factors mainly affecting precision are resin activation and extraction of fractions from resins. Table 5-1 lists the standard deviation values for triplicate fractionations of two asphalts.

RESULTS AND DISCUSSION

To achieve results comparable to those obtained in preparative IEC separation of asphalts, a scaled-down method should use the same charge-to-resin ratios as for the preparative method. For the cation, first anion, and second anion resins, these ratios are approximately 0.067 g/mL, 0.046 g/mL, and 0.021 g/mL, respectively. Charges of asphalt in the scaled-down procedure were calculated based on these ratios.

The principal time saving in the scaled-down procedure results from the larger number of separations that can be run using a given batch of activated resin. The activation procedure is tedious, taking an entire week. Two full preparative runs can be made using the amount of resin activated in one preparation in the procedure used [SHRP 1994b]. In the Fast IEC procedure, approximately eight full runs can be made using the same resin activation preparation.

Significant time savings were not achieved during the actual separation. Asphalts appear to be products of molecular association, and time for equilibria to be established must be allowed [Selucky et al. 1981]. Because sample size and amounts of resin used are smaller, it takes somewhat less time to perform the extraction and solvent removal steps in the scaled-down method.

Table 5-1 lists mass percentages of four IEC fractions of eight SHRP asphalts using the scaled-down, or Fast IEC method. All of these asphalts were subjected to one or both preparative IEC separations in the SHRP Binder Characterization and Evaluation A-002A Project. It was mentioned above that two different IEC separation procedures were employed. Different polar fractions are generated by each method. Only the neutral fractions are the same. Results of these separations have been published [SHRP 1993a] and are listed for convenience of reference in tables 5-2 and 5-3. Values in tables 5-2 and 5-3 are averages of several runs.

Preparative IEC separation into amphoteric, acid, base, and neutral fractions was performed only for asphalts AAD-1, AAG-1, AAK-1, and AAM-1. Therefore comparison of the Fast IEC results for the other four asphalts cannot be made directly with a preparative procedure, except for the neutral fractions. Asphalt AAA-1 was separated into neutral, strong, and weak acid, and strong and weak base fractions by preparative IEC. These results indicate that AAA-1 contains relatively large amounts of neutral materials and more acids than bases. Asphalts characterized by large amounts of strong acids in one preparative IEC separation contain large amounts of amphoterics in the other preparative IEC separation. The Fast IEC results show that AAA-1 has large amounts of neutrals, large amounts of amphoterics, and more acids than bases.

Preparative IEC separation of AAB-1 into neutral, strong and weak acids, and strong and weak bases would indicate that this asphalt is relatively rich in basic components, although acids predominate. However, more bases than acids are detected in AAB-1 by Fast IEC. The Fast IEC data also show that AAB-1 contains more neutral and amphoteric materials than might have been expected based on the preparative IEC separation.

Asphalt AAC-1 was separated only into acids, bases, and neutrals by preparative IEC due to problems with wax precipitation in the mixed solvent. The yield of neutral materials in the Fast IEC separation is virtually identical with that observed in the preparative separation. Asphalt AAC-1 is characterized by fewer amphoteric materials than most of the other asphalts. In this separation of AAC-1, a different batch of activated resins was used than for all of the other Fast IEC separations but one of AAD-1, discussed below.

In the Fast IEC separations of AAA-1, AAB-1, and AAC-1, toluene replaced benzene in all operations.

Three different separations of AAD-1 were performed using Fast IEC. In run 1, benzene was used. In runs 2 and 3, toluene replaced benzene. In run 3, a new batch of activated anion resin was used, whereas the same batch was used for all other separations except for the separation of AAC-1 discussed above. Amounts of neutral and amphoteric materials, as well as total recoveries, are similar to what was observed when AAD-1 was separated into neutral, amphoteric, acid, and base fractions by preparative IEC. Averages of acid and base fractions also were similar to those observed in the preparative IEC separation.

Asphalt AAF-1 was separated into neutral, strong and weak acids, and strong and weak bases by preparative IEC. In the Fast IEC separation, more neutral materials are observed than in the preparative IEC results. The preparative IEC results indicate that AAF-1 should contain relatively more acids than bases, and the Fast IEC results confirm this prediction. Toluene replaced benzene in the Fast IEC separation of AAF-1.

Results of three Fast IEC separations of AAG-1, a lime-treated asphalt, are listed in table 5-1. Based on preparative IEC data, AAG-1 should contain relatively few amphoterics, and large amounts of bases and acids. These characteristics are reflected in the Fast IEC results for AAG-1. Presumably some of the acids in AAG-1 are weak and do not react with lime. Otherwise, no acids would be detected in AAG-1 at all as they would have been neutralized.

The Fast IEC separation of AAM-1 yielded results similar to those observed in the preparative separation for amphoterics and acids, but with somewhat more neutrals and fewer bases.

CONCLUSIONS

The results show that in most cases, mass fraction data obtained in the Fast IEC method are similar to equivalent data obtained in the preparative IEC methods. Both methods serve to "fingerprint" asphalts by quantifying relative amounts of non-polar, acidic, basic, and amphoteric materials. The amounts of these materials vary considerably among asphalts, and their relative amounts serve to classify asphalts according to various properties of interest. It is also important that toluene can replace benzene in all operations, although this results in slightly longer extraction time.

An obvious extension of the Fast IEC method is to reduce separation time itself. This was not done because of apprehensions that correspondence with the benchmark preparative data would not be achieved. Shortening actual separation time may result in insufficient contact time of asphalt with resins, and also the increased pressures required might not be practical using existing glass equipment. However, some reduction of separation may be possible using other equipment. The principal time saving in the Fast IEC method as it now stands is the large reduction in the resin activation effort, because many more runs can be performed from a given batch of resin. Some time also was saved in extraction of polar materials from the resins and solvent removal. The much smaller hood space requirement for the downsized equipment also is an advantage.

The Fast IEC method also should be useful in generating samples for subsequent experiments that require small amounts of materials, such as differential scanning calorimetry.

Table 5-1. Separation of SHRP core asphalts by “Fast” IEC.

Asphalt	Run no., mean, std. dev.	Yield of IEC fraction, mass %				Total recovery, mass % of original sample
		Neutral	Acid	Base	Amphoteric	
AAA-1	1	60.6	8.9	7.1	20.3	96.9
AAA-1	2	62.3	7.5	6.8	20.3	96.8
AAA-1	mean	61.4	8.2	7.0	20.3	96.8
AAB-1	1	61.1	6.6	10.3	19.9	97.9
AAC-1	1	60.6	8.6	12.2	18.3	99.7
AAD-1	1	55.5	7.4	7.6	24.1	94.6
AAD-1	2	55.3	7.7	6.9	24.5	94.4
AAD-1	3	51.6	8.4	9.7	23.1	92.9
AAD-1	mean	54.1	7.8	8.1	23.9	94.0
AAD-1	std. dev., σ	1.8	0.4	1.2	0.6	0.8
AAF-1	1	62.9	10.3	7.8	19.3	100.3
AAG-1	1	55.9	10.9	14.5	17.0	98.3
AAG-1	2	56.4	11.3	14.4	17.6	99.7
AAG-1	3	56.0	11.9	16.1	15.7	99.7
AAG-1	mean	56.1	11.4	15.0	16.8	99.2
AAG-1	std. dev., σ	0.2	0.4	0.8	0.8	0.7
AAK-1	1	55.3	8.3	7.9	23.6	95.1
AAM-1	1	59.8	9.3	11.8	18.5	99.4
AAM-1	2	56.3	9.3	12.1	19.6	97.3
AAM-1	mean	58.0	9.3	12.0	19.0	98.4

Table 5-2. Separation of SHRP core asphalts by preparative IEC,[1] conventional method.

Asphalt	Yield of IEC fraction, mass %							Total recovery, mass %
	Neutral	Strong acid	Weak acid	Strong base	Weak base	Acid	Base	
AAA-1	59.6	18.0	8.6	6.2	5.0			97.2
AAB-1	56.9	15.3	8.6	9.1	6.7			96.5
AAC-1	60.2					23.2	13.6	97.2
AAF-1	56.8	16.9	9.9	6.2	7.6			97.7

[1] The data are averages reported in SHRP 1993a, Table 1.1, and Supplementary Table 1.19.

Table 5-3. Separation of SHRP core asphalts by preparative IEC,[1] amphoterics method.

Asphalt	Yield of IEC fraction, Mass %				Total recovery, mass %
	Neutral	Acid	Base	Amphoteric	
AAD-1	53.6	8.0	9.4	24.9	95.6
AAG-1	52.4	14.4	12.5	18.5	98.2
AAK-1	54.6	7.9	9.9	22.9	94.6
AAM-1	55.3	9.3	14.0	18.6	97.8

[1] The data are averages reported in SHRP 1993a, Table 1.8.

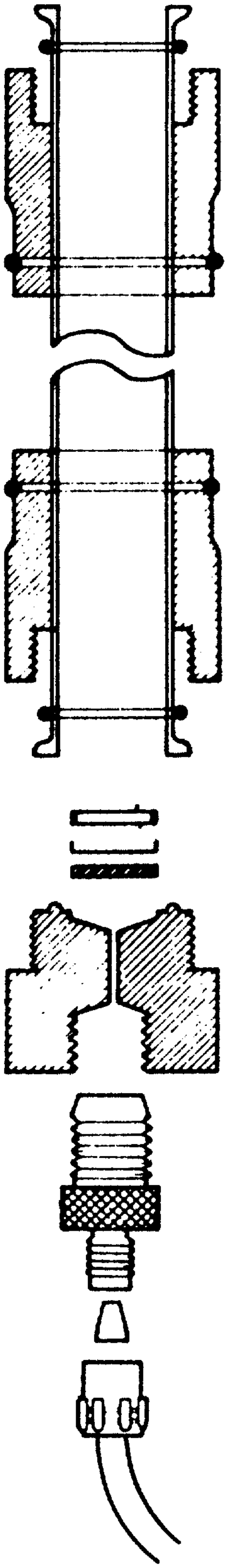


Figure 5-1a. Schematic diagram of a fast ion exchange chromatography column with lower Teflon® end plate, reproduced with permission of the supplier.

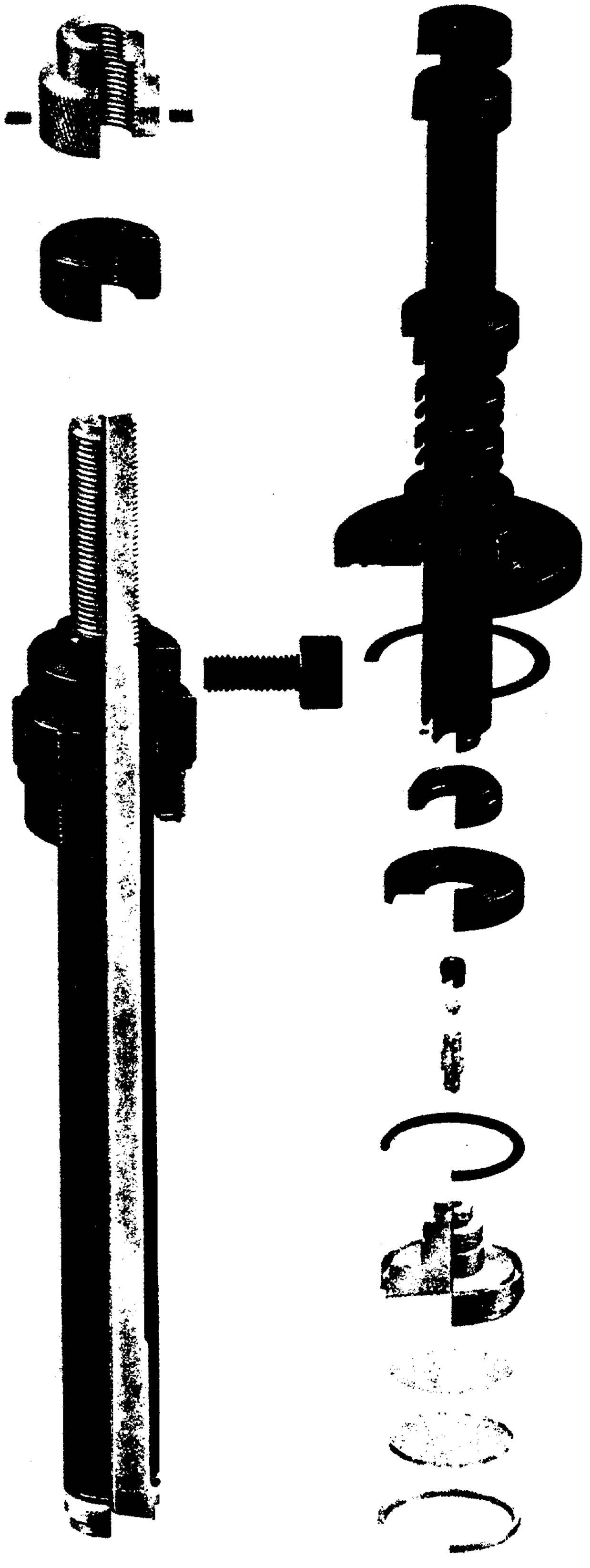


Figure 5-1b. Cross-sectional view of the plunger assembly used in fast ion exchange chromatography separation, reproduced with permission of the supplier.

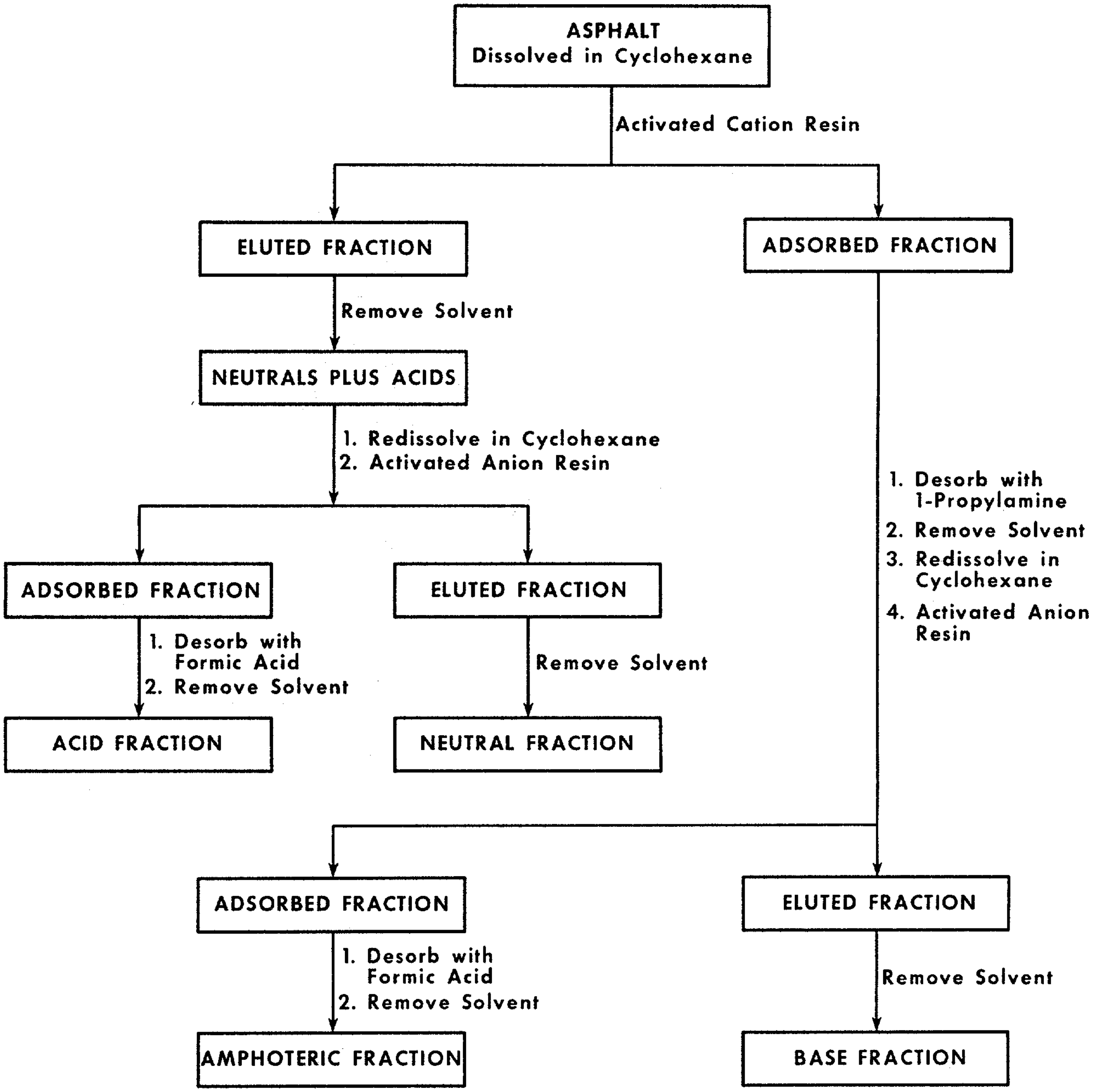


Figure 5-2. Flow sheet for separation of asphalts into amphoteric, base, acid, and neutral fractions by Fast IEC.

METHOD 6. ASPHALT AGING AND TESTING USING MICROWAVE ENERGY

ABSTRACT

This section describes experiments performed under the direction of S. W. Bishara to employ microwave heating as a method for shortening asphalt aging times from 20 hours in the standard PAV test. During the course of this research, important correlations between asphalt chemical composition and times required for samples of asphalts to reach 150°C (302°F) in the microwave were observed. Total polarity and sulfur content determine asphalt dielectric heating rates. Other work describes attempts to optimize experimental variables using a microwave oven to accelerate asphalt aging.

Since this volume was written, the microwave method for oxidative aging of asphalts has been developed into a fully utilizable procedure. The details of the technique are now available [Bishara et al. 1999].

INTRODUCTION

The early stages of the SHRP program saw considerable time spent on the kinetics of aging the core asphalts at 60°C (140°F) using the pressure aging vessel (PAV). However, the long period of time (144 hr) required to cause laboratory aging comparable to field aging was a major concern for producers and suppliers. For organic reactions, the rule of thumb is that the reaction rate doubles for every 10°C (18°F) increase in temperature. Raising the aging temperature to 100°C (212°F) allows reducing the treatment time to 20 hr (or less) according to the rule of thumb. Nevertheless, there is still concern among some producers and suppliers about the length of time needed to complete all specification testing, with aging to constitute a considerable percentage thereof. Furthermore, Liu et al. [1997] reported recently that because the road ages at moderate temperatures and low pressures, and the PAV (AASHTO PP1) uses high temperature and high pressure, there are expected differences between PAV and road aging. There is, therefore, a basic need for an alternative method for asphalt aging that may be faster than the 20-hr, 100°C (212°F) PAV procedure, and that may effect an aging more comparable to road aging.

Recent work at Kansas Department of Transportation (KDOT) [Bishara and McReynolds 1995, 1996] described the use of microwave energy for short- and long-term aging of 18 asphalts used on Kansas roads. A domestic microwave unit was used to treat a relatively small amount (10 or 16 g) of asphalt placed in a Petri dish. Different sets of microwave treatment conditions (time and power level) were selected to simulate rolling thin film oven (RTFO) and 20-hr, 100°C (212°F) PAV aging. After microwave treatment, rheological measurements were carried out at high, intermediate, and low test temperatures (by Superpave® binder specification) to compare microwave aging with RTFO and PAV aging. It was found that microwave radiation could simulate RTFO. However, trials to simulate the PAV aging resulted in asphalts that were as much as 6°C or 10.8°F (one Superpave® grade) lower than the equivalent PAV treatment. That is, microwave aging is less severe than the 20-hr, 100°C (212°F) PAV aging.

It is important to note that historical studies have shown that longer time, lower temperature PAV aging is more predictive of road aging than shorter time, higher temperature PAV aging [Branthaver et al. 1993]. It then follows logically that simulating long-term aging by microwave radiation may prove to agree with the more realistic 144-hr, 60°C (140°F) PAV aging than with the 20-hr, 100°C (212°F) PAV aging. Therefore, results obtained in this research using microwave energy to simulate long-term aging have been compared with results of the 144-hr, 60°C (140°F) PAV aging.

In the previous work at KDOT with the household microwave unit, there were numerous shortcomings:

- Household units have no temperature control. Although the output power can be set for the sample to attain a given temperature after a certain time period, the reproducibility of attaining the same temperature was poor. Furthermore, different asphalts would require different settings to attain the same temperature within a given time period.

- Household microwave units have no pressure control. All microwave treatments were carried out on samples placed in uncovered, quartz Petri dishes - at atmospheric pressure. Quartz was selected because it has a very low, 6×10^{-5}, dissipation factor, tan δ, that is, ϵ''/ϵ', or the ratio of energy transformed into thermal energy (dielectric loss) to that obstructed by the test material. The low dissipation factor of quartz guarantees that all microwave energy passes to the sample and not be partially absorbed by the container.

- One main concern about the lack of pressure control during microwave treatment is the difference in altitudes between various potential laboratories; some are located at sea level whereas others are several thousand feet above sea level, leading to a wide variation in the value of atmospheric pressure at each location. Another concern related to the lack of pressure control and the use of open sample containers is the possibility of loss of some volatile constituents during the microwave treatment.

- Domestic microwave ovens, like the one used in the previous work [Bishara and McReynolds 1995, 1996], control the power output by turning the magnetron on and off according to a duty cycle, i.e., a time on/time off program. For home-style microwave ovens the time base is usually 10 seconds. The oven attains, say, 50 percent power level by turning the magnetron on for five seconds then off for five seconds. This relatively long off period is not desirable because significant heat losses, and hence temperature fluctuation, may occur [Neas and Collins 1993].

Because of the aforementioned limitations of household microwave units, the purchase of a scientific microwave instrument was deemed necessary. The last 10 years have seen an ever-increasing use of microwave (dielectric, in-situ) heating in organic synthesis, the undergraduate laboratory, and industrial production. Several books and reviews describe these developments. More than 250 papers have been published to document the enhancement of reaction rates for a wide variety of organic reactions, sometimes together with an increased reaction yield. Application of microwave irradiation for sample decomposition (by wet digestion) has been extended to areas such as elemental analysis, solid content analysis, botanical, biological, food, and pharmaceutical samples [Neas and Collins 1993]. EPA methods #3015 and 3051 use microwave-assisted acid digestion for decomposition of sediments, sludges, soils, and oils.

RESULTS

As expected, the increased application of microwave radiation went hand-in-hand with technological improvements. Microwave instruments now available, including the purchased MDS 2100, provide temperature and pressure controls and are custom designed with composite sample vessels that can tolerate up to 1400 kPa (200 psi) pressure. The lid of such a vessel has openings for pressure safety valve, gas inlet, and a built-in fiberoptic temperature probe. The latter is protected from contamination by the sample through the use of a thermowell that encases the probe but allows just enough contact for sensing the temperature. The temperature of a sample inside the vessel can be measured continuously during microwave treatment or controlled to increase gradually over a specified time period to reach a preselected temperature. The gas inlet allows connection to a compressed air cylinder with a pressure gauge to control air pressure inside the vessel [Neas and Collins 1993].

The typical microwave instrument used for scientific purposes consists of five major components: the microwave generator (the magnetron), the wave guide, the microwave cavity, the mode stirrer, and a turntable. Microwave energy is produced by the magnetron, propagated through the wave guide, and focused into the microwave cavity where the mode stirrer distributes the incoming energy in various directions.

In the MDS 2100 unit, the turntable includes a carousel that can hold up to 12 composite vessels, each has a capacity of 50 mL. The turntable has a direct drive alternating system, that is, it rotates 360° in one direction then reverses to the opposite direction and rotates 360°, and so on. This guarantees an equal and even exposure of all vessels to the microwave radiation. The instrument has four cavity inlet/outlet ports to allow connecting the sample vessels to an outside gas source, e.g., compressed air cylinder. Because use can be made of more vessels than ports, a system of Tefzel tee-shaped connections was used. A printer provides a hard copy of data in tabular and graphic forms for temperature variation with time of treatment.

In the period from the end of September to the end of November 1996 some exploratory work was performed. This work is summarized as follows:

<u>Measurement of the power output of the instrument.</u> This was carried out as outlined in the manufacturer's manual (and as reported in EPA methods #3015 and 3051). As received, the unit has a switch to enable the power output to be about 800 or 900 Watts.

<u>Uncontrolled dielectric heating rate.</u> To explore the behavior of the eight core asphalts when subjected to 800-W microwave radiation, each asphalt was irradiated with microwaves and allowed to heat up to a preselected temperature (120, 130, 140, or 150°C [248, 266, 284, or

302°F]). It was found that the time required to reach the set temperature varied considerably from one asphalt to the other. For example, to reach a preselected temperature of 150°C (302°F), with the instrument fan at 100 percent speed, asphalt AAK-1 took 14 minutes whereas asphalt AAM-1 could not exceed 140°C (284°F) even after 3-hr treatment as shown in table 6-1. Repeating the same treatment for a target temperature of 150°C (302°F) but using a power output of 900 W caused asphalt AAM-1 to reach the 150°C (302°F) after 111.5 minutes, while asphalt AAK-1 took 13 minutes (table 6-2). Because each of the eight core asphalts has a time period characteristic for it to reach a preselected temperature, say 150°C (302°F), this may serve as a simple, rapid binder characterization test. A minimum microwave power output of 900 W may be necessary.

Uncontrolled dielectric heating rate versus total polarity. In SHRP report A-368, Branthaver et al. [1993] used ion exchange chromatography (IEC) to separate asphalt into strong acids, weak acids, strong bases, weak bases, neutrals, and amphoterics. The latter fraction was further subdivided into strong acid-strong base, strong acid-weak base, weak acid-strong base, and weak acid-weak base amphoterics. Each of the nine fractions was assigned an arbitrary value that is multiplied by the fraction's mass percent; the sum of the products is the relative total polarity of the given asphalt. The total polarity for each of four of the eight core asphalts was calculated [Branthaver et al. 1993].

Plotting total polarity versus the microwave treatment time required for each of the four core asphalts to reach 150°C (302°F) gave a curve that would be fit with a non-linear, power fit equation with a coefficient of determination, r^2 of 0.998. The high r^2 value allows excellent prediction of total polarity of the other four core asphalts, and other asphalts as well, by measuring the microwave treatment time a given asphalt needs to reach the preselected temperature [Bishara and Mahoney 1998].

Uncontrolled dielectric heating rate versus sulfur and total sulfide contents. The microwave treatment time required for an asphalt to reach a preset temperature of 150°C (302°F) was found to vary with its sulfur and total sulfide contents. For the eight core asphalts, treatment time varied with sulfur content according to a linear, power fit equation with r^2 value of 0.93; treatment time varied with total sulfide content according to a non-linear, power fit equation with r^2 value of 0.94. However, table 6-3 shows that asphalt AAG-1 heats much faster than would be predicted from its sulfur or total sulfide content. Excluding AAG-1, the other seven core asphalts show a microwave treatment time that varies with sulfur content according to an equation with r^2 value of 1.00; the same treatment time varies with total sulfide content according to an equation with r^2 value of 1.00 [Bishara and Mahoney 1998].

It was first thought that asphalt AAG-1 exhibits a faster dielectric heating rate due to its lime treatment. But further testing on SHRP non-core asphalts showed that those few asphalts with Ni:V > 1 (like AAG-l) heat faster than the rest, and follow a different equation for the variation of microwave treatment time with sulfur content; the r^2 value is 1.00 [Bishara and Mahoney 1998].

The curve fits enable excellent prediction of sulfur and total sulfide content of asphalt through measuring the microwave treatment time necessary for a given asphalt to reach a preset temperature, e.g., 150°C (302°F).

Simulation of asphalt aging. To enhance dielectric heating, and accordingly shorten the time necessary for simulating the PAV aging, the microwave instrument manufacturer, upon request from KDOT, installed a more powerful transformer that increased the power output from 900 to about 1250 W.

The preliminary experiments described above showed that polarity and sulfur contents of a given asphalt determine its dielectric heating rate. In the laboratory aging process, however, all asphalts must be subjected to the same conditions, that is, to the same pressure, microwave power level setting, and for the same period of time. To satisfy the condition of the same time period, a controlled heating rate is essential. Obviously the heating rate selected must be slower than the rate of the slowest-heating asphalt, which is AAM-1. Increasing the power output to 1250 W, and turning the instrument fan off, causes asphalt AAM-1 to be able to reach 150°C (302°F) in 25 minutes compared with 111.5 minutes for a power output of 900 W and a fan speed of 100 percent (tables 6-2 and 6-4). For AAM-1, 36 minutes are necessary to reach 190°C (374°F). Selecting a ramp time of 45 minutes, then, guarantees that all asphalts reach a target temperature of 190°C (374°F), or lower, in the 45-minute time period. Following the ramp, the instrument may be programmed to hold the temperature for any desired length of time.

Three 60-g samples of each of two asphalts, AAD-1 and AAM-1, were distributed equally among six composite vessels and subjected to a ramp of 45 minutes to reach 190°C (374°F), then followed by a set of different power levels and treatment times at 190°C (374°F). This was done to search for the microwave setting that most closely simulates PAV aging. Tables 6-5 and 6-6 list the $G^* \cdot \sin \delta$, S, and m values for asphalts AAD-1 and AAM-l, respectively, following microwave treatment, and their comparison with those obtained after 144-hr, 60°C (140°F) PAV aging. The limited data available so far show that at the intermediate temperature, microwave aging is less severe than PAV aging for asphalt AAD-1 (table 6-5); AAM-1 (table 6-6) exhibits the same phenomenon but to a lesser extent.

Work is continuing to identify the optimum microwave conditions (output power, fan speed, temperature, sample weight, and treatment time) that simulate the 144-hr, 60°C (140°F) PAV aging. So far, all trials have used air pressure of 1400 kPa (200 psi) or less - the maximum pressure the available composite vessels can handle. This relatively low pressure could be responsible for the always lower stiffness measurements obtained for microwave aging. It is becoming more evident that purchasing a 4200 kPa (600 psi) set of vessels will be necessary.

Some work has also been carried out to simulate the RTFO aging by irradiation with microwaves. Open containers (quartz Petri dishes) were used to hold the asphalts. Some minor modifications had to be made to the turntable to allow four Petri dishes (each charged with 40-g asphalt) to be irradiated simultaneously.

To account for the variability among asphalts of the dielectric heating rate, a heating ramp of 45 minutes was applied to reach 100°C (212°F), and a second ramp of 45 more minutes to reach 163°C (325.4°F). The ramps were followed by a set of different treatment time periods, as shown in table 6-7. More work is needed to refine the procedure. However, because high urgency exists for a rapid, long-term aging procedure, more attention will first be dedicated to simulating the PAV aging. To this end, the ongoing work will investigate the chemical and physical changes occurring during the microwave treatment. Besides measuring the intermediate and low temperature stiffness, the asphaltene content and total polarity will be monitored.

Table 6-1. Variation of dielectric heating rate with asphalt for target temperatures of 120, 130, 140, or 150°C, power output 800 W, fan speed 100%.

Asphalt	Time, min, to reach target temperature			
	120°C	130°C	140°C	150°C
AAK-1	10.0	11.0	13.0	14.0
AAM-1	28.5	39.0	72.5	-- [1]

[1] Asphalt AAM-1 could not exceed 140°C even after 3-hr treatment.

Table 6-2. Variation of dielectric heating rate with asphalt. Target temperature = 150°C, power output 900 W, fan speed 100%.

Asphalt	Time, min, to reach target temperature
AAK-1	13
AAM-1	111.5

Table 6-3. Variation of dielectric heating rate with sulfur content. Target temperature = 150°C, power output 900 W, fan speed 100%.

Asphalt	Sulfur, % [1]	Sulfide, % [2]	Time, min, to reach 150°C
AAC-1	1.9	0.5	44.5
AAG-1	1.3	0.4	28.0
AAM-1	1.2	0.2	111.5

[1] SHRP report A-367, p. 120.

[2] SHRP report A-368, p. 185.

Table 6-4. Variation of microwave treatment time for asphalt AAM-1 to reach some preselected temperatures (uncontrolled heating rate), power output about 1250 W, fan off.

Set temperature, °C	Time, min, to reach set temperature
150	25:00
190	36:00

Table 6-5. Effect of microwave treatment time, power level, and air pressure on $G^* \cdot \sin \delta$, S, and m for AAD-1, fan off.

Aging conditions	PAV aging		Microwave treatment[1]		
	144 hr at 60°C		3.25 hr at 190°C using 90% power	3.25 hr at 190°C using 70% power	4.00 hr at 190°C using 70% power
Test temperature, °C	16	13	13	13	13
$G^* \cdot \sin \delta$, kPa	4,976	7,446	3,849	3,969	4,367
Test temperature, °C	-18	-24	-18		
S, MPa	207	464	130		
m	0.348	0.281	0.413		

[1] Following a heating ramp of 45 min to reach 190°C. All treatment time at 840 kPa (120 psi) pressure.

Table 6-6. Effect of microwave treatment time, power level, and air pressure on $G^* \cdot \sin \delta$, S, and m for AAM-1, fan off.

Aging conditions	PAV aging		Microwave treatment[1]	
	144 hr at 60°C		3.25 hr at 190°C using 90% power	
Test temperature, °C	22	19	16	19
$G^* \cdot \sin \delta$, kPa	3,742	5,113	5,487	4,009
Test temperature, °C	-12	-18	-12	-18
S, MPa	174	357	164	351
m	0.309	0.256	0.338	0.282

[1] Following a heating ramp of 45 min to reach 190°C. All treatment time at 840 kPa (120 psi) pressure.

Table 6-7. Effect of microwave treatment time on $G^*/\sin\delta$ for asphalts AAD-1 and AAM-1, fan off.

Asphalt	Aging conditions	RTFO aging		Microwave treatment[1]		
				10 min at 163°C using 90% power		20 min at 163°C using 90% power
AAD-1	Test temperature, °C	58	64	52	58	--[2]
	$G^*/\sin\delta$, kPa	4.03	1.87	4.58	2.11	--[2]
AAM-1	Test temperature, °C	64	70	58	64	--[2]
	$G^*/\sin\delta$, kPa	2.34	1.09	3.32	1.63	--[2]

[1] Following a heating ramp of 45 min to reach 100°C and another ramp of 45 min to reach 163°C.

[2] These conditions caused equipment problems, e.g., melting of door lining material and the motor drive shaft.

METHOD 7. NON-AQUEOUS POTENTIOMETRIC TITRATION (NAPT) OF ORGANIC ACIDS IN ASPHALT

ABSTRACT

A non-aqueous potentiometric titration (NAPT) technique has been used to determine the amounts of strong organic acids in virgin asphalts and oxidized asphalts. The method allows the semi-quantitative determination of two major classes of compounds—moderately strong acids such as carboxylic acids and an unidentified strongly acidic material thought to be produced by the oxidation of sulfur-containing compounds. The method allows the fast determination of these classes of compounds in the chemically complex asphalt matrix without the requirement of prior separation steps. Weak acids, such as phenols, are not quantitatively determined by the method.

INTRODUCTION AND APPLICABILITY

The goal of this research was to apply the non-aqueous titration techniques previously used in the analysis of petroleum and coal-derived liquids to the analysis of organic acids in asphalts. To be useful for the asphalt industry the method should be fast, quantitative, reproducible, and easily performed by a laboratory technician. Data obtained from the simple titration technique are valuable for defining the kinds and amounts of organic acids, especially carboxylic acids, found in virgin asphalts, oxidized asphalts, and chemically modified asphalt mixtures. The ability to measure the kinds and amounts of these acids accurately in asphaltic matrices is important because the acids may directly influence performance behavior such as moisture susceptibility and the solubility of asphalt additives such as crumb rubber.

According to the Lowry-Bronsted definition, acids are molecules that dissociate to yield positively charged protons (H^+) and bases are molecules that accept protons. Mineral acids, such as hydrochloric acid, are almost completely dissociated into protons and the corresponding negatively charged anions (chloride ion in the case of hydrochloric acid) when dissolved in water. The relative amounts of protons, anions, and undissociated acid are related by

$$K_{acid} = \frac{[H^+][A^-]}{[HA]} \tag{7-1}$$

in which K_{acid} is an equilibrium constant and the other terms are concentrations of protons, anions, and undissociated acid. Organic acids found in petroleum are much weaker acids than mineral acids, and dissociate to protons and corresponding acid anions to a very slight extent. Therefore the value of K_{acid} is small for organic acids. In an analogy with pH values commonly used in chemistry, the negative logarithm of K_{acid} values, designated as pK_a, may be used to measure relative strengths of acids. A lower value pK_a indicates a strong acid, and a higher value a weak acid. The two most common acid compound types in petroleum, carboxylic acids and phenols, have pK_a values of 4-5 and 10-12, respectively, when measured in water. Thus phenols are much weaker acids than carboxylic acids.

Potentiometric titrations involve the measurement of changes in electric potential of an indicating electrode immersed in a solution while titrant is added to the solution. Since there is no way to measure the absolute potential of a single electrode it is also necessary to employ a reference electrode in potentiometric titration work.

In the potentiometric titration of acids or bases or their solutions, changes in hydrogen ion concentration (or in theory, activity) caused by addition of an acidic or basic titrant are monitored by changes in the electromotive force in an electrode that is sensitive to hydrogen ion concentration. In terms of pH, which is the conventional measure of hydrogen ion concentration, the change in electromotive force of the indicator electrode responsive to hydrogen ion is:

$$E = E_{ref} - 0.0591\mathrm{pH} \qquad (7\text{-}2)$$

For most potentiometric acid-base titrations, a glass electrode is used as the indicator electrode, and its electromotive force E is measured against that of a suitable reference electrode, E_{ref} (in this work a silver/silver chloride electrode). Thus, pH (acidity) changes can be recorded as titrant is added to a solution.

The great majority of potentiometric titrations are performed in aqueous media. However, asphalts are not water soluble. Therefore, if titrations of acids and bases in asphalts are to be performed, a much less polar solvent must be used. Any such operation is classified as a non-aqueous potentiometric titration (NAPT).

Solvents that dissolve asphalts are much less polar than water and therefore have much lower dielectric constants than water. A consequence of this is that charged ions are not as effectively solvated as in water, and acidities and basicities are less pronounced in solvents of low dielectric constant compared with water.

In the titration of organic acids in asphalts the titrant used most often has been tetrabutyl ammonium hydroxide, an organic base. The solvent for the asphalt is often a mixture of organic solvents, such as chlorobenzene and ethanol, which has a much lower dielectric constant than water. The solvent systems are chosen so that components of the asphalt do not precipitate during the course of the titration. In mixed organic solvents, strengths of organic acids are not the same as in water. However, relative acidities of various compound classes and of members of a compound class remain the same. For example, phenols will exhibit different acid strengths in chlorobenzene/ethanol compared with water, although individual phenols will exhibit the same relative acidity with respect to one another [Huber 1967]. However, this proportionality may not exist for substances that are not chemically similar. The acidity of members of a given compound class may change much more in an organic solvent than members of another compound class (compared with water) even though relative acidities of the various members are similar within the class.

One reason for the different acidity of organic acids in non-aqueous solvents of low dielectric constant compared with water is the phenomenon of homoconjugation. Homoconjugation is unimportant in water. As acids are titrated with base, the anion formed does not become solvated as it would in water, but instead complexes with undissociated acid molecules to form a stable complex. The result of this phenomenon is that sharp end points are not observed in the titration of mixtures of different kinds of organic acids in non-aqueous solvents. The asphalt matrix itself also affects the sharpness of the end points, and the acid types in asphalts appear to form more of a continuum with respect to acid strength than do the bases. Nevertheless, a semi-quantitative measure of the amounts and kinds of acids present in an asphalt solution may be obtained by plotting electrode response in millivolts vs. amount of titrant added.

Tetrabutylammonium hydroxide (TBAH) was first used as a titrant for organic acids in the 1950s by Deal and Wyld [1955], Cundiff and Markunas [1956], van der Heidje and Dahmen [1957], Harlow and Wyld [1958], and Harlow and Bruss [1958]. Buell [1967] used TBAH in benzene/pyridine solvent as the first practical method of titrating acidic compound types such as carboxylic acids, phenols, mercaptans, carbazoles, and amides in petroleum fractions. He used the method as a way of differentiating between weak and very weak acids in petroleum for the purpose of evaluating separation and treatment processes. Nakajima and Tanobe [1973] used TBAH in benzene/pyridine and TBAH in isopropyl alcohol/pyridine to analyze weak and very weak acids in bituminous materials. More recently Dutta and Holland [1983] used TBAH in methanol/toluene/isopropanol to determine carboxylic acids and phenols in coal and coal-derived liquids. The techniques described in the above publications were developed to quantify acids in specific materials. In most cases the analyses were compromised by ill-defined end points, caused by the multiplicity of individual compounds[1] or by sterically hindered functional groups that did not titrate at all. For these reasons, non-aqueous titration of acids has not been widely used by the asphalt industry. The method described herein is an adaptation for asphalts of techniques discussed above. It uses TBAH in toluene as titrant for solutions of asphalts in chlorobenzene and ethanol. It suffers from the same complications experienced by earlier workers. The method is satisfactory for the analysis of the stronger acids in asphalts but does not quantify weak acid compound types. In most cases the end point for the titration of weak acids is not discerned. For weakly acidic components of asphalts the method is probably best described as being semi-quantitative. Yet with these limitations, the method is useful for comparing the amounts of some of the acidic compound types in asphalts, especially the moderately strong carboxylic acids and the stronger acids that appear to be generated when asphalts are subjected to oxidative aging.

PROCEDURE

A Standard Operating Procedure is provided at the end of this section. Some experimental details are described below.

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[1] Recently Jennings et al. [1995] observed that carbon-13 nuclear magnetic resonance spectra of asphalts do not exhibit peaks corresponding to carboxylic acid carbon atoms even though the presence of acids is unequivocally demonstrated by other methods. The failure to observe distinct carboxylic acid carbon peaks in the spectra is due to the diverse substituents adjacent to the acid group. This substituent diversity spreads the nuclear magnetic resonance peaks; likewise the electrode response, in the case of titration, as the acidity of each of the many carboxylic acids is slightly different from all others.

Apparatus

Equipment

The equipment used was a Metrohm 665 Dosimat titrating unit connected to a Metrohm 670 Titroprocessor. A glass pH electrode and a silver/silver chloride reference electrode were used for making measurements. The reference electrode was filled with a saturated solution of lithium chloride in ethanol.

Reagents

A list of reagents is provided in the Standard Operating Procedure described at the end of this chapter.

Titrations

All titrations were conducted using subsurface addition (solutions of asphalts form films on droplets when exposed to air) of titrant and were started at an addition rate of 200 µL/min. The rate was automatically reduced by the instrument control system as the end points were approached. The instrument located the half neutralization points using pre-established sensitivity parameters and carried out the necessary calculations. Half neutralization points are reported as milliequivalents per gram (meq/g). Corresponding values for mL of titrant used and millivolt (mV) reading for each half neutralization point can also be printed.

Asphalts studied in this project are those selected for investigation during the Strategic Highway Research Program. The asphalts are identified by special code numbers, e.g., AAA-1, AAB-1, AAD-1, etc. Aged SHRP asphalts were prepared using the thin film oven (TFO) procedure, or the TFO and pressure aging vessel (PAV) oxidation [SHRP 1994b]. The PAV aged samples were prepared under various conditions of temperature, time, and pressure in an atmosphere of air.

RESULTS AND DISCUSSION

After a review of the literature and preliminary testing of several solvent systems recommended in the literature, the titration method using TBAH/toluene titrant and chlorobenzene/ethanol diluent was adapted for asphalt samples. The method is similar to that used by Dutta and Holland [1983] for the determination of acidic groups in coal and coal-derived liquids.

Titration of Model Compounds

Model compounds representing the major acidic compound types found in petroleum and asphalt were titrated to determine the millivolt (mV) range of specific compound types. The model compounds tested were organic carboxylic acids and phenols, which represent the principal acidic components of petroleum. Carboxylic acids are moderately strong organic acids.

Phenols are weak acids. Solutions of the compounds at the 0.01 M level in chlorobenzene-ethanol were prepared. Aliquots of 5 mL or 10 mL of the solutions were titrated with 0.1 N solution of TBAH titrant. The instrument records millivolt readings as titrant is added to the solution. If acidic materials are present, the base in the titrant solution neutralizes them. As this process of neutralization approaches completion, inflections in the recorded titration curve are detected by the instrument. The millivolt readings at these inflections serve to identify specific acid types, such as carboxylic acids and phenols. Each type will be characterized by specific millivolt readings. Because carboxylic acids are stronger acids then phenols, the inflection points corresponding to the former will be at less negative millivolt readings than those corresponding to the latter. Specifically, the half-neutralization potentials in millivolts and corresponding volumes of titrant were recorded. These data then are used to calculate the concentrations of identifiable acid types in solutions.

Two different sets of electrodes were used, which yielded different mV values for each of the model compounds. It was not determined why this should be so. Accordingly, one particular electrode was chosen for analysis of the asphalt solutions. Titration data for model compound solutions using this electrode are listed in table 7-1. Based on these data, the two carboxylic acids, palmitic and benzoic, are stronger acids than the two phenols, 1-naphthol and t-butyl phenol. Based on the molarity of the solutions, it would be expected that approximately 0.5 mL titrant would largely neutralize 5 mL model compound solution. So, for 10 mL model compound solution, the half-neutralized potential would be that mV reading at which 0.5 mL titrant has been added.

Table 7-1 also lists titration data for two mixtures of model compounds, palmitic acid with 1-naphthol, and benzoic acid with 4-t-butyl phenol. It was observed that the mV readings for the end points of carboxylic acids in the mixtures had shifted from the end points observed when each compound was titrated by itself. This may be due to interaction between carboxylic acid anions and phenols in a solvent of much lower dielectric constant than water. The observation illustrates the changes in behavior that are observed even in simple mixtures of compounds and shows why data obtained from a complex mixture such as asphalt should probably be described as being semi-quantitative. For example, asphalts contain bases as well as acids, and these bases and acids interact. The result of the interactions would be expected to influence end points in potentiometric titrations.

Titration of Neat, Unaged Asphalts

Titration data for the unaged SHRP asphalts are shown in table 7-2. The results indicate that, as expected, moderately strong organic acids exhibit observable end points. No weak organic acids (such as phenols) were observed to have distinct end points. Undoubtedly phenols and other weak acids are present in these asphalts but were not detected as a class because the end points of individual compounds were spread over a continuum. The titrator measures changes of direction of a titration curve and apparently did not detect changes in direction of the curve generated by the titration of weak acids. Based on the data in table 7-2, asphalts AAD-1 and AAK-1 have significant amounts of what are probably carboxylic acids, the concentrations of which are reported in milliequivalents per gram (meq/g). Half neutralization potentials are in the same general range (-170 to -254 mV) as those of palmitic and benzoic acids reported in table

7-1. This conclusion is supported by infrared spectrometric data [SHRP 1993a]. The acids in AAD-1 appear to be stronger than those in AAK-1, based on mV readings, which are less negative for AAD-1. A less negative mV value indicates stronger acidity. Asphalt AAG-1 contains few acids, as would be expected for a lime-treated asphalt. None of the other asphalts appear to contain large amounts of carboxylic acids.

Titration of Asphalts Aged for 144 Hours

Titration data for five SHRP asphalts, mildly oxidized, are listed in table 7-3. The oxidative aging was performed at 60°C (140°F) for 144 hours in a pressure vessel (300 psi) after a preliminary TFO treatment. Again, only moderately strong organic acids were detected. As shown by the amount of titrant used, some additional acids appear to have been generated by the 144 hour oxidation. End points for weak acids were not detected.

Titration of Asphalts Aged for 400 Hours

Asphalts AAD-1, AAG-1, and AAM-1 were oxidized more extensively for 400 hours at 60°C (140°F) in a pressure vessel (300 psi) after prior TFO treatment. Table 7-3 lists half neutralization potentials in mV and volumes of titrant for titrations of these materials. All extensively oxidized asphalts exhibit two end points. One corresponds to small amounts of quite strong acids titrating at about -10 to -60 mV, and the second end point corresponds to the expected large amounts of moderately strong carboxylic acids titrating in the -200 to -300 mV range. The strong acids also were detected in inverse gas liquid chromatographic analyses (IGLC) of aged asphalts, as discussed in Volume I. The identity of the strong acids is speculative. It is possible that they may be formed by the oxidation of sulfur compounds, probably sulfides, which undergo a reaction pathway involving a Pummerer rearrangement to form sulfonic acids. The possibility of strong acids being formed from the oxidation of sulfur compounds such as thiols and disulfides has been shown by Pedley et al. [1987] in studies involving the oxidative formation of gums in fuels. In any event, sulfur-containing acids (sulfonic or sulfinic) are much stronger than typical carboxylic acids found in petroleum and may be reasonably expected to be generated as a result of oxidative processes. Preliminary aqueous extraction experiments have shown the pH of water into which strong acids were extracted to be in the range of about 3.2 to 3.5. This shows that the strong acids are water soluble, which sulfur acids would likely be. The high acidity (low pH) of the aqueous solution could not result from the presence of typical carboxylic acids found in asphalt. The ability to detect and measure the amounts of strong acids in oxidized asphalts could have significant implications for understanding the mechanisms that cause stripping and moisture damage in asphalt pavements.

Data Calculation and Precision

The method is sensitive to the particular electrodes used. The mV readings appear to be somewhat asphalt dependent. Results are reported in terms of meq/g acids in asphalts versus mL titrant. The acids in asphalts exist as a continuum of strengths. Discrimination between strong and weak acids is somewhat arbitrary. Until there is a larger database, precision cannot be estimated.

SUMMARY

A non-aqueous potentiometric titration technique has been used to measure the variety of moderately strong and strong organic acids in virgin asphalts and oxidized asphalts. The method allows the semi-quantitative determination of two major classes of compounds—moderately strong acids such as carboxylic acids, and an unidentified strongly acidic material thought to be produced by the oxidation of sulfur-containing compounds. The method allows the fast determination of these classes of compounds in the chemically complex asphalt matrix without the requirement of prior separation steps. Weak acids, such as phenols and amides, were not determined by the method because an inflection point of the titration could not be detected. The reason that no inflection point was found may be that the weak acids consist of a large number of chemical species differing from one another only slightly in acidity. This would result in the observed titration curves that vary monotonically, but exhibit no inflection points. A standard operating procedure was developed for the method.

Table 7-1. Titration of model compound solutions (0.01 M) with TBAH (0.1 M).

Model compounds	Run no.	Half neutralization potential, mV	Titrant, mL
palmitic acid	1	-256.0	0.448
palmitic acid	2	-255.3	0.484
benzoic acid	1	-255.4	0.458
benzoic acid	2	-236.4	0.450
1-naphthol	1	-331.8	0.507
1-naphthol	2	-336.0	0.539
4-tert-butylphenol	1	-350.3	0.737
4-tert-butylphenol	2	-350.8	0.704
palmitic acid & 1-naphthol	1	-154.6 -326.2	0.427 0.888
palmitic acid & 1-naphthol	2	-192.8 -340.1	0.434 0.878
benzoic acid & 4-tert-butylphenol	1	-165.3 -340.1	0.419 0.998
benzoic acid & 4-tert-butylphenol	2	-175.4 -342.9	0.424 1.013

Table 7-2. Titration of unoxidized asphalts.

Asphalt	Sample size, mg	Half neutralization potential, mV	Titrant, mL	Concentration of acids in asphalt, meq/g
AAA-1	500	-199	0.142	0.029
AAB-1	500	-197	0.072	0.015
AAC-1	500	-170	0.057	0.011
AAD-1[1]	200 200	-173 -196	0.105 0.115	0.053 0.058
AAF-1	500	-254	0.117	0.024
AAG-1[1]	200 200	-90 -103	0.045 0.045	0.023 0.023
AAK-1[1]	200 200	-238 -234	0.105 0.101	0.053 0.051
AAM-1[1]	200 200	-226 -185	0.061 0.056	0.031 0.028

[1] Replicate determinations.

Table 7-3. Titration of oxidized asphalts.

Asphalt	Aging procedure	Sample size, mg	Half neutralization potential, mV	Titrant, mL	Concentration of acids in asphalt, meq/g
AAB-1	60°C/144 hr TFO/PAV	500	-281	0.131	0.026
AAD-1	60°C/144 hr TFO/PAV	200[1] 200[1]	-211 -237	0.123 0.125	0.062 0.063
AAG-1	60°C/144 hr TFO/PAV	200[1] 200[1]	-202 -193	0.124 0.128	0.062 0.064
AAK-1	60°C/144 hr TFO/PAV	200[1] 200[1]	-229 -247	0.119 0.114	0.059 0.057
AAM-1	60°C/144 hr TFO/PAV	200[1] 200[1]	-222 -243	0.075 0.073	0.038 0.037
AAB-1	60°C/400 hr TFO/PAV	500	-51 -284	0.045 0.171	0.009 0.025
AAD-1	60°C/400 hr TFO/PAV	200	-10 -300	0.050 0.310	0.025 0.115
AAG-1	60°C/400 hr TFO/PAV	200	-60 -230	0.050 0.240	0.025 0.120
AAM-1	60°C/400 hr TFO/PAV	200	-25 -275	0.050 0.155	0.025 0.077

[1] Replicate determinations.

STANDARD OPERATING PROCEDURE WRI-218

Procedure Title: Tetrabutyl Ammonium Hydroxide (TBAH) Titration for Acids in Asphalt

I. APPLICABILITY

This method is applicable to any asphalt or asphalt fraction that does not precipitate during the titration.

II. SUMMARY

This method is used for the determination of strong acids in asphalt using tetrabutyl ammonium hydroxide. The millivolt readings generated by the titration appear to be electrode specific and will drift slightly within individual pairs of electrodes. The cutpoint for strong acids will have to be determined for a specific electrode combination by running the appropriate reference compounds (i.e., palmitic acid, benzoic naphthol). Data are reported as milliliters (mL) of titrant used, millivolt (mV) reading at each end point and milliequivalents/gram (meq/g) of material titrated.

III. EQUIPMENT AND REAGENTS

A. Equipment

Metrohm 665 Dosimat titrating unit and a Metrohm 670 Titroprocessor.
Glass pH indicator electrode and Silver/Silver Chloride (Ag/AgCl) reference electrode.

B. Reagents and chemicals

Tetrabutyl ammonium hydroxide (TBAH), 1.0 M in methanol* (Aldrich Chemical Co., 1001 W. St. Paul Avenue, Milwaukee, WI 53233)
Ethanol (absolute), HPLC grade
Chlorobenzene, HPLC grade (Aldrich Chemical Co.)
Acetone (Aldrich Chemical Co.)
Lithium chloride (LiCl) (Aldrich Chemical Co.)
Drierite ($CaSO_4$) (Aldrich Chemical Co.)
Ascarite (NaOH)* (Aldrich Chemical Co.)
2-propanol, HPLC grade (Mallinckrodt Chemical Co., St. Louis, MO 63160)
Palmitic acid (Aldrich Chemical Co.)
Benzoic Acid (Aldrich Chemical Co.)

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* CAUTION: The solid and solutions of this material are toxic and damaging to flesh, especially eye tissue. Wear safety glasses or goggles when handling this material.

1-Naphthol (Aldrich Chemical Co.)
4-t-Butyl Phenol (Aldrich Chemical Co.)

IV. PREPARATION

A. Preparation and maintenance of electrodes.

1. The Ag/AgCl reference electrode should be kept filled with a saturated solution of lithium chloride (LiCl) in ethanol. The electrode should be stored in ethanol. Vents on the electrode should be covered when not in use for an extended period of time. If the electrode has been stored in ethanol for more than a few days a drop of electrolyte may need to be released from the tip of the electrode.

2. The pH electrode should be stored in distilled water.

B. Preparation of carbon dioxide and moisture trap.

The TBAH titrant is moisture sensitive and reacts with carbon dioxide in air. Solutions of the titrant must be protected from these two substances. Insert a thin layer of glass wool into trap. Fill trap half full with Ascarite or sodium hydroxide pellets. Insert another thin layer of glass wool. Finish filling with Drierite. Insert another thin layer of glass wool. Place cap on trap. Install trap in lid of autotitrator reagent (TBAH) bottle. Flood titration reagent bottle with dry argon.

C. Preparation or cleanup of buret.

Disconnect tubing from top of buret. Slide base plate forward to disengage buret plunger. Unscrew collar and remove buret. Clean buret as needed.
After cleaning, insert plunger into buret leaving approximately 2 cm of shaft exposed. Slide base plate back until plunger pin is seen. Place buret on base plate engaging pin into flat side of plunger shaft. Slide base plate fully to rear. Place collar over buret and tighten. Reconnect tubing to top of buret (do not fit too tightly).

D. Preparation of diluent (10 percent ethanol/chlorobenzene).

Add 50 mL absolute ethanol to 500 mL graduated cylinder then add 450 mL chlorobenzene. Transfer to volumetric flask with stopper for storage. Cover with dry argon.

E. Preparation of titrant (0.1 N).

Note: TBAH (available from Aldrich Chemical) is received in a Sure/Seal bottle with a rubber septum. Care should be taken to maintain positive argon pressure in this bottle. TBAH is hygroscopic and also very sensitive to carbon dioxide contamination. There are several accepted methods for transferring reagents while maintaining positive pressure. (See Aldrich Technical Bulletin Number AL-134, Handling Air-Sensitive Reagents.) One method is to charge a syringe with argon. Insert needle of syringe into Sure/Seal bottle. Discharge argon into bottle and withdraw reagent (TBAH) into syringe. Remove syringe from bottle and inject reagent into volumetric flask.

Flood a 100 mL volumetric flask with argon. Add 4 mL of 2-propanol to volumetric flask. Add 10 mL of 1.0 molar TBAH to volumetric flask. Fill to 100 mL line with toluene. Flood volumetric flask with argon again and agitate mixture (titrant).

The reagent bottle on the autotitrator should be flooded with argon before titrant is transferred into it. Transfer titrant into titration bottle. Maintain a slow constant flow of argon thru reagent bottle once titrant has been added.

F. Preparation of reference acid standard (0.01 N).

Add 1 formula weight in mg (palmitic acid, 256.4mg) to 100 mL volumetric flask. Dilute to 100 mL with diluent.

V. PROGRAM SETUP

A. Turn on instrument. Select page 1 by typing **P1 <R>**. This will bring up the following screen.

```
        METROHM TITROPROCESSOR  (5.670.0033)      METHODS        PAGE    1A

0       NEW
1       @         Dynamic Titration
2       @         Monotonic Titration
3       @         SET (Set Endpoint Titration, 2 endpoints)
4       @         DYNT for Acids in Asphalts
5       @         DYNT for Acidic Standards
6       @         DYNT for Bases in Asphalts
7       @         DYNT for Basic Standards
8
9
10      @         BURETTE PURGE
```

This screen contains the various methods that have been programmed into the METROHM 670 titroprocessor. Select method 10 to purge. Select method 5 for running blanks and model compounds. Select method 4 for running samples. The @ indicates that the method has been secured and any editing to the method will not be permanent. The DYNT is an acronym for dynamic titration.

B. Calibration/Standardization.

From page 1 select method 5 by typing **ME5 <R>**. This will bring up the following screen, page 8 of method 5.

```
DYNT for Acidic Standards                      METHOD 5      PAGE 8
                                               MONITORING
1      REMARKS         xxxxxxxxxxxxxxxxxxxxxxxxxxxxxxx
2                      xxxxxxxxxxxxxxxxxxxxxxxxxxxxxxx
3      NAME            xxxxxxxx
4      RUN#            xxx
5      MEAN
6      AUTO START#     NO  :.. of 999
7      AUTO FF NO

       SILO P9  LEVEL: .. of 999
8      CLOSED  a       b                c                  d          e
       SAMPLE DATA     MTHD   ID1 or S3 ID2 or S2  S1 VAR  SO SIZE(m,v)
9      ACTUAL LINE

                                                           *READY*
```

The only lines that may need to be edited are lines 1 through 4. Lines 1 and 2 would have information about the sample (blank, type or quantity of sample, ID, etc.). Line 3 would contain the operator's name or initials. Line 4 could be edited if you wanted to start with a specific run number.

To edit line 2 type **EL2 <R>**. At the bottom of the screen you can type the information needed. Press **<R>** to end data entry on that line and move to the next line. To skip a line just press **<R>**. To terminate the editing mode press **CTRL Q**. At this point the program is ready and blanks or model compounds could be run. See section **VI Titration.**

C. Samples.

From page 1 select method 4 by typing **ME4 <R>**. This will bring up page 8 of method 4. This screen will look similar to page 8 of method 5 except the title line will read:

```
DYNT for Acids in Asphalt
```

Edit any lines necessary on this screen (lines 1 thru 4) in the same manner as used for method 5. At this point the program is ready and samples could be run. See section **VI Titration.**

Blanks and standards can be run from this method, but it will print out an unnecessary report.

D. Program calculations and variables.

The formula for calculation of milliequivalents/gram can be expressed as:

meq/g = volume of titrant (mL)* normality of titrant / grams of sample

The formulas used by the instrument for calculations can be found on page 6 of method 4.

DYNT for Acids in Asphalts METHOD 4 PAGE 6
CALC. STATEMENTS

	a RES. QUANTITY	b R#, I#, Cx FORMULA	c DPL	d UNIT
1	meq/g EP1	R1=E1*C1/C2*C3	4	meq/g
2	meq/g EP2	R2=E2*C1/C2*C3-(R1)	4	meq/g
3	meq/g EP3	R3-E3*C1/C2*C3-(R1+R2)	4	meq/g
4	meq/g EP4	R4=E4*C1/C2*C3-(R1+R2+R3)		4
meq/g				
5	meq/g EP5	R5=E5*C1/C2*C3-(R1+R2+R3+R4)	4	meq/g
6	meq/g EP6	R6=E6*C1/C2*C3-(R1+R2+R3+R4+R5)	4	meq/g
7	meq/g EP7	R7=E7*C1/C2*C3-(R1+R2+R3+R4+R5+R6)	4	meq/g
8	meq/g EP8	R8=E8*C1/C2*C3-(R1+R2+R3+R4+R5+R6+R7)	4	meq/g
9				
10				

The variables used in these formulas can be found on page 7 of method 4.

DYNT for Acids in Asphalt METHOD 4 PAGE 7
CALC. STATEMENTS

	a C# CALC. VAR	b COMMENT	a Cx COM. VAR	b COMMENT
1	C1 0.1000	N of titrant	21 CA	
2	C2 .500000	G of sample	22 CB	
3	C3 1000.00	correction fact	23 CC	
4			24 CD	
5			25 CE	

Variable C1 is the normality of the titrant being used (0.1 N TBAH).
Variable C2 is the sample mass in grams, currently set at 500 mg of sample.
Variable C3 is a correction factor for an instrument error in calculating meq/g.
These variables will have to be edited if there is a change in sample mass or normality of titrant. Editing can be done using the EL or EV functions at the bottom of the screen.

VI. TITRATION

Titrations are carried out at a rate of 200 µL/min, and this is automatically reduced as the end point is approached. A plot is produced on the screen of the Titroprocessor as the titration progresses. The instrument locates the end points and carries out the necessary calculations. Results are printed out with the titration curve.

Note: If it is going to take longer than 1 or 2 minutes to prepare sample for titration, wash both electrodes with chlorobenzene. Wash the pH electrode with acetone. Place the electrodes in their respective storage tubes. Wash the pH electrode with acetone and chlorobenzene before reuse. Wash the reference electrode with chlorobenzene before reuse.

Note: After each run, wash the reference electrode with chlorobenzene. Wash the pH electrode with chlorobenzene and acetone, then return it to storage tube after each run. This will rehydrate the glass membrane and stabilize the pH electrode. Wash the pH electrode with acetone and chlorobenzene before reuse.

A. A trap has been installed on the titrant reagent bottle. Argon gas flow (enough positive pressure to protect titrant from air) has been established and the titrant reagent bottle has been flooded with argon. Titrant has been transferred to the reagent bottle. All tubing connections on the autotitrator have been made.

B. If the reagent bottle has just been filled or if it contains titrant from a previous day and the system has been allowed to stand for a few days, it may be necessary to cycle the piston to discharge the 10 mL of titrant contained in the buret and refill it. From page 1 select **ME10**. Be sure that both the glass pH electrode and the reference electrode are in a beaker of diluent (chlorobenzene-ethanol). Purge the buret by pressing the red **START** button. If system integrity and argon flow is maintained, the titrant should remain good for a week or more. Additional titrant can be added to the bottle as needed during this time.

C. Titration using blanks and model compounds (palmitic acid, etc.).

At the beginning of each day or after a break of 30 minutes or more, a titration should be made using blank solutions. If using the 10 percent ethanol/chlorobenzene diluent as the blank, there should be no titratable end points detected. Occasionally there may be an end point on a blank. If this occurs and less than 0.050 mL of titrant has been consumed, it can be disregarded as noise.

Note: The tip of the buret can be cleared of any air bubbles before a titration by expelling a small amount of titrant. Press the **GO** button on the Dosimat or use the remote. Occasionally a bubble will appear in the tubing; this bubble should also be expelled. After expelling bubbles, press the **FILL** button to reset Dosimat. Wash the buret tip with chlorobenzene.

1. From page 1 bring up method 5 by typing **ME5 <R>** for running blanks and model compounds.

2. Edit any lines necessary on page 8 of method 5 using the **EL#** function at the bottom of the page.

3. For blank determination, add 25 to 30 mL of diluent and small stir bar to a 50 mL beaker. Place beaker on stirrer (for model compounds add 5 mL of 0.01 N reference palmitic acid standard solution and 20 to 25 mL of diluent).

4. Wash electrodes and buret tip. See notes at start of section **VI Titration**. Place electrodes and buret tip into the solution in 50 mL beaker.

5. Start titration by pressing the red **START** button.

6. After completion of titration press the **BREAK** button. This will terminate the titration and print the report. Wash electrodes. See notes at start of section **VI Titration**.

D. Titration of samples.

1. From page 1 bring up method 4 by typing **ME4 <R>** for samples.

2. Edit any lines necessary on page 8 of method 4 using the **EL#** function at the bottom of the page.

3. Accurately weigh 500 ± 0.5 mg of asphalt sample into a 50 mL beaker.
   Add 30 mL of diluent and stir using a magnetic stirrer.
   Dissolution of sample should be complete in 10 minutes; if not, increase time according to the experimental plan for those samples.

4. After sample is in solution, remove electrodes from storage tubes.
   Wash pH electrode with acetone to remove surface water.
   Wash both electrodes and buret tip with chlorobenzene.
   Place electrodes and buret tip into the solution in 50 mL beaker.
   Start titration by pressing the red **START** button.

5. After completion of titration, press the **BREAK** button. This will terminate the titration and print the report.

6. Repeat these steps 2 thru 5 for each additional sample. Both electrodes should be washed and returned to their respective storage tubes after each asphalt sample run.

V. DATA REPORT

End points are reported as meq/g. Corresponding values for mL of titrant used and mV reading for each end point can also be reported. The course of the titration may be recorded on chart paper.

VI. QA/QC

A. A set of blanks of ethanol-chlorobenzene diluent and reference acid standards (e.g., palmitic acid) should be run at the start of each day.

B. Comparative duplicates of unknown samples are run during each day as established by the specific experimental plan.

C. A set of blanks and model compounds can be run at the end of each day as dictated by the experimental plan.

METHOD 8. SUPERCRITICAL FLUID EXTRACTION (SFE) OF ASPHALT-AGGREGATE MIXES

The technique of supercritical fluid extraction (SFE) was evaluated as an alternate method for the quantitative extraction of asphalts from asphalt-aggregate mixtures. The primary purpose of these experiments was to isolate screenable aggregate without the use of chlorinated hydrocarbons. During the examination of the technique three possible supercritical solvents (carbon dioxide, sulfur hexafluoride, and propane) were tested. No supercritical solvent, even with the addition of modifiers, could completely extract asphalt from the aggregate. Propane extraction yields were better than the other solvents tested with the percentage extracted slightly greater than 75. However, propane is quite flammable, can be destructive to the instrument seals, and is not environmentally friendly. Generally, the recovery of asphalt by the SFE systems tested was too low, even with the addition of SFE modifiers, to be considered of practical use for asphalt-aggregate mixes. Carbon dioxide, the readily disposable solvent of choice, gave extraction efficiencies that were generally less than 50 percent. Details of extraction procedures and conditions are given in a topical report [Barbour et al. 1997].

METHOD 9. SHALE OIL-MODIFIED ASPHALT (SOMAT) TEST STRIP

ABSTRACT

Presented below is a description of the types and sources of the samples collected during the conduct of a field project in Grand Teton National Park. In addition, the experimental methods that were used to determine the chemical and physical properties of these samples are described or referenced. The experimental methods used in the analysis of the aggregate, core, and binder samples are, for the most part, those recommended by the American Association of State Highway and Transportation Officials (AASHTO). Also included are supplementary data, presented in the form of tables or figures, upon which conclusions presented in Volume I were, in part, based.

INTRODUCTION

Briefly, an objective of this project is to compare the performance of a shale oil-modified asphalt (SOMAT) test strip with a polymer-modified control strip. The project site is located about 33.8 km (21 miles) north of the south boundary of Grand Teton National Park on U.S. Highway 89. What is presented below is a description of the types and sources of the samples collected during the conduct of the project that is described in Volume I, chapter 6. In addition, the experimental methods that were used to determine the chemical and physical properties of these samples are described or referenced. The experimental methods used in the analysis of the aggregate, core, and binder samples from both pavements are, for the most part, those recommended by the American Association of State Highway and Transportation Officials (AASHTO). The experimental methods used in the analysis of the environmental samples (air, water, hot mix, and soil), the results of which are only briefly discussed in Volume I, chapter 6, have been published [WRI 1994; Thomas et al. 1997]. Also included here are supplementary data, presented in the form of tables or figures, upon which the conclusions presented in Volume I, chapter 6, were, in part, based.

SAMPLE COLLECTION AND METHODS OF ANALYSIS

Sample Collection

Various samples of the construction materials were obtained during the reconstruction of the highway. These included eight 18.9-L (5-gallon) samples of aggregate obtained from the cold aggregate feed belt, one 3.8-L (1-gallon) sample of shale oil modifier (SOM) used in each of the two lifts, one 3.8-L (1-gallon) sample of the performance-based asphalt-6a (PBA-6a) from the first lift and one 0.95-L (1-quart) sample of PBA-6a from the second lift, two 3.8-L (1-gallon) samples of the PBA-base asphalt before the addition of Kraton® D 1184 (obtained from Sinclair Refinery separately), one 18.9-L (5-gallon) sample of SOMAT from each of the two lifts, one 3.8-L (1-gallon) sample of SOMAT from each of the two lifts, one 3.8-L (1-gallon) sample of AC-20 from the first tanker and one 0.95-L (1-quart) sample of AC-20 from the second tanker (used for blending with SOM), one 18.9-L (5-gallon) sample of the control asphalt (PBA-6a) from each of the two lifts, five 18.9-L (5-gallon) cans of SOMAT loose mix from each of the two lifts, and five 18.9-L (5-gallon) samples of the PBA-6a loose mix from each of the two lifts. The samples described above were obtained for either archival purposes and/or baseline measurements.

The day after the reconstruction of the highway was completed, September 17, 1993, personnel from Nichols Consulting Engineers (NCE) and WRI marked the location of the required cores in the control (PBA-6a) and test (SOMAT) sections of the highway. The core locations were identified using a waterproof, silver paint. The identification of the cores included the core location with respect to section, that is, a designator as to whether the core was taken from one of the four control sections (C1, C2, C3, and C4) or one of the two test sections (S1 and S2). This designator was followed by the core number (C1 to C15, which identify the 102-mm [4-inch] cores and A1 to A4, which identify the 152-mm [6-inch] cores). The reader is referred to figure 9-1 for an example of the coring pattern. In addition, an arrow on the top of the core indicated the direction of the traffic flow. A total of 108 cores were identified, 70 in the four control sections and 38 in the two test sections. On September 18th, all 108 cores were drilled and collected. This included twenty-four 152-mm (6-inch) cores and eighty-four 102-mm (4-inch) cores. Three of the 102-mm (4-inch) cores in the coring pattern from each of sections C3 and C4 were not drilled or collected (see figure 9-1) because they were not required for testing. The data obtained from these 108 cores are the baseline values to which all future data will be compared. Cores from the pavement sections were also obtained in 1994 and 1995. However, in these cases cores were not taken from control sections C3 and C4. Additional cores will only be taken from these control sections if it appears that the information obtained from the cores taken from sections C1 and C2 are insufficient to explain the observed distress of the control sections. The distribution of the cores for analysis and the type of analyses that are being conducted are shown in table 9-1.

Table 9-1. Distribution and type of analyses that were conducted on the cores obtained from U.S. Highway 89.

Recipient	Number	Type of analysis
WRI	8	Rheological Analyses, Aging Tests, Infrared Analyses, and Elemental Analyses
NCE		
Braun Intertec	78	Moisture Susceptibility, Resilient Modulus, Bulk and Maximum Specific Gravity, Asphalt Content, and Gradation of Aggregate
Oregon State University	18	Fatigue/Permanent Deformation
FHWA	4	Archive

Methods of Analysis

For acceptance of the highway, the Western Federal Lands Highway Department (WFLHD) required numerous tests be conducted on the construction materials. During construction of the pavement, the materials tested included cold aggregate feed, loose mix after being laid but before compaction, and cores taken from the compacted pavement. The AASHTO tests conducted on these materials consisted of the following. The asphalt content (T-164), sieve analysis (T-30), and moisture content (T-110) were determined for the loose mix samples. The sand equivalency (T-176) and the results of the fracture test to determine the percentage of fractured faces (FLH; T-507) were determined for the cold aggregate feed samples. T-507 is a WFLHD test procedure for determining the percentage of fractured faces in a gravel. It is conducted by visually determining the percentage of material in the aggregate that contains a sharp edge. The bulk specific gravity (T-166) and degree of compaction (T-230) were determined for the core samples. In addition, the density of the pavement during compaction was monitored. This was done using a Troxler nuclear gauge. The pavement density was monitored lineally about every 61 m (200 feet) with locations selected randomly across the new pavement. WFLHD accepted 90 percent of the maximum theoretical value. However, the values obtained were usually about 93 to 94 percent of the maximum.

On October 20 to 22, 1993, personnel from NCE and WRI conducted a non-destructive, baseline evaluation of the pavement in the four control (PBA-6a) and two test (SOMAT) sections. The methods used to evaluate the pavement included: a distress survey, falling weight deflectometer (FWD) testing, and transverse and longitudinal profile measurements of the six sections.

A distress survey of the highway that contained the control and test sections was conducted by personnel from NCE 1 month after construction. During the survey, the guidelines presented in the publication, SHRP-P-338, were followed [SHRP 1993b]. The conclusion was that the new pavement was in excellent condition. Distress surveys were also conducted every year after construction to monitor the advent of distress. It was originally planned that distress surveys would only be conducted in 1993, 1994, 1995, and 1998. However since cracking was noted in the control and test sections in 1995, it was decided that more frequent monitoring was required to track the extent of crack growth. Consequently, distress surveys were conducted in 1996 and 1997. During the conduct of a distress survey the severity and extent of cracking, surface deformation (rutting and shoving), potholes (including patch deterioration), and surface defects (bleeding, polished aggregate, and raveling) were evaluated.

FWD testing of the pavement was conducted to determine the structural capacity of the recently constructed pavement. From these results the stress-strain properties of the pavement can be determined. The load that was applied to the pavement that resulted in the deflections simulates the load of a 40 kN (9,000 pound) dual tire. This baseline data will be compared with data that will be collected in 1998.

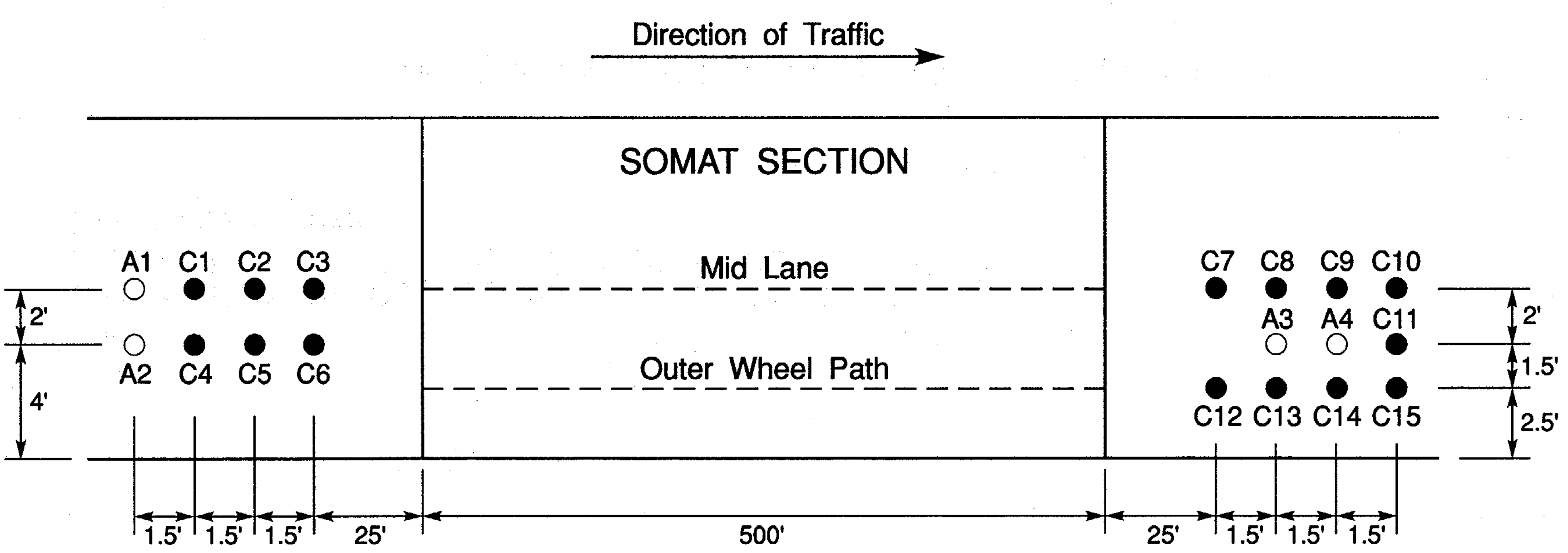
Transverse and longitudinal profiles were obtained for the six sections. Transverse profiles were obtained every 15.2 m (50 feet) including the beginning of each section. The transverse profiles were made using a KJ Law profilometer (dipstick). The measurements were made by measuring the slope of the pavement in hundredths of a millimeter (thousandths of an inch) every 304.8 mm (1 foot) from the fog line to the center line and then back to the fog line. Thus, 24 (12 x 2) measurements were made across the 3.7-m- (12-foot-) wide driving lane. The data were then treated according to the SHRP guidelines [SHRP 1993b]. Transverse profiles have been obtained for every year from 1993 to 1998.

The longitudinal profiles for the outside and inside wheel paths were obtained using the SHRP profilometer van. NCE, which is the western regional subcontractor of FHWA, was responsible for conducting this test. Nine runs, the maximum required according to SHRP guidelines [SHRP 1994c], were made through the six sections. See figure 9-2 for the orientation of the sections. A more detailed discussion of these non-destructive tests is contained in the topical report delivered to FHWA in December 1995. Shown in the figure are the stations that were set up for the project. The units for the stations are in feet from the base location of the project for the 1993 construction season. The convention is, for example, 1121+50 (the start of section S2) which means one hundred and twelve thousand and one hundred feet plus fifty feet or 112,150 feet to the base location of the project.

DISCUSSION

As shown in table 9-1, the bulk of the cores that were obtained by NCE and WRI were distributed to three different laboratories for analysis. Braun Intertec conducted the majority of the tests on the cores. These tests included asphalt content and gradation of the aggregate using Superpave® standards P04 and P14, respectively. In addition, they determined the bulk specific gravity and maximum specific gravity using P02 and P03, respectively. The resilient modulus was determined using P07, and the moisture susceptibility of cores was determined using P05. Oregon State University evaluated the fatigue and permanent deformation characteristics of cores taken from the control and test sections. The method used was a modification of the fatigue test in ASTM method D 4123. The modification allows for the evaluation of a specimen to resist permanent deformation. The test was conducted at 25°C (77°F) and at constant stress. The vertical deformation after repetitive loads and the number of repetitions to sample failure were recorded. Failure is defined as when a lead-based foil tape glued around the diametral axis of the core and perpendicular to the loading axis of the core is broken due to the application of a load.

The analytical methods employed at WRI used to evaluate the binders obtained from cores and loose mix included AASHTO method PP6 to grade or verify the Superpave® performance grade of the binders. To evaluate the extent of aging of the binder that had occurred during hot mix processing and hauling, loose mix and core samples from the control and test sections were extracted with toluene - ethanol (85 - 15 percent) to recover the binder. After solvent removal, infrared analysis of these samples and the original binder samples were then conducted using a Perkin Elmer 983G infrared spectrophotometer to evaluate the extent of chemical aging (oxidation). Dynamic rheological measurements of the extracted and original binder samples, obtained using a Rheometrics 605 mechanical spectrometer, were used to assess physical hardening. Original binder samples were aged using the rolling thin film oven (RTFO) test (ASTM D 2872/AASHTO method T240) and AASHTO method PP1 using a pressure aging vessel (PAV). These data from the laboratory aging of the binders were then, in part, compared with that obtained from the extracted loose mix and core samples to compare the RTFO aging with hot mix plant aging. Rheological properties at various temperatures were also obtained following AASHTO method TP1 using a bending beam rheometer (Cannon) and method TP5 using a dynamic shear rheometer (Rheometrics). The elemental composition of SOM was determined using conventional analytical techniques. In addition, infrared analysis to determine the weight percentage of SOM and dynamic rheological measurements to determine the master curve were obtained to characterize the binders.



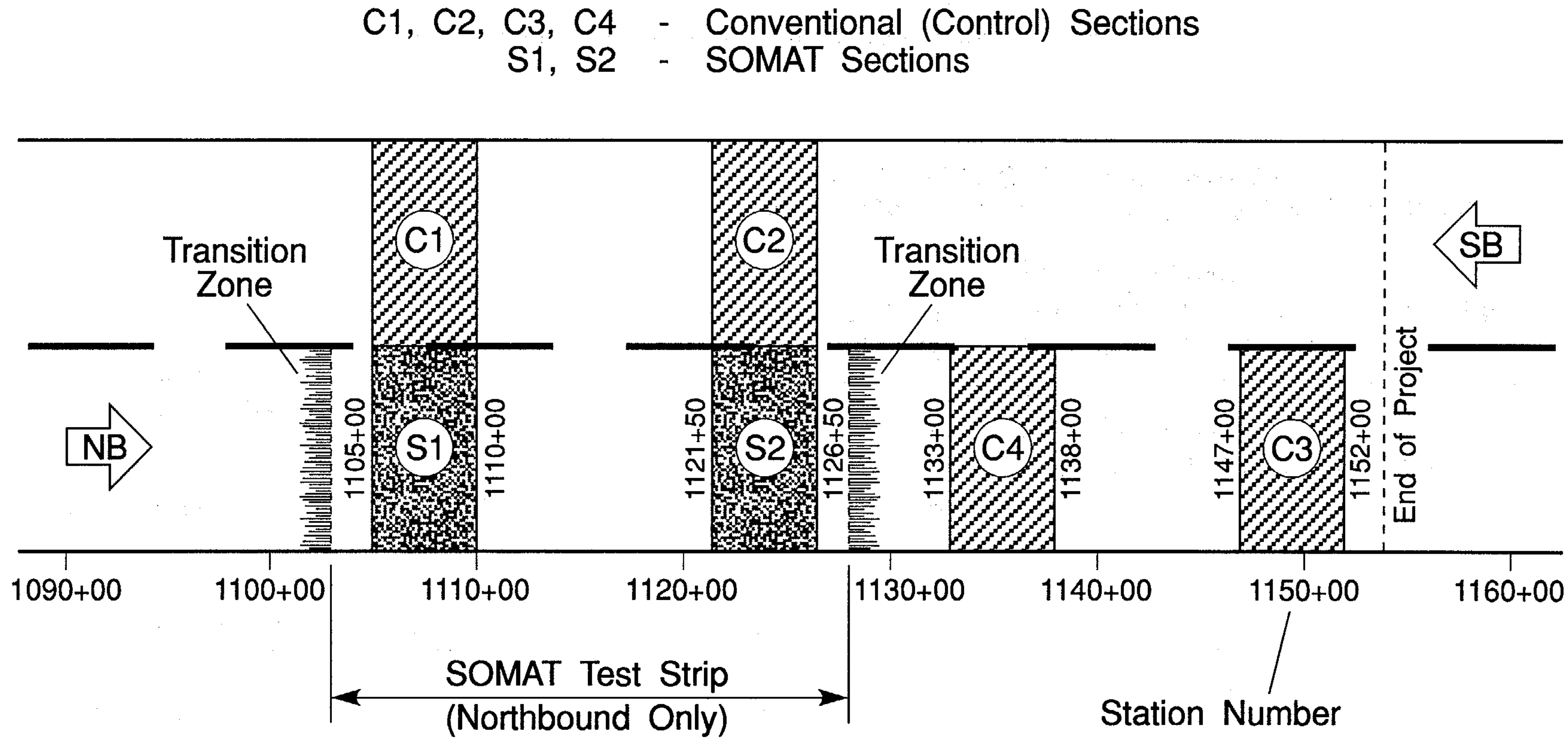
● 4" OD Core of Pavement Surface

○ 6" OD Core of Pavement Surface

C1-C3, C7-C9 - Moisture Susceptibility
C4-C6 - Fatigue/Permanent Deformation
C12-C14 - Resilient Modulus
A1, A3 - Maximum Specific Gravity
A2, A4 - Extraction/Gradation
C10, C15 - Rheological and Chemical Tests
C11 - FHWA TFHRC

Note: Cores C10, C11 and C15 Are Not Required for Conventional Sections C3 and C4.

Figure 9-1. Orientation of the coring pattern for the test sections.



Note:

19 Cores Each Are Required from Sections S1, S2, C1, C2
16 Cores Each Are Required from Sections C3, C4
(See Coring Diagram)

Figure 9-2. Orientation of the monitoring sections, U.S. Highway 89.

SUPPLEMENTARY DATA

The following tables and figures are the supplementary information that was referred to in Volume I, chapter 6, in the section entitled "Shale Oil-Modified Asphalt Test Strip."

Table 9-2. Indirect tensile strength of cores taken from the two pavement sections.

Year	Section	Indirect tensile strength, kPa		Tensile strength ratio
		Dry	Wet	
1993	C1	427	346	0.81
	C2	312	273	0.88
	C3	492	435	0.88
	C4	477	373	0.78
	S1	663	472	0.71
	S2	625	476	0.76
1994	C1	681	624	0.92
	C2	595	626	1.05
	S1	857	845	0.99
	S2	838	811	0.97
1995	C1	691	704	1.02
	C2	670	633	0.94
	S1	1021	1002	0.98
	S2	1070	1063	0.99

Table 9-3. Resilient modulus data for cores taken immediately after construction (1993).

Section	Instantaneous resilient modulus, MPa			Total resilient modulus, MPa			Indirect tensile strength, kPa
	5°C	25°C	40°C	5°C	25°C	40°C	
C1	3268	2053	634	2547	1357	401	519
C2	2365	1441	484	1913	979	307	361
C3	3498	2045	637	2802	1400	413	432
C4	3156	1359	427	2611	994	281	345
S1	4361	2335	788	3493	1661	538	542
S2	3209	2036	736	2612	1478	490	517

Table 9-4. Resilient modulus data for cores taken 2 years after construction (1995).

Section	Instantaneous resilient modulus, MPa			Total resilient modulus, MPa			Indirect tensile strength, kPa
	5°C	25°C	40°C	5°C	25°C	40°C	
C1	10,211	7470	1971	8323	5072	1183	772
C2	11,846	4640	1945	11,129	3217	1187	672
S1	13,503	7189	3036	11,050	4786	1811	934
S2	13,273	7340	2304	10,721	4573	1395	968

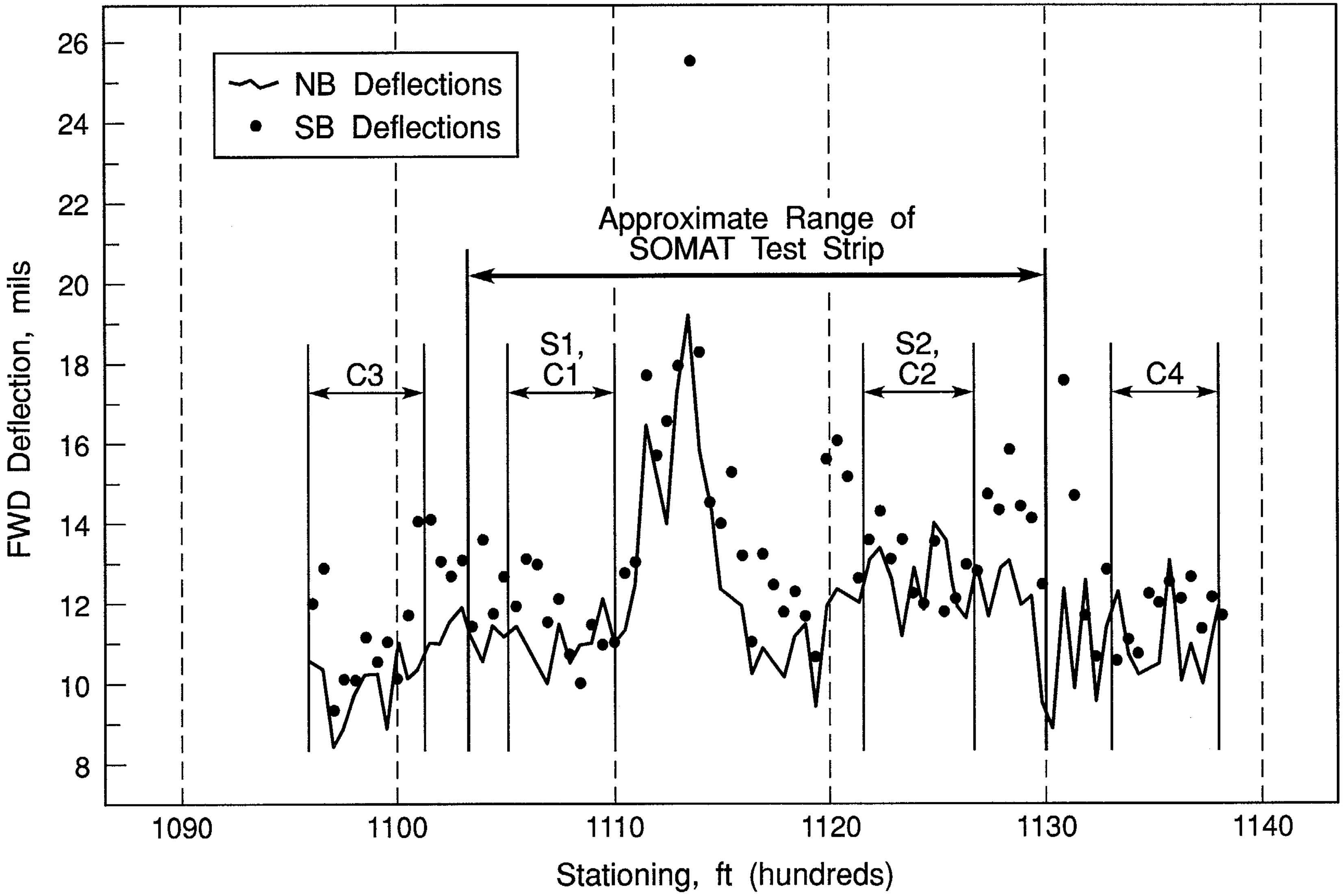


Figure 9-3. Maximum deflections in the north and southbound directions in the vicinity of the planned SOMAT test strip, U.S. Highway 89.

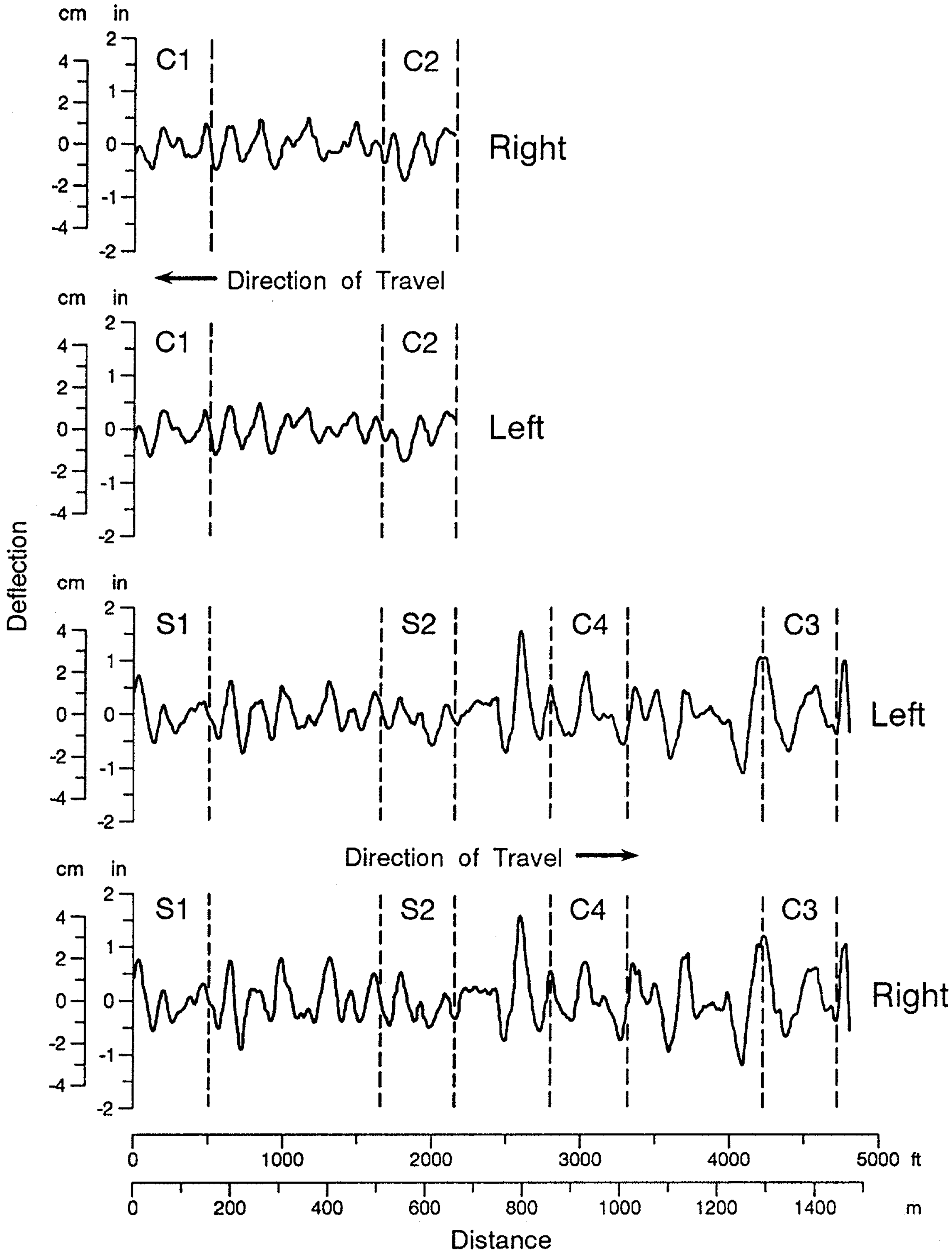


Figure 9-4. Longitudinal profile of the six sections that are being monitored (1993).

METHOD 10. IMPACT OF MOISTURE ON ASPHALT RHEOLOGY AND AGING

ABSTRACT

Presented below are the experimental methods that were used to determine the chemical and physical properties of samples that were stored either in the presence of water or in an inert atmosphere for different lengths of time. Also included are supplementary data, presented in the form of figures, upon which the conclusions presented in Volume I were, in part, based.

INTRODUCTION

One objective of this project is to evaluate the impact of water on the physical properties of asphalts. Presented here are the experimental methods that were used to determine the chemical and physical properties of the samples that were studied during the conduct of the project that is described in Volume I, chapter 5. The description of the methods is broken into two sections. These sections discuss those methods that deal with the treatment of asphalt with water and those methods that deal with the attenuated total reflectance (ATR) infrared spectroscopic analysis of samples that were stored in an inert atmosphere for extended periods of time. In addition, the calibration chart for the determination of water in asphalt is included in the first section. Also included here are supplementary data, presented in the form of figures, upon which some of the conclusions presented in Volume I, chapter 5, were, in part, based.

EXPERIMENTAL METHODS

Treatment of Asphalts with Water

The object of this study is to answer the following fundamental question. Does the incorporation of water into asphalt binders disproportionately produce different building materials from binders that were originally graded alike? To address this question three methods of incorporating water into the asphalts were evaluated. These methods included: (1) soaking the asphalt samples in a sealed container of water at room temperature (about 20°C/68°F), (2) soaking the asphalt samples in a sealed container of water at an elevated temperature (60°C/140°F), and (3) exposing the asphalt samples to a controlled humidity and temperature, ASTM method D 1412 [ASTM 1992]. For all series of experiments, a control experiment was conducted in which the water was removed from the container but all other variables were the same. Each sample for testing was formed into a pellet by pouring approximately 0.8 grams of asphalt into a silicone rubber mold that was about 19 mm in diameter (a penny was used to form the mold). This resulted in a pellet that was suitable for rheological analysis using 25 mm plates. The container used to evaluate methods 1 and 2 was a 500-mL canning jar. The jar was sealed with a rubber gasket and metal bail. To minimize the oxidation of the samples, the containers were purged with an inert gas (nitrogen or argon) or evacuated. Method 3 utilizes a vacuum desiccator. The samples were stored in the containers for known periods of time after which a sample was removed, and the sample, while still in the mold, was placed in a freezer for about 20 minutes. Freezing the sample was done to aid in handling the sample during the subsequent analyses. Because of the potential of losing water during the annealing process, all pellets were not annealed before rheological analysis. Rheological analyses were conducted using either a Rheometrics 605 mechanical spectrometer or a Bohlin dynamic shear rheometer. All data were obtained at 58°C (136°F) and 10 radians per second. Infrared analysis of the samples was conducted using a Perkin Elmer 983G infrared spectrophotometer. The level of oxidation was assessed by integrating the carbonyl peak at 1,700 cm^{-1} and the sulfoxide peak at 1,030 cm^{-1}. The concentration of the asphalt was 50 mg per 1 mL of carbon disulfide, and the spectrum was obtained using a matched set of 0.75-mm pathlength, sodium chloride cells. Artificial aging of the samples was conducted using the rolling thin film oven (RTFO) test (ASTM D 2872/AASHTO method T240) and AASHTO method PP1 using a pressure aging vessel (PAV).

Several methods were evaluated to determine the amount of water that was incorporated into the asphalt pellets. These included Karl Fischer titration, infrared spectroscopy in carbon tetrachloride [Petersen 1967], and reaction with 2,2-dimethoxypropane followed by infrared spectroscopy [Netzel et al. 1996; Critchfield and Bishop 1961]. The use of the latter procedure involving reaction of water with 2,2-dimethoxypropane followed by infrared spectroscopy resulted in the most reliable data. In this latter procedure, water reacts with 2,2-dimethoxypropane in the presence of an acid, methanesulfonic acid, to produce acetone and methanol. The intensity of the carbonyl peak in acetone is measured by infrared spectroscopy, and this value is compared to a calibration chart to obtain the percentage of water. As a result of the reaction one mole of water produces one mole of acetone. The analysis of a sample was conducted as follows. One-half of a gram of asphalt was dissolved in carbon tetrachloride (CCl_4). To this solution was added 0.5 mL of 2,2-dimethoxypropane and 1.0 mL of 0.2 N methanesulfonic acid in methanol. This solution was diluted to 100 mL with CCl_4 in a volumetric flask and allowed to stand with occasional shaking for about 15 minutes before analysis. The carbonyl peak at 1715 cm^{-1} resulting from the production of acetone was integrated. The reference blank contained the same quantities of reagents dissolved in CCl_4 except for the 0.5 grams of asphalt, and the spectrum was obtained using a 0.95 mm pathlength, sodium chloride cell. The reader is advised that the reaction is extremely efficient, and the reaction does not start until the methanesulfonic acid is added to the solution. The calibration chart used for unaged asphalts, based on AAG-1, is shown in figure 10-1. The correlation coefficient for the data is 0.9998 and is based on the amount of water in the asphalt.

To assess the impact of water during PAV aging, three RTFO-aged SHRP asphalts (AAD-1, AAG-1, and AAM-1) were PAV aged in the presence of water for different lengths of time and at different temperatures. As a control the asphalts were also aged for the same lengths of time and at the same temperatures with no water added to the aging vessel. Other than these modifications, the standard Superpave® PAV procedure was followed. The variables incorporated into the PAV-aging procedure are: temperatures of 60 and 80°C (140 and 176°F) and lengths of aging of 0, 6, 10, and 20 days. For those experiments that were conducted in the presence of water, 20 mL of deionized water was poured into a PAV pan, and the pan was placed in the aging vessel during the aging of the three asphalt samples. Rheological analyses were conducted using a Rheometrics 605 mechanical spectrometer. All data are reported at 60°C (140°F) and 10 radians per second. The amounts of carbonyl and sulfoxide were determined by infrared analysis, as described above, using a Perkin Elmer 983G infrared spectrophotometer.

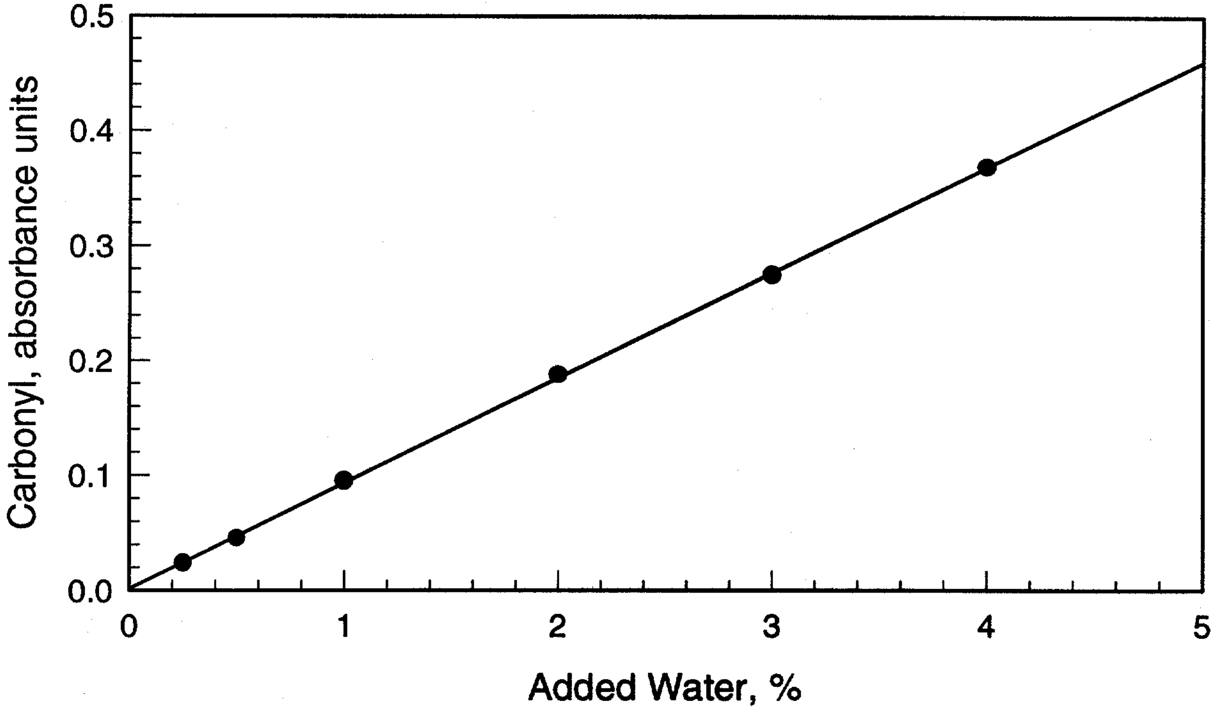


Figure 10-1. Calibration chart for water added to unaged asphalt AAG-1.

Infrared Reflectance Spectroscopy (ATR Experiments)

The investigation of the premise that asphalt molecules slowly migrate to and possibly orient themselves with respect to the aggregate surface was investigated using infrared reflectance spectroscopy. In this technique the infrared beam reflects off of the sample rather than traveling through the sample as in the more common absorption or transmission infrared spectroscopy. The depth of analysis of the sample is typically about 10 μm. For the investigation described here, a Bio-Rad FTS-45 Fourier transform infrared (FTIR) spectrometer was used for all analyses. A liquid vessel cell, model 68 obtained from Buck Scientific, was equipped with an attenuated total reflectance (ATR) crystal. The ATR crystal used with the liquid vessel cell was a zinc selenide (ZnSe) parallelogram with a 45° face angle and dimensions of 6 x 6 x 60 mm. When an analysis is being conducted the infrared beam enters the crystal perpendicular to the face, travels through the crystal penetrating the sample to a depth of about 10 μm, and then exits the crystal face to the detector. Win-IR software supplied by Bio-Rad Digilab was used to collect the spectra, and QuantBasic for GRAMS\386 obtained from Galactic Industries Corporation was used to analyze the spectra.

Prior to each use of the FTIR, the accessories in the sample chamber were removed and the alignment of the instrument was checked using a single-beam scan and a 100 percent transmission scan. The results of this instrument check were logged daily to ensure the FTIR was operating correctly.

The following procedure was used to clean the ZnSe crystal prior to loading with asphalt. It was soaked in toluene for 30 minutes, rinsed with dichloromethane, and wiped with lint free lens paper. To ensure the complete volatilization of the solvents used in cleaning, the crystal was swept with a heat gun. Teflon® sheeting was used as gasket material for both the end and the top plates of the liquid vessel cell. The liquid vessel cell was then assembled using the Teflon® gaskets to secure the crystal in place. The mirrors were adjusted to maximize the alignment of the infrared beam through the crystal. A background spectrum was recorded at this time and used throughout the experiment. All spectra were collected as single-beam scans with a resolution of 8 cm^{-1}, the aperture open, a gain of one, and the number of scans set at 128. The sample chamber was purged with nitrogen for 5 minutes before each spectrum was collected.

The liquid vessel cell was filled with dry asphalt as follows. The asphalt sample was heated at 150°C (302°F) for 40 minutes and then the hot asphalt was poured into the liquid vessel cell with the crystal in place. The top Teflon® gasket was put into place and the top plate was screwed securely to the sample cell. The asphalt samples were scanned while still hot and then allowed to cool to room temperature and scanned again. No differences were noted between these spectra. The sample cells were placed in an air-tight container and purged with argon before being stored at the various experimental temperatures. During analysis, the containers were removed from the oven and the cells were allowed to cool to room temperature under a blanket of argon. After infrared analysis the sample cells were replaced in the container under argon and returned to storage in the oven at the designated temperature.

At the end of the experiment, the top plate of the liquid vessel cell and the top Teflon® gasket were removed. The amount of the asphalt and appearance of the crystal were recorded.

(The appearance of the crystal was noted because the manufacturer did not guarantee its integrity at elevated temperatures and for extended periods of time. Fortunately, the integrity of the crystal was not affected by being in the presence of asphalt at elevated temperatures for extended periods of time.) While the asphalt was still warm, the bulk of the remaining asphalt was removed with a Teflon® coated spatula. A 50-mg sample of the asphalt was saved and dissolved in carbon disulfide for further infrared analysis. The crystal, still secure in the liquid vessel cell, was cleaned by rinsing in toluene until the solvent was colorless. The crystal/liquid vessel cell assembly was then transferred to a dichloromethane wash and rinsed until this solvent was also colorless. This washing process was continued until the recorded spectrum and the original background spectrum were identical.

To analyze the data, the spectra were first converted from single-beam scans to absorbance spectra by subtracting the background spectrum. The relative amount of carbonyls and sulfoxides was obtained by calculating the ratio of the peak height of the carbonyl at 1,700 cm^{-1} and the peak height of the sulfoxide at 1,030 cm^{-1} with the peak height of the alkyl stretch at 2,920 cm^{-1}. A QuantBasic® method to analyze the spectra was created for each of the three regions of interest. The baseline of the carbonyl region was drawn between 1,730 cm^{-1} and 1,602 cm^{-1}, with the maximum peak height measured in the region of 1,705 cm^{-1} to 1,695 cm^{-1}. The baseline of the sulfoxide region was drawn between 1,045 cm^{-1} and 1,020 cm^{-1}, with the maximum peak height measured in the region of 1,035 cm^{-1} to 1,025 cm^{-1}. The baseline of the alkyl region was drawn between 3,100 cm^{-1} and 2,700 cm^{-1}, with the maximum peak height measured in the region of 2,925 cm^{-1} to 2,916 cm^{-1}.

Since this was intended to be a preliminary investigation, the easiest method available, peak heights, was used for quantification of the carbonyl, sulfoxide, and alkane peaks. However, the accumulated data for all of the runs are stored in the memory of the computer, thus, if needed a different method of data calculation, for example comparing peak areas, could be done in the future.

SUMMARY

Several methods were evaluated with regard to the incorporation of water into asphalt. The method that was chosen involved the soaking of asphalt pellets in water at 60°C (140°F). The analyses of the pellets were conducted using standard rheological and infrared techniques. The determination of water in the pellets was conducted using a method that relies on the quantitative reaction of water with 2,2-dimethoxypropane. In addition to evaluating the effects of water on the rheological properties of asphalt, the migration of compounds to a surface was studied. Infrared reflectance spectroscopy was used to monitor the migration of carbonyl-containing compounds to a ZnSe crystal surface.

SUPPLEMENTARY DATA

The following figures are the supplementary information that was referred to in Volume I, chapter 5, in the section entitled "The Impact of Moisture on Asphalt Rheology and Aging."

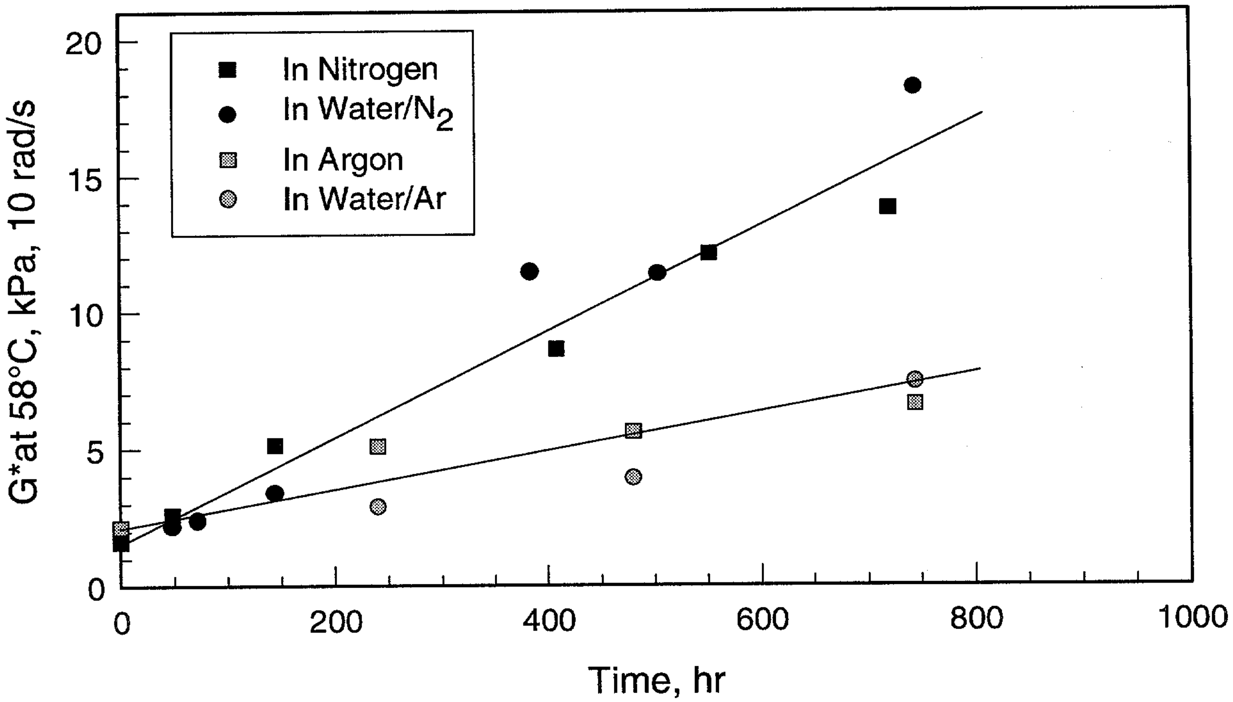


Figure 10-2. The impact of the environment at 60°C on G* of unaged AAD-1.

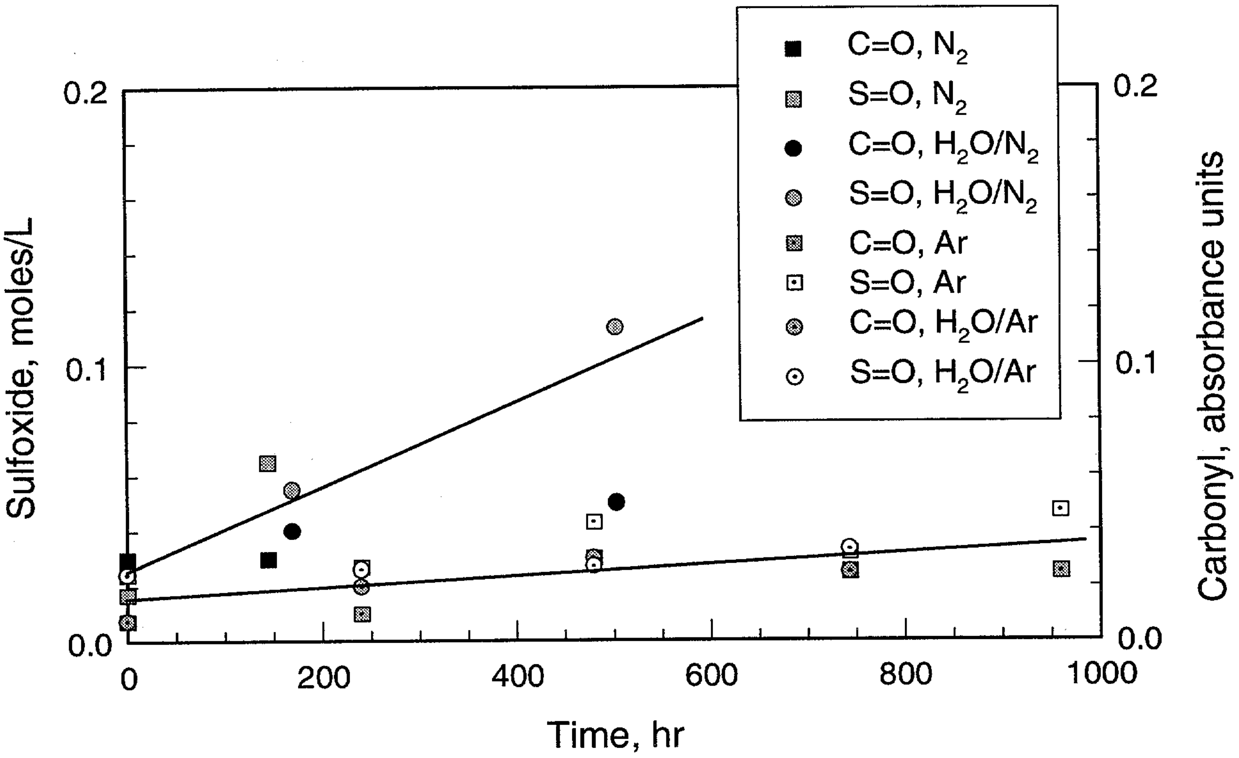


Figure 10-3. A plot showing the amount of each functional group in unaged AAD-1. All samples stored at 60°C.

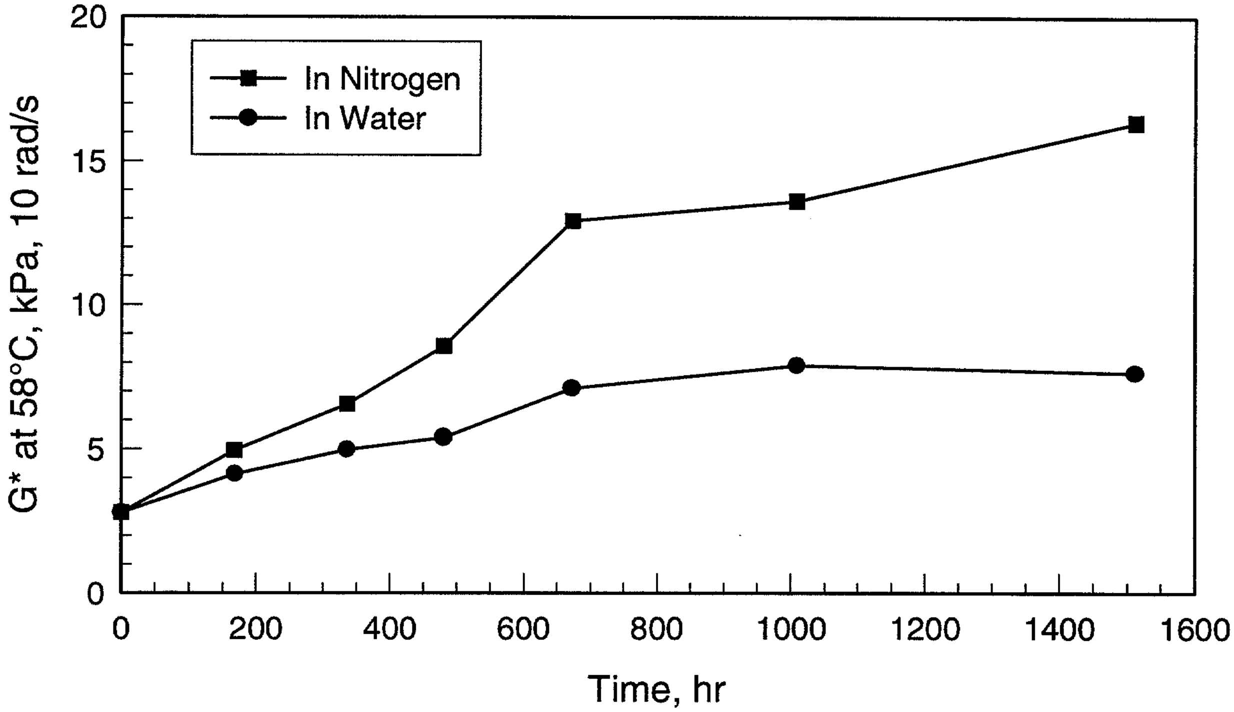


Figure 10-4. The impact of the environment at 60°C on G* of unaged AAG-1.

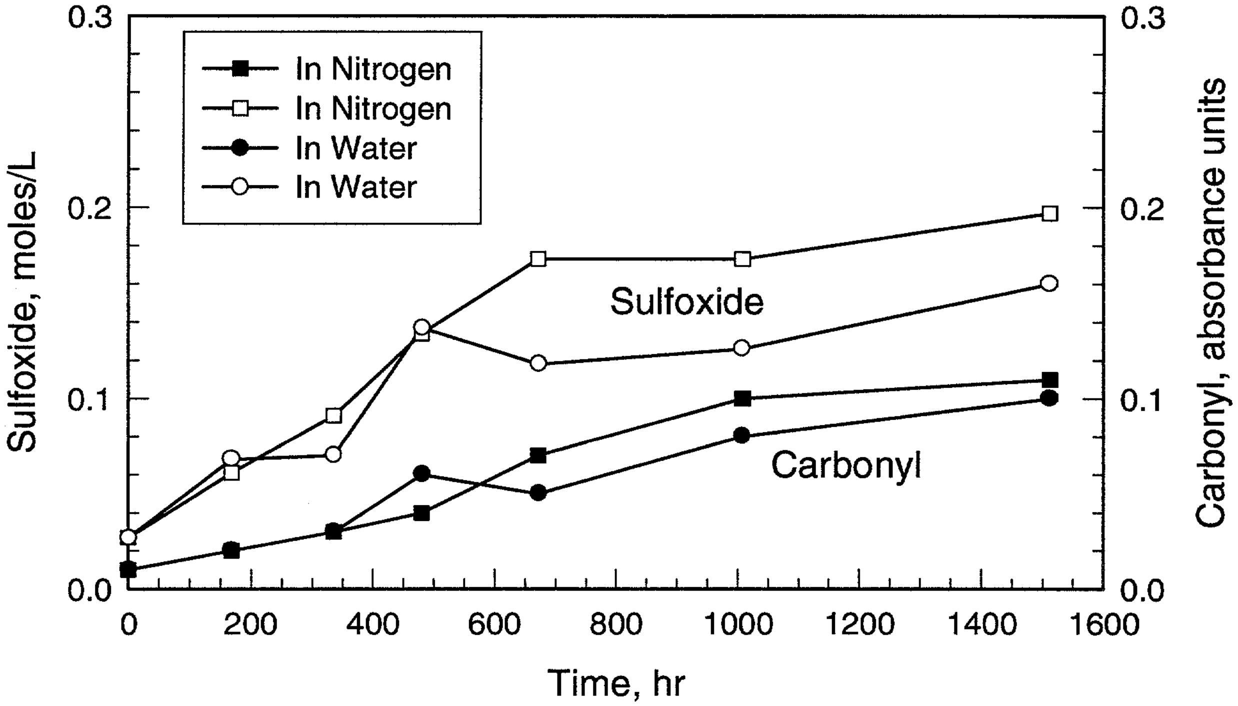


Figure 10-5. A plot showing the amount of each functional group in unaged AAG-1. All samples stored at 60°C.

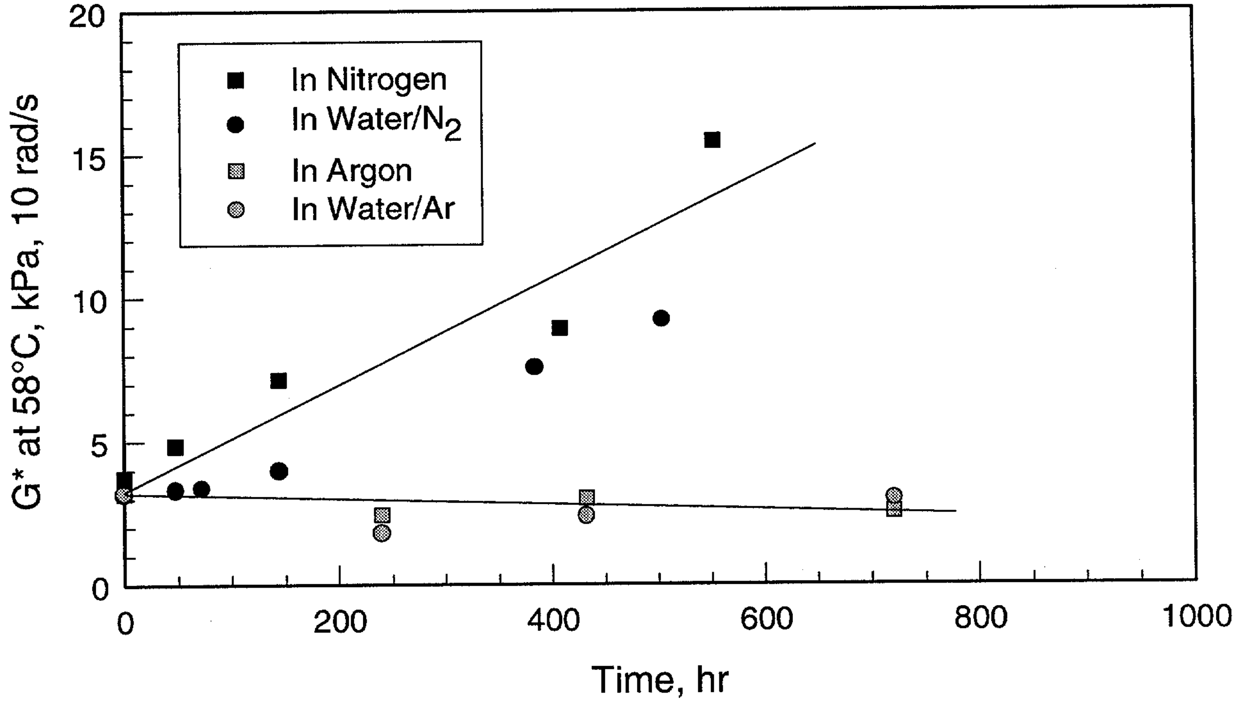


Figure 10-6. The impact of the environment at 60°C on G* of unaged AAM-1.

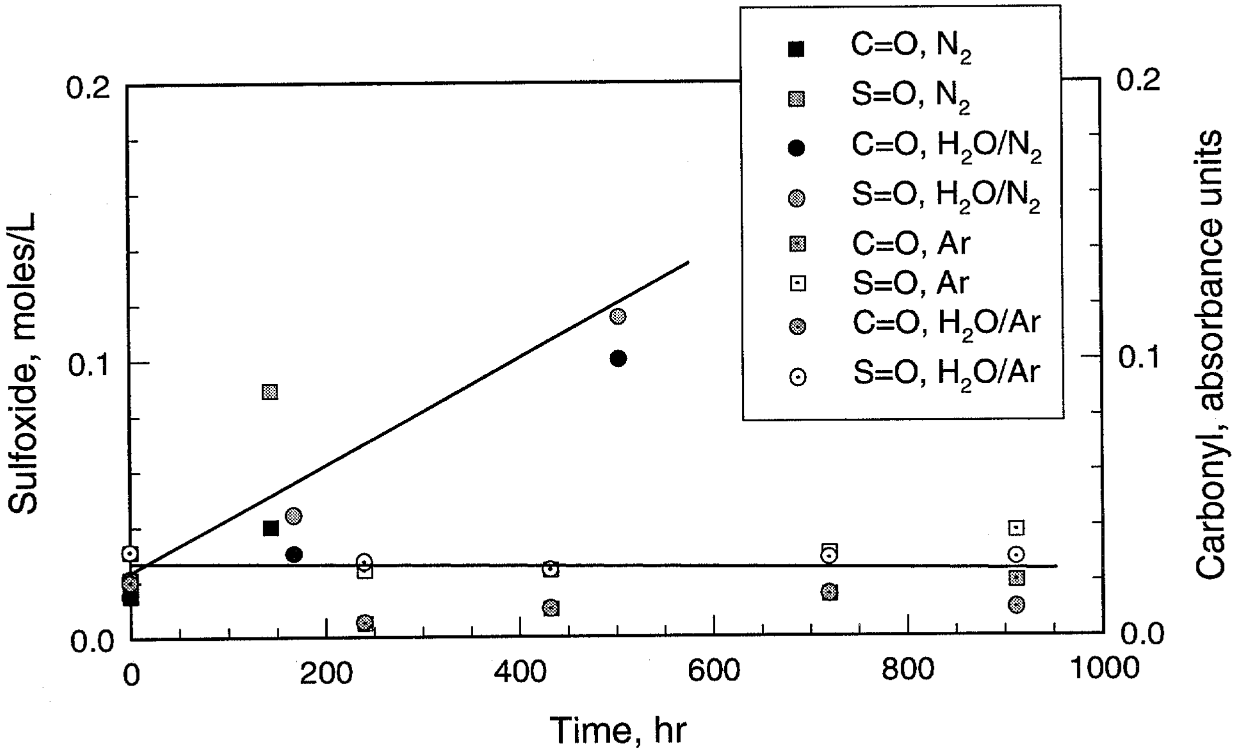


Figure 10-7. A plot showing the amount of each functional group in unaged AAM-1. All samples stored at 60°C.

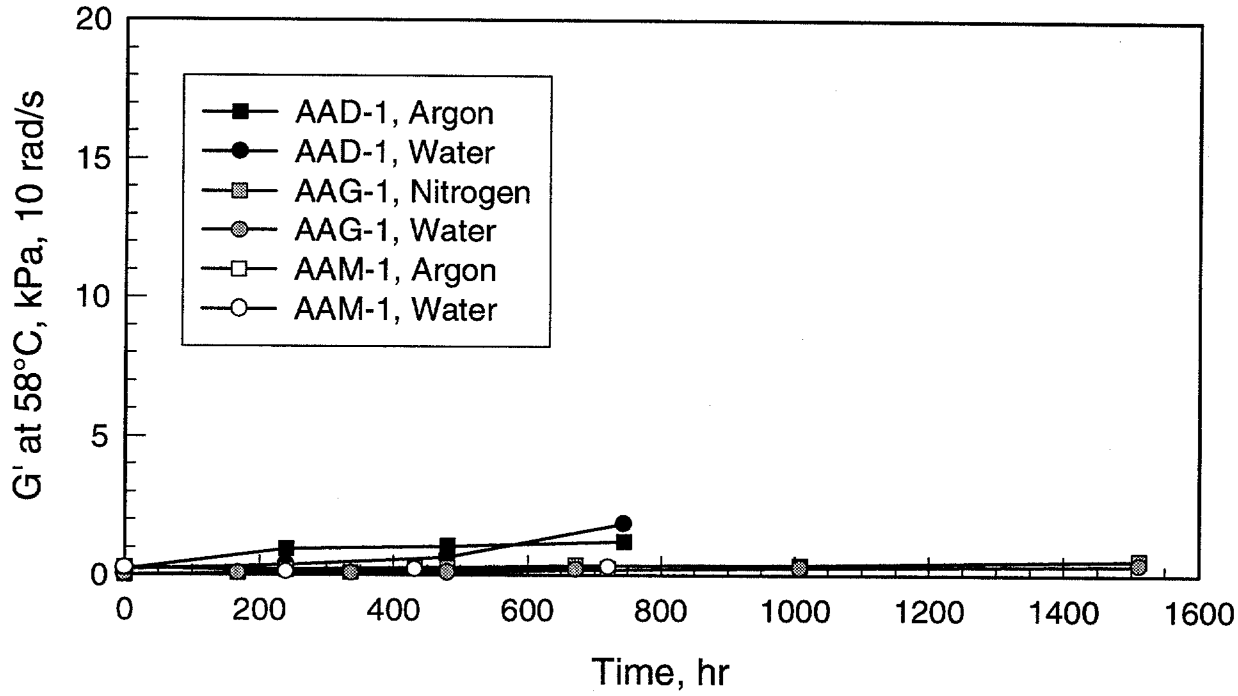


Figure 10-8. The impact of the environment at 60°C on G' of unaged AAD-1, AAG-1, and AAM-1.

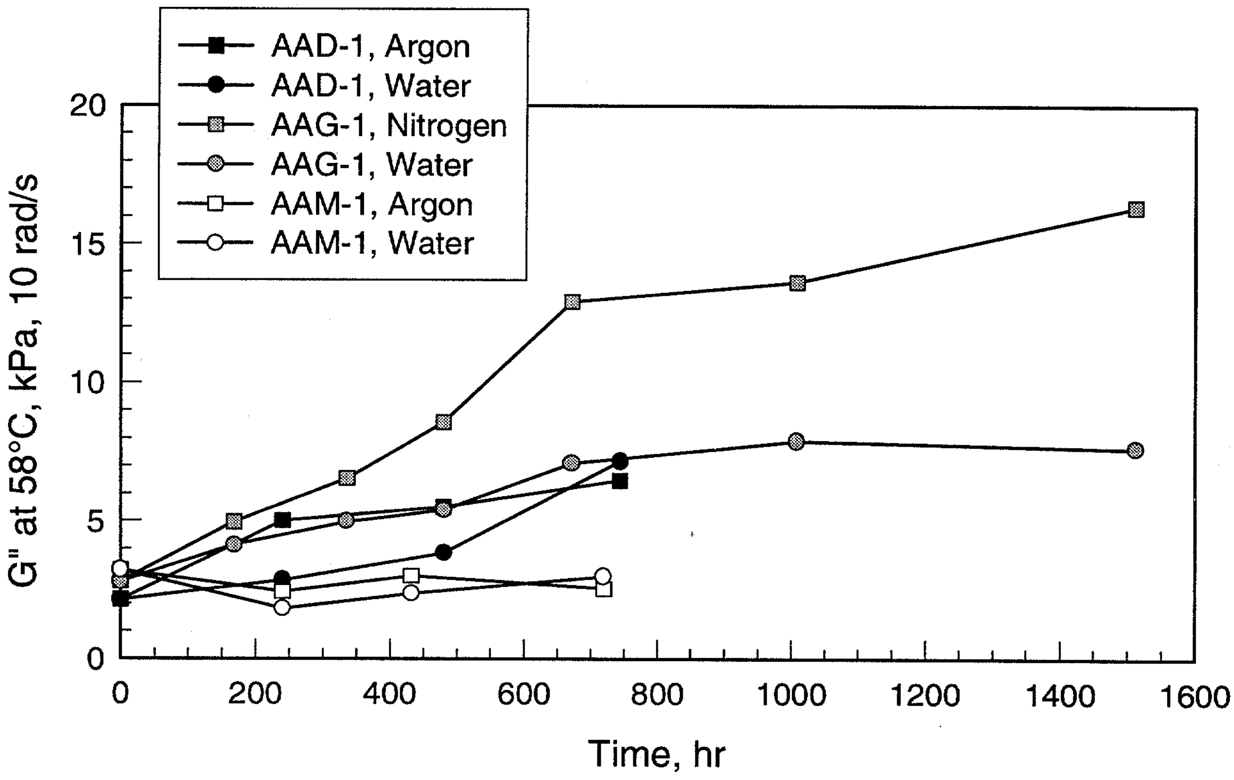


Figure 10-9. The impact of the environment at 60°C on G" of unaged AAD-1, AAG-1, and AAM-1.

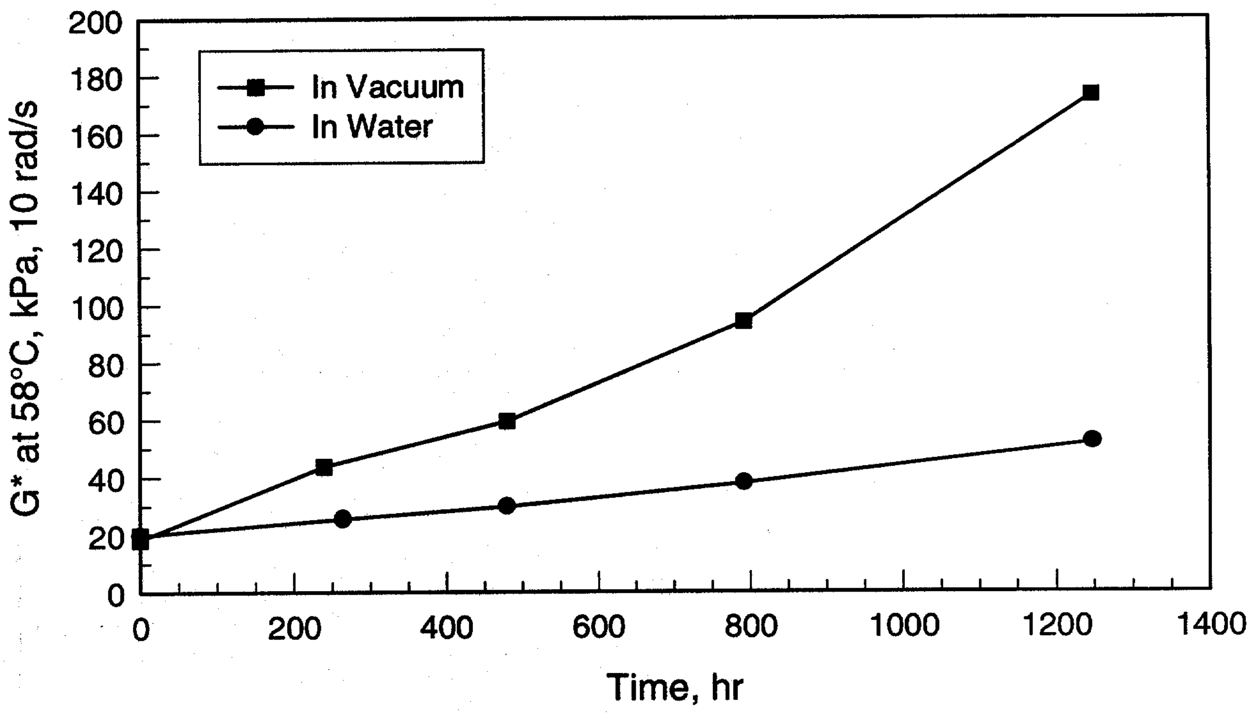


Figure 10-10. The impact of the environment at 60°C on G* of RTFO/PAV-aged AAD-1.

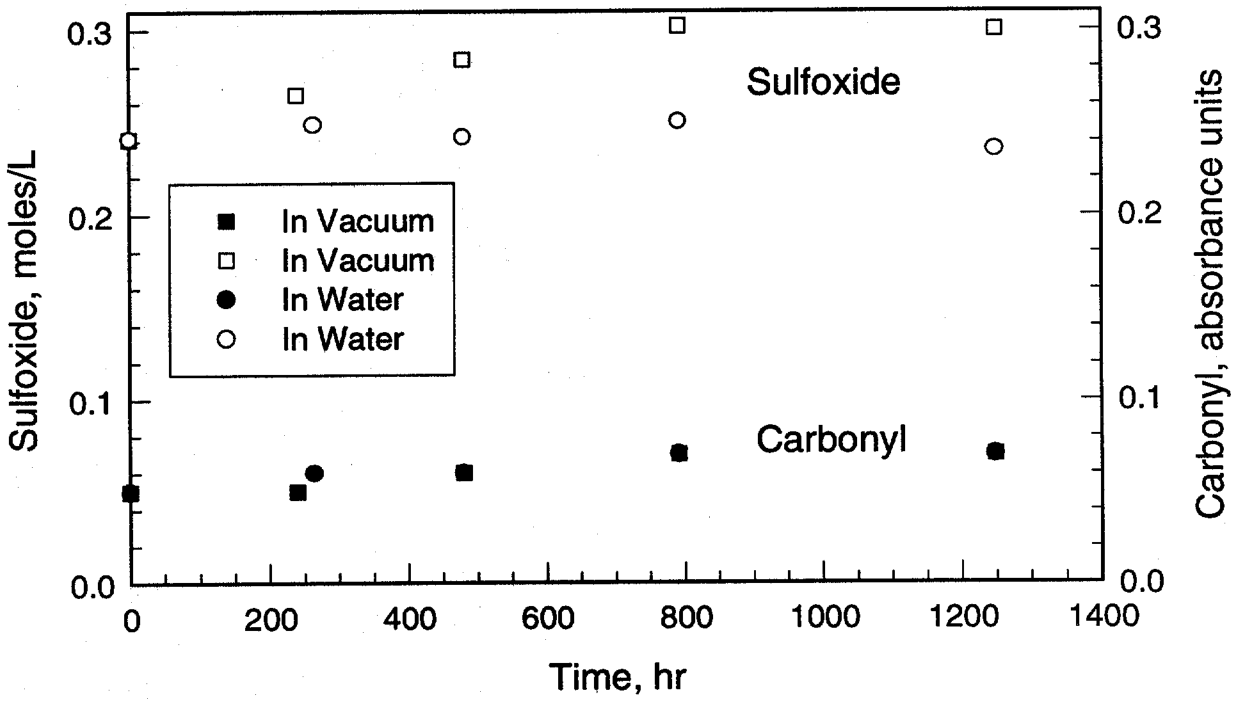


Figure 10-11. A plot showing the amount of each functional group in RTFO/PAV-aged AAD-1.
All samples stored at 60°C.

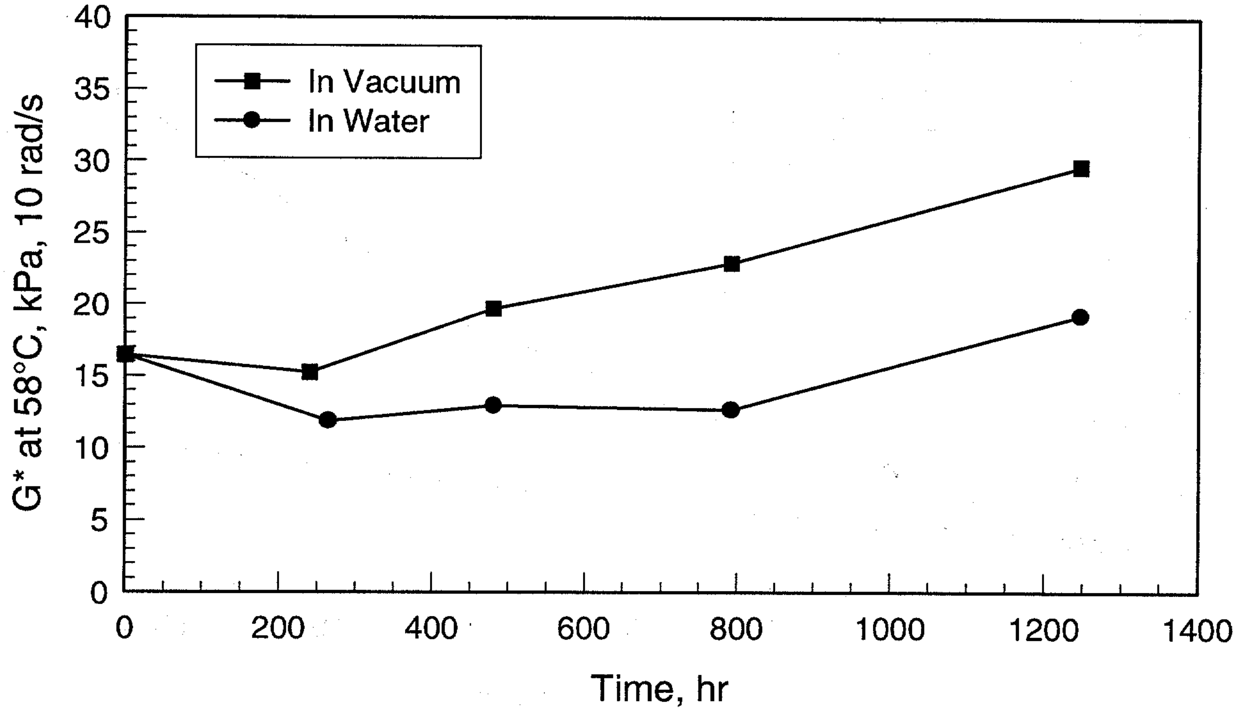


Figure 10-12. The impact of the environment at 60°C on G* of RTFO/PAV-aged AAG-1.

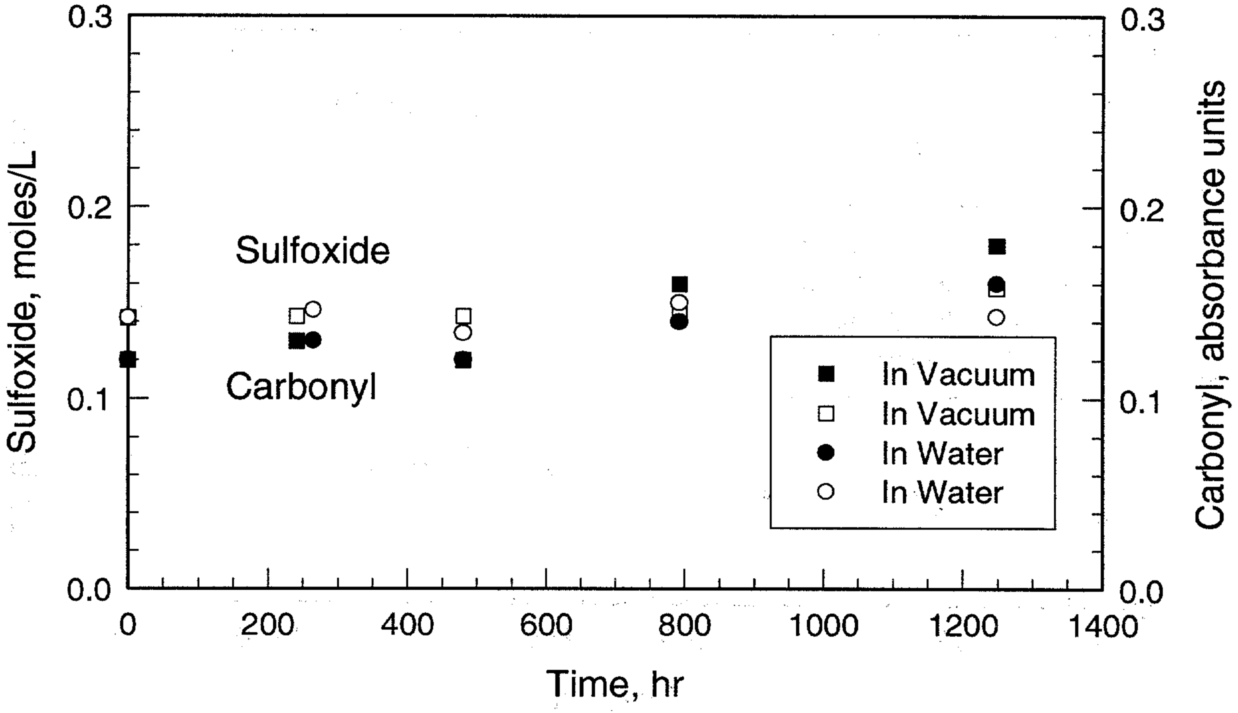


Figure 10-13. A plot showing the amount of each functional group in RTFO/PAV-aged AAG-1. All samples stored at 60°C.

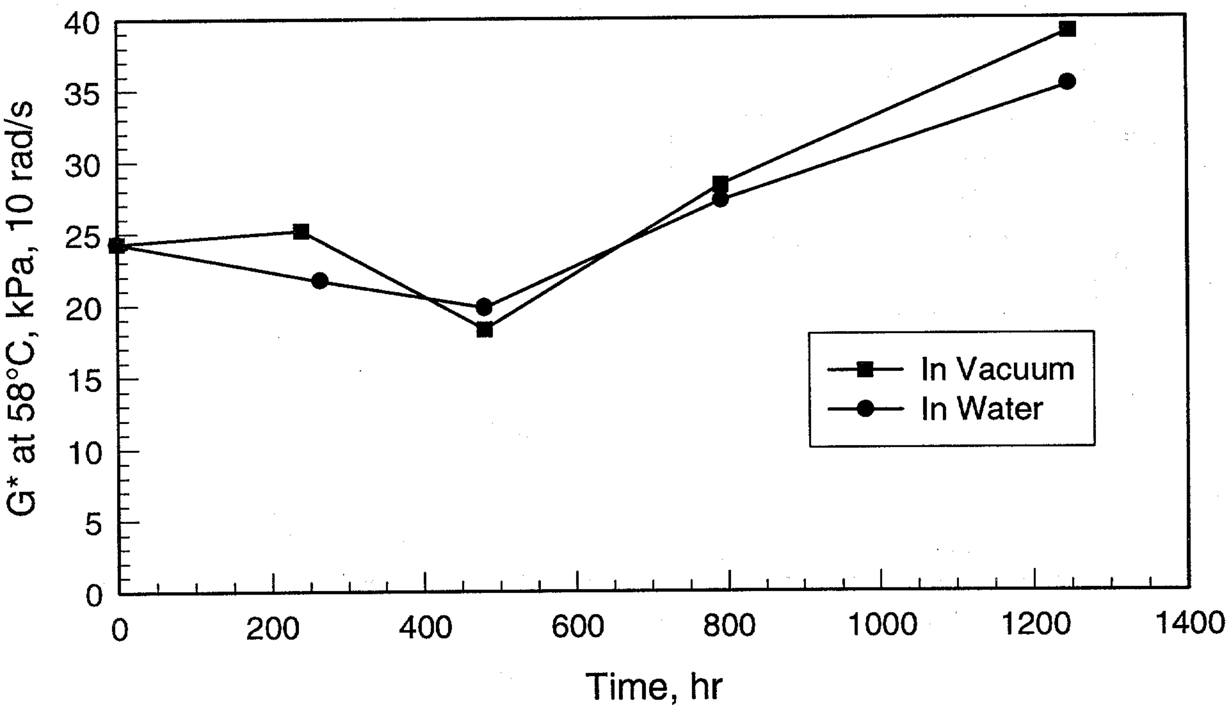


Figure 10-14. The impact of the environment at 60°C on G* of RTFO/PAV-aged AAM-1.

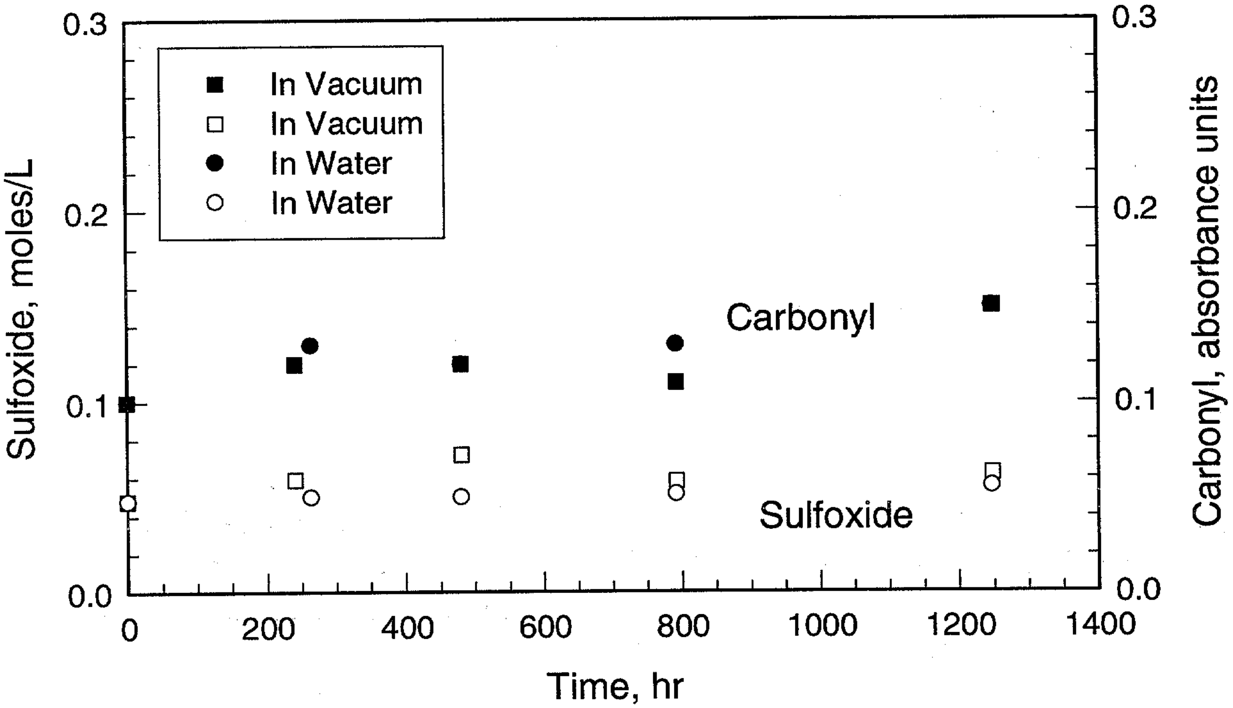


Figure 10-15. A plot showing the amount of each functional group in RTFO/PAV-aged AAM-1. All samples stored at 60°C.

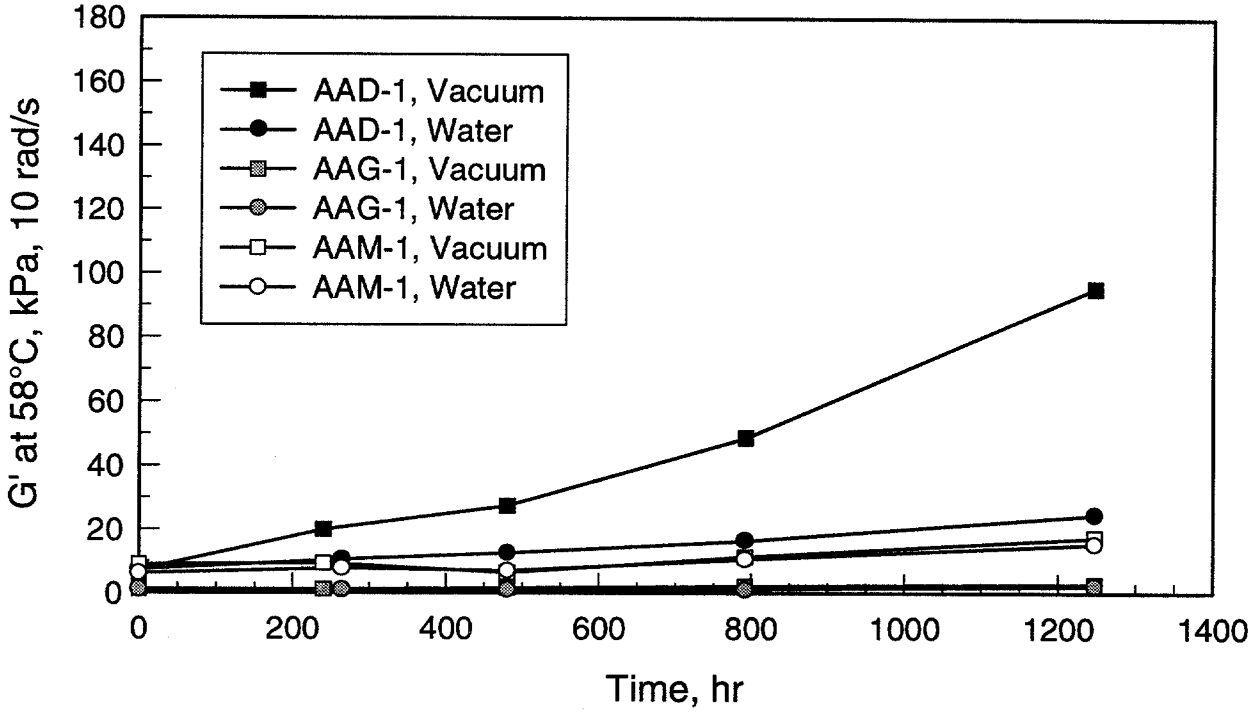


Figure 10-16. The impact of the environment at 60°C on G' of RTFO/PAV-aged AAD-1, AAG-1, and AAM-1.

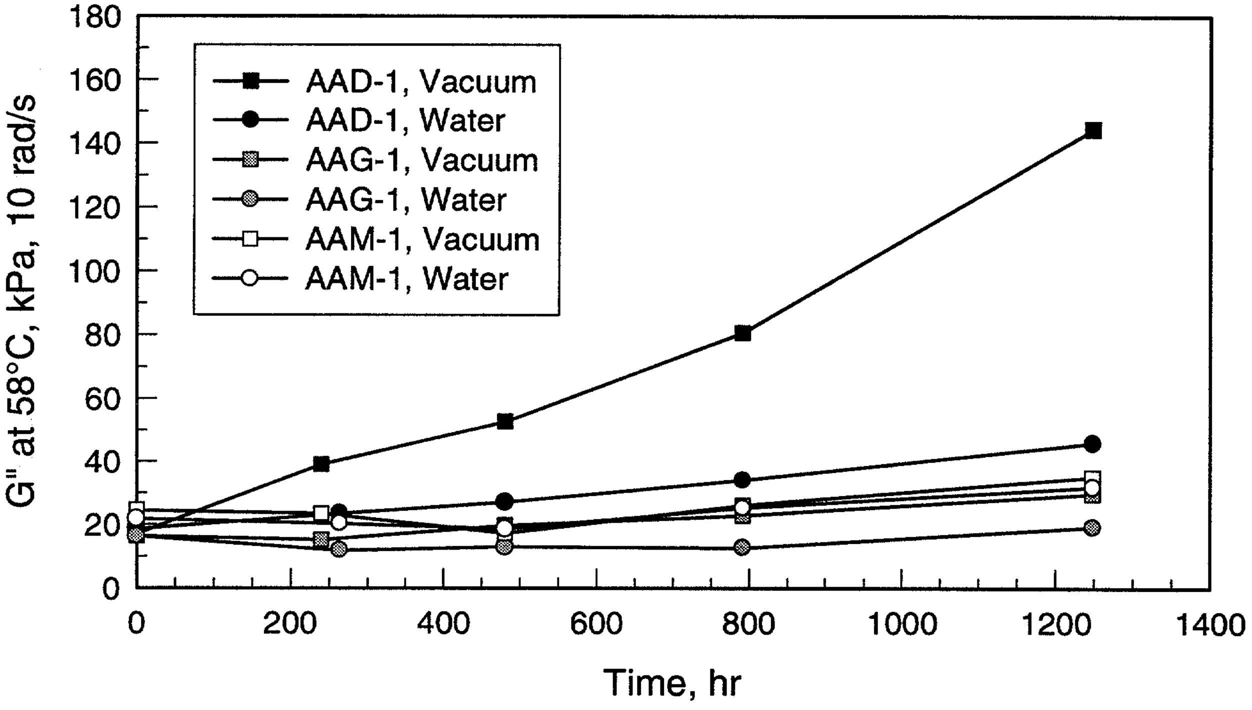


Figure 10-17. The impact of the environment at 60°C on G" of RTFO/PAV-aged AAD-1, AAG-1, and AAM-1.

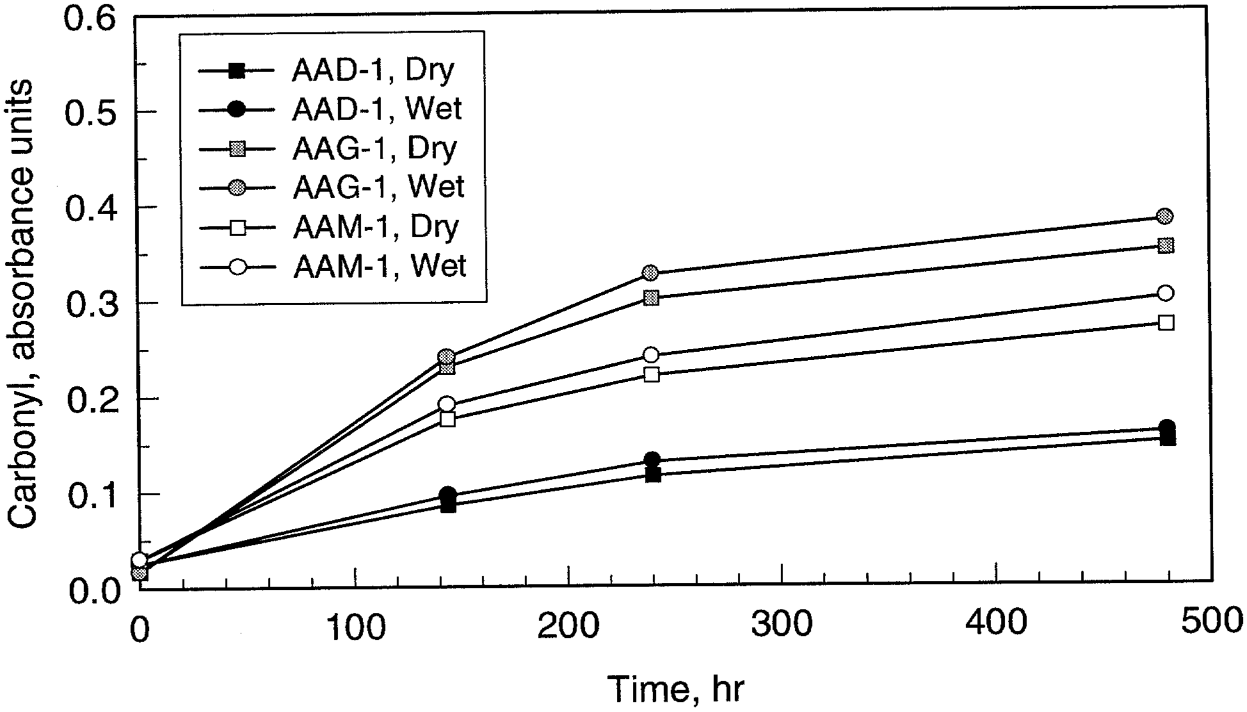


Figure 10-18. A plot showing the increase of carbonyl for RTFO-aged SHRP asphalts. All asphalts PAV aged at 80°C.

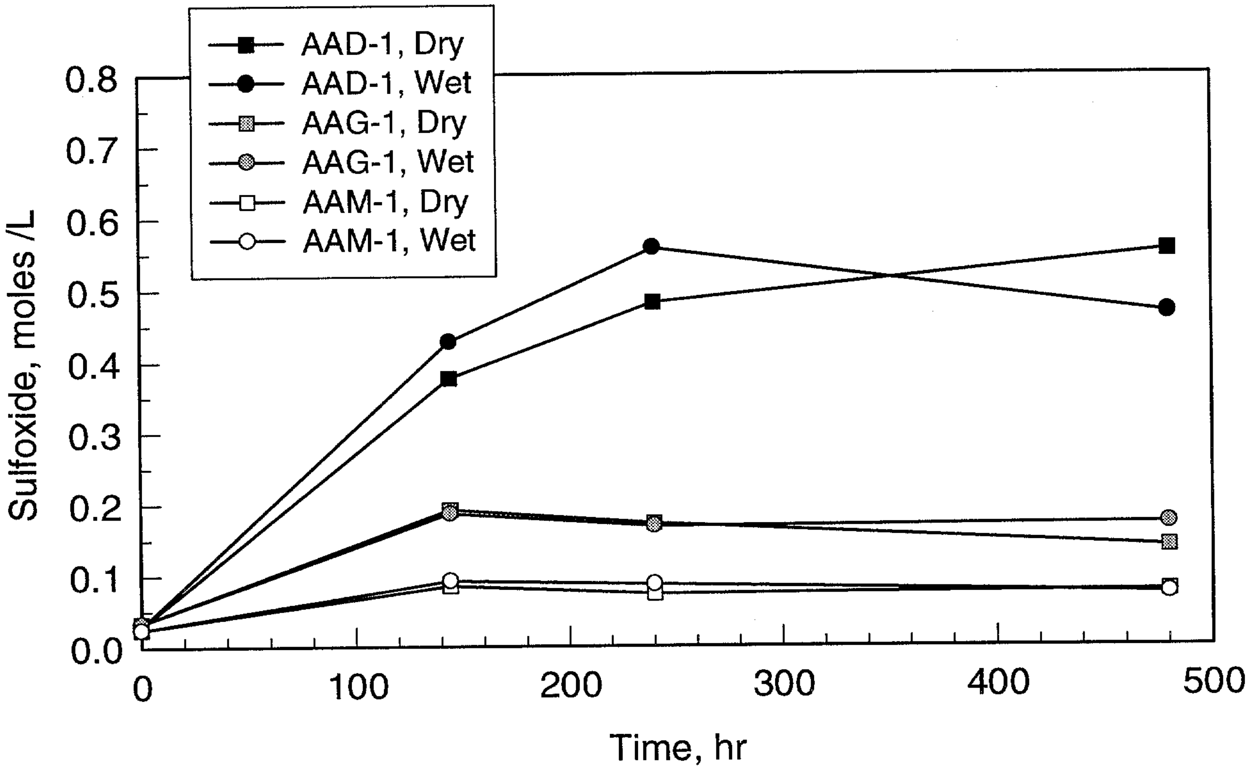


Figure 10-19. A plot showing the increase of sulfoxide for RTFO-aged SHRP asphalts. All asphalts PAV aged at 80°C.

MISCELLANEOUS STANDARD METHODS USED IN THIS PROJECT TO WHICH MODIFICATIONS WERE MADE OR WHICH ARE NOT FULLY DESCRIBED ELSEWHERE

METHOD 11. ION EXCHANGE CHROMATOGRAPHY USING AMBERLYST® AND AMBERLITE® RESINS

INTRODUCTION AND APPLICABILITY

During the Strategic Highway Research Program (SHRP), ion exchange chromatography (IEC) was used as a preparative technique to separate solutions of asphalts into various polar and non-polar fractions. In one procedure, solutions of asphalts are separated into a non-polar neutral fraction and three polar fractions: acids, bases and amphoterics. The relative amounts of these fractions were related to various asphalt properties [SHRP 1993a]. Thus, in addition to being a preparative method, IEC was used to "fingerprint" asphalts. The published method [SHRP 1994b] was modified to serve largely as a characterization procedure, and that modification is reported as method 5 in this volume. This was done because of the expensive material and time requirements inherent in the SHRP procedure.

For some studies, not all of the polar and non-polar components of asphalts generated by IEC are necessary. In such a case, a modified preparative procedure using less expensive resins and requiring less operator time may be used. The modified procedure is especially applicable to the isolation of non-polar neutral fractions from which waxes may subsequently be isolated. The disadvantage of the modified procedure described below is that it is not useful as a characterization method because there is not sufficient discrimination among polar fractions.

IEC can be used to separate relatively large (16.0 g in the method described in SHRP 1994b) samples of asphalt into several fractions. In a single separation of an asphalt by IEC, the fractions obtained are basic, amphoteric, neutral, and acidic. IEC utilizes the differences in the polarity of individual molecules to separate solutions of asphalt into chemically defined components. In the separation of asphalt into the four fractions listed above, a solution of an asphalt flows through a column packed with activated cation resin (see figure 5-2, this volume, for a flow sheet). Cation resins are small beads that have acidic active sites. These beads attract the molecules of the asphalt that contain basic functional groups. They also attract any amphoteric molecules of the asphalt. Amphoteric molecules contain acidic and basic functional groups. They will adhere to either cation or anion resins, whichever they encounter first. Since, in the separation method described here, they first come into contact with the cation resin, they will adhere to it, along with molecules containing only basic functional groups. The eluate from the cation column contains the neutral and acidic fractions of the asphalt. The base plus amphoteric fraction is retained on the cation resin.

The cation resin is then stripped by treatment with a compound more basic than any that are found in the asphalt. This strongly basic compound releases the basic and amphoteric materials of the asphalt from their bonds with the cation resin by a simple displacement reaction. Solvent is removed from these two combined fractions and they may then be separated from each other using an anion resin.

A solution of the neutral and acidic portion of the asphalt passes through a second column, this one containing activated anion resins. Anion resins are small beads with basic sites.

They will attract and bind any acidic molecules. The neutral molecules will pass through the column. The eluate from the second column consists of the neutral fraction and solvent. Removal of solvent (usually performed on a rotary evaporator) yields the neutral fraction, which comprises 50-60 percent of most asphalts.

The anion resin is stripped in an analogous manner to the cation resin. The acidic molecules are displaced from the resin with a compound that is more acidic than any component of an asphalt. This step of the process yields the acid fraction and solvents. After solvent removal, the acid fraction, a tacky substance comprising 5-15 percent of most asphalts, is obtained.

PROCEDURE

Apparatus

Equipment

500 mL wide mouthed flask
Trip scale, weighing ± 0.1 g
Balance, with accuracy to four places
Heating/magnetic stir plate
Magnetic stir bar
600 mm X 40 mm column with stopcock and fritted glass bottom
Glass wool
Berkshire sand
1,000 mL beaker
500 mL packing reservoir
Funnel
800 mL beaker
2 -1 L pear shaped heavy walled flasks
Rotary evaporator equipped with a water bath
Rotary evaporator equipped with an oil bath
2,000 mL Buchner funnel
Rubber tubing
2,000 mL vacuum flask
100 mL amber bottle
600 mm X 25 mm column with stopcock and built in 300 mL packing reservoir
100 mL round bottom flask
20 mL vial
Heat lamp

Reagents
Amberlyst® - 15 Cation Resin (Aldrich Chemical Co., 1001 W. St. Paul Avenue, Milwaukee, WI 53233)

Amberlite® - IRA 904 Anion Resin (Fluka Chemical Corp., 980 South 2nd Street, Ronkonkoma, NY 11779)
Cyclohexane (EM Sciences, P. O. Box 70, Gibbstown, NJ 08027)
Sodium Hydroxide (J. T. Baker Chemical Co., Phillipsburg, NJ 08865)
Hydrochloric Acid (J. T. Baker)
Methanol, 98.8% Reagent Grade (Aldrich Chemical Co.)
Toluene, HPLC Grade (Spectrum Chemical Co., 755 Jersey Avenue, New Brunswick, NJ 08901)
Isopropylamine, 99% (Aldrich Chemical Co.)

Setup, Sample Preparation, and Procedure

The first step in this method is sample preparation. A 500 mL wide mouthed flask is used for ease of handling as it is especially convenient for pouring the asphalt. This flask is tared on a balance with accuracy to four decimal places. The asphalt is warmed with a heat lamp, so that the asphalt will flow. Heating asphalt should be kept to a minimum as heating can cause the asphalt to oxidize. The flask is placed on a trip scale during pouring of the asphalt. When 25 ± 0.5 g asphalt has been transferred to the flask, pouring is discontinued. The asphalt is allowed to cool, and the flask and its contents are weighed on a balance and the weight is recorded to four decimal places. The weight of the flask is subtracted from the weight of the flask plus asphalt to determine the weight of the asphalt. Cyclohexane (200 mL) is then added to the flask. The flask is left covered overnight in a fume hood to allow the asphalt to dissolve. If the asphalt sample has not completely dissolved by the next morning it is placed on a heating/stir plate. It is warmed gently and stirred with a magnetic stir bar until it is dissolved. The sample is removed from the hot plate and the magnetic stir bar is removed. This completes the sample preparation.

The column should now be prepared. A small piece of glass wool is placed in the bottom of a large glass column (600 mm X 40 mm I.D., equipped with stopcock and fritted glass plate at the bottom) and is tamped down. Berkshire sand is poured on top of the glass wool. The top of the sand layer should be 5.0 cm above the glass wool. The sand and glass wool are added to prevent small resin particles from clogging the glass frit. Approximately 400 mL of dry Amberlyst® 15 strongly acidic macroreticular ion exchange resin (cation resin) are poured into a large beaker. Approximately 800 mL of deionized water is then poured over the resin beads. This causes an exothermic reaction. Heat and fumes are briefly produced. Therefore, this procedure should be performed in a fume hood. Protective gloves should be worn. The column is then fitted with a 500 mL packing reservoir. A funnel is placed on top of the packing reservoir. The aqueous slurry of resin beads is poured into the funnel. Deionized water should be used to rinse all resins from the beaker and into the column. A large beaker is placed under the column and the stopcock is opened. The water flows through the column, causing the resin beads to settle. Water is run through the column until the eluate from the column runs clear (approximately 1000 mL). At first, the eluant water is light brown in color.

The resin now needs to be activated. The resin is activated via a series of washes. The washes are performed by filling the packing reservoir with the appropriate solution while the stopcock of the column is closed. The stopcock is then opened and the solution flows through the column. The eluate is collected in a beaker and the solutions are disposed of appropriately. The resin bed should always be covered by a liquid to prevent the resins from drying out (this deactivates them). In addition, the uncovered anion resin reacts with atmospheric carbon dioxide. In most cases, the packing reservoir must be refilled several times to get the desired volume of each solution through the column. All solutions (the reagents listed below are common laboratory chemicals and may be purchased from a large number of vendors) should be prepared with deionized water. The first series of washes consists of acid/base and aqueous washes:

1. 1,500 mL 1 N sodium hydroxide (NaOH) solution
2. 700 mL deionized water
3. 1,500 mL 1 N hydrochloric acid (HCl)

4. 700 mL deionized water
5. 1,500 mL 1 N NaOH - when the last of this solution has been run through the column, but there is still solution covering the resins, the stopcock is closed for 5-10 minutes.
6. 700 mL deionized water
7. 1,500 mL 1 N HCl - after adding most of this solution, the stopcock is closed for 5-10 minutes as in step 5.
8. 1,500 mL water

The second set of washes consists of a series of organic solvent washes. Each solution is poured into the column, and after most has passed through, the stopcock is closed for 5-10 minutes.

9. 500 mL 50:50 methanol (MeOH):water
10. 500 mL 75:25 methanol:water
11. 1,000 mL methanol
12. 1,000 mL toluene
13. 2,000 mL cyclohexane

When the last of the cyclohexane has passed through the column, the resins have been activated. The column should be stoppered and capped until the sample is ready to be loaded. The column can be left overnight without the resins deactivating. If this is done, an additional 700 mL of cyclohexane should be run through the column before the sample is loaded onto the column.

The sample is loaded by pouring the dissolved asphalt sample through the funnel into the packing reservoir. The stopcock should be closed. The flask containing the sample should be rinsed with cyclohexane and the rinse poured into the funnel. This should be repeated until the rinse in the flask is clear. This is to ensure that all of the sample gets into the column for separation and is very important in terms of recovery of the sample. A 1-L, pear-shaped flask is placed under the column to collect the eluate. The stopcock is carefully opened to allow a slow drip to come from the column. The pear-shaped flask is removed and is replaced with a small graduated cylinder and, using a stopwatch, the flow rate is adjusted to 3 mL of eluate from the column per minute. The pear-shaped flask is returned to underneath the column. The sample is allowed to flow through the column until the liquid has reached a level that is approximately ½"

(1.27 cm) above the top of the resin bed. The stopcock is closed and the eluate in the pear-shaped flask is poured back into the reservoir. This eluate will be colored and, therefore, contains asphalt components. Nevertheless, these initial eluates are poured back onto the resin bed because it has been found that a better separation is achieved. The flask is rinsed with cyclohexane and the rinse also is poured into the reservoir. This is repeated until the rinse from the flask is clear. The flask is placed back under the column and the stopcock is slowly opened. The flow rate should be adjusted to a very slow drip, the best approximation of 3 mL/minute possible. The sample solution again flows through the column until the liquid level reaches approximately ½" (1.27 cm) above the top of the resin bed. The stopcock is closed and the flask is removed. The cyclohexane is removed from the eluate in the pear-shaped flask via rotary evaporation using a water bath. The bath temperature is set at approximately 80°C (176°F) and a vacuum of approximately -10 in (-25.4 cm) Hg is used. When the cyclohexane has been removed from the flask, the recovered cyclohexane is poured back onto the column to finish eluting the acids and neutral fractions through the column. The same pear-shaped flask is replaced under the column. The stopcock is opened and the cyclohexane is allowed to flow slowly through the column. This process is repeated until the eluate from the column is clear. When the eluate is clear, the stopcock is closed, making sure to leave a least ½" of solvent on top of the resin bed. The sample in the flask contains the base-free component, that is, the combined acid and neutral fractions. This sample should be reduced via rotary evaporation to an approximate volume of 200 mL. This sample will be further separated using an anion column. The base plus amphoteric materials remain adsorbed on the cation resin.

The base plus amphoteric fractions must be desorbed from the cation resin. The resin is transferred to a 2,000 mL Buchner funnel. This is accomplished by placing the funnel in a large beaker and then inverting the column over the funnel. Rubber tubing is attached to the end of the column and air is gently forced through the tubing and the column. This causes the resin to slide out into the funnel. The funnel is then placed on top of a 2,000 mL suction flask. Then, 1 liter of toluene is poured onto the resins and the filtrate, which is black, is collected in the suction flask. The filtrate is transferred to a pear-shaped flask and the toluene is removed via rotary evaporation (approximately 80°C (176°F), approximately -15 in (-38 cm) Hg). The recovered toluene is poured back over the resins. This procedure is repeated until the filtrate reaches a constant light brown color. The toluene is then properly disposed of or, usually, the toluene is redistilled and reused. Then, 1 liter of a 54:38:8 solution of toluene:methanol:isopropyl amine is prepared. This solution is poured over the cation resin and is collected in the vacuum flask. The filtrate, which is black, is transferred to the same pear-shaped flask that was previously used. The solvent is removed via rotary evaporation with the water temperature at 80°C (176°F) and the vacuum is started at approximately -5 in (-12.7 cm) Hg and is gradually increased to approximately -15 in (-38 cm) Hg. The vacuum must be very slowly and carefully reduced as the methanol and isopropyl amine vaporize at a much lower vacuum than toluene. The toluene also has a tendency to boil over in the rotary evaporator, a phenomenon known as "bumping." Lowering the vacuum too quickly can easily cause this sample to bump. Once the solvent is removed, it is poured back over the resins. It is recollected, re-evaporated and again pored over the resins. This process is repeated until the eluate from the resins is an unchanging light brown color. When this constant color is attained, the solvent is removed one final time and is properly disposed of. Approximately 800 mL of toluene is then poured over the cation resin. The filtrate, which has again darkened, is collected in the same vacuum flask and transferred to the same pear-shaped flask. The toluene is removed via rotary evaporation with the water temperature at approximately 80°C (176°F) and a vacuum of approximately -15 in (-38 cm) in Hg. The reclaimed toluene is poured back over the resin. The filtrate is collected, transferred to the pear-shaped flask, and the solvent is again removed. This process is repeated until the filtrate is an unchanging light brown color. When this constant color has been achieved the resins are allowed to dry and are then disposed of. A container (usually a 100 mL amber bottle) is labeled and weighed. The filtrate is transferred to this container with a pipette and is rinsed in with toluene (it may be necessary to first reduce the volume via rotary evaporation). The container and sample are placed on a nitrogen evaporator overnight. The sample is then placed on a rotary evaporator equipped with boiling water (100°C; 212°F) at full vacuum for 1 hour. The sample is then transferred to a rotary evaporator equipped with a hot oil bath (130°C; 199.4°F) at full vacuum for 1 hour. The sample usually puffs up, taking on the appearance of a meringue. It is extremely difficult to remove all the solvent from this fraction. Additional time on the oil rotary evaporator is often required. The sample is then cooled and weighed. The weight of the empty container is subtracted from the weight of the container plus the sample to determine the weight of the recovered sample. This weight is divided by the original weight of the asphalt that was separated to determine the percent of the asphalt that is basic and amphoteric. The basic and amphoteric sample preparation is now complete.

The neutral and acid fractions can now be separated. The cyclohexane eluate from the cation column contains the sample and it is already in solution in the appropriate solvent.

A small piece of glass wool is placed in the bottom of a small column (600 mm X 25 mm), equipped with a packing reservoir, and is tamped down. Approximately 2 inches (5 cm) of Berkshire sand is poured through a funnel placed on top of the column.

Approximately 200 mL of Amberlite® IRA 904 ion exchange strongly basic resin beads (anion resin) are mixed in a large beaker with approximately 600 mL of deionized water. The stopcock of the column is closed and the resin/water mixture is poured into the column. The resin is completely rinsed into the column with additional water. A large beaker is placed under the column, the stopcock is opened, and the resin packs as the water flows from the column. The stopcock is closed when the water level is about 2 inches above the top of the resin bed and the column should be approximately 2/3 full with resin. The resin is now ready to be activated. The resin is activated via a series of acid/base washes using deionized water. The resin should always be covered by a liquid to prevent deactivation. All solutions should be poured through the funnel into the packing reservoir. The solutions are allowed to flow through the column and are collected in a beaker under the column and are then properly disposed of.

The acid/base aqueous washes:

1. 500 mL 1N HCl
2. 200 mL deionized water
3. 500 mL 1 N NaOH solution
4. 200 mL deionized water

5. 500 mL 1 N HCl - when the level of this solvent has reached a level of approximately ½" above the level of the resins, the stopcock is closed for 5-10 minutes.
6. 200 mL deionized water
7. 500 mL 1 N NaOH solution - after this solution is mostly through the column, the stopcock is closed for 5-10 minutes as described above.
8. 500 mL deionized water

Organic washes: after each one is mostly through the column, the stopcock is closed for 5-10 minutes as described above.

9. 100 mL 50:50 methanol:water
10. 100 mL 75:25 methanol:water
11. 200 mL methanol
12. 200 mL toluene
13. 400 mL cyclohexane

The resin in the column is now activated. The sample must be run the same day as the activation because the resins will deactivate if left overnight. The sample, which is the eluate from the cation column, is poured onto the column. The flask is rinsed with cyclohexane and the rinse is poured onto the column. This is repeated until the rinse from the flask is clear. A 1-L, pear-shaped flask is placed under the column. The stopcock is opened to allow a slow drip of liquid from the column. The pear-shaped flask is then replaced with a 10 mL graduated cylinder and, using a stopwatch, the flow rate is adjusted to 2 mL/minute. When this has been achieved, the pear-shaped flask is put back under the column. The sample solution is allowed to flow through the column until the sample solution level is approximately ½" (1.27 cm) above the top of the resin bed. The stopcock is closed and the eluate collected in the flask is poured back onto the column. The pear-shaped flask is rinsed with cyclohexane and is poured into the funnel. This is repeated until the rinse in the flask is clear. The stopcock is reopened to allow a drip rate approximating that determined previously. The sample solution is allowed to flow through the column until the liquid level is approximately ½" (1.27 cm) above the top of the resin bed. The column is stoppered and the flask is removed. The cyclohexane is removed via rotary evaporation, the water temperature is approximately 80°C (176°F) with a vacuum of approximately -10 in (-25.4 cm) Hg. The recovered cyclohexane is poured onto the column and is allowed to percolate through as before. The eluate is collected in the same flask. This is repeated until the eluate from the column is clear. The eluate contains the neutral fraction and the acid component is retained on the resins. The solution containing the neutral fraction is transferred to a labeled and weighed 100 mL round bottomed flask. The sample is completely divested of solvent via rotary evaporation as previously described. The sample is cooled and weighed and the weight of the flask is subtracted from the weight of the sample plus flask to determine the weight of the neutral fraction. The weight of the sample is divided by the original weight of the asphalt separated to determine the percentage of the asphalt that is recovered as the neutral fraction.

The acid fraction must be stripped from the resins. A 500 mL solution of 60:40 toluene:methanol is prepared. Carbon dioxide is bubbled through this solution for 15 minutes to acidify the solution, which is then poured onto the column. A pear-shaped flask is placed under the column and the stopcock is opened so that the solution drips slowly from the column. When the solution level is approximately ½" (1.27 cm) above the top of the resin bed, the stopcock is closed and the column is stoppered. The pear-shaped flask is attached to a rotary evaporator and is immersed in a water bath. The bath temperature should be approximately 80°C (176°F). At the beginning of this process of solvent removal, a slightly reduced pressure is applied. As solvent is removed from the flask, a progressively stronger vacuum is applied. After most solvent has been removed, the pressure should be approximately -15 in" (-38 cm) Hg. The recovered solution is poured back onto the column. The stopper is removed from the column, the stopcock is reopened, and more solution is collected. This is repeated until the eluate from the column is clear. When the eluate is clear, all of the solution is allowed to drip from the column as the resins no longer need to be covered by liquid. The solution containing the acid fraction is reduced in volume via rotary evaporation. The sample is then transferred to a labeled and weighed container (20 mL vial). The sample is placed on the nitrogen evaporator overnight and is then completely dried via rotary evaporation as previously described. The flask containing the sample is cooled and weighed and the weight of the flask is subtracted from the weight of the sample plus the flask to determine the weight of the acid sample. The weight of the sample is divided by the weight of the original amount of asphalt separated to determine the percent of the whole asphalt that comprises the acid fraction.

Data Calculation and Precision

Only weights of IEC fractions are recorded. Reproducibility is within a few mass percent for the various fractions. Since the method is purely preparative and only used to generate samples, this is not a serious disadvantage.

SUMMARY

A preparative IEC method using less expensive materials and taking less time than the published SHRP method was developed. The method is useful for generating neutral and possibly some polar fractions for other studies. It is not recommended for characterization studies.

METHOD 12. PRECIPITATION OF WAXES FROM NEUTRAL FRACTIONS OBTAINED BY ION EXCHANGE CHROMATOGRAPHY OF ASPHALTS

INTRODUCTION AND APPLICABILITY

The procedure outlined below describes the precipitation of waxes from neutral fractions obtained by ion exchange chromatography (IEC) of asphalts [SHRP 1994d]. Waxes are long-chain saturated hydrocarbons that are fairly abundant in some asphalts. Recently, it has been shown that waxes greatly influence asphalt physical properties (Volume I, chapter 3). Thus, a method for isolation of waxes from asphalts so that the waxes can be subjected to various investigations was developed in this program. Sufficiently pure samples of waxes cannot be obtained directly from asphalts by solvent precipitation due to co-precipitation of asphaltenes.

PROCEDURE

Apparatus

<u>Equipment</u>

100 mL round-bottom flask
trip scale (balance), capacity: 300 g, precision: 4-place
250 mL volumetric flask
5 mL Hamilton syringe
250 mL 10 - 20 μm fritted glass funnel (ACE Glass) with cooling jacket
Two 500 mL vacuum flasks
Two 20 mL containers
Rotary evaporator with a water bath
Rotary evaporator with an oil bath
Nitrogen evaporator (solvent evaporation under nitrogen flow)

<u>Reagents</u>

Toluene, spectrophotometry grade (EM Sciences, P. O. Box 70, Gibbstown, NJ 08027)
Methyl ethyl ketone (MEK), ACS grade (J. T. Baker, Phillipsburg, NJ 08865)

Setup, Sample Preparation, and Procedure

A 100 mL round-bottom flask is taped, labeled, and weighed with the weight recorded to four decimal places. A sample of the IEC neutral fraction of the asphalt to be dewaxed is heated and the sample is poured into the round-bottom flask. A trip scale is used during pouring to make sure that no more than 5 grams[1] of sample is transferred into the round-bottom flask. The sample is allowed to cool and the round-bottom flask is weighed with the weight recorded to four decimal places. The weight of the flask is subtracted from the weight of the flask plus sample to determine the weight of the sample. Then, 10 mL of toluene is added to the flask,[2] the flask is capped, and is allowed to sit overnight.

The dissolved sample is transferred to a 250 mL volumetric flask using a 5 mL Hamilton syringe. Toluene is used to rinse the sample residue from the round-bottom flask and the syringe into the volumetric flask. The amount of rinse toluene used is carefully controlled. The total amount of toluene used is in the ratio of 3.75 mL toluene for each 1 gram of sample. The total amount of toluene is determined by this ratio, the amount used to dissolve the sample is subtracted from the total, and the remainder is used to transfer the sample. Methyl ethyl ketone (2-butanone) is then added to the volumetric flask in a ratio of 11.25 mL MEK for each 1 gram of sample. The flask is then placed in a methanol/ice bath (approximately -25°C [-13°F]) for 1 hour. The sample is then poured into a 250 mL 10 - 20 μm fritted glass vacuum funnel connected to a circulating cold water bath (approximately 0°C [32°F]), resting on a 500 mL vacuum flask. The filter funnel has an inlet and outlet in its outer wall so that the cooling solution can circulate between the inner and outer walls of the funnel. The waxes adhere to the filter plate while the dewaxed material in solution passes through. Vacuum is applied. MEK (25 mL) is added to the volumetric flask. The flask is placed in the methanol/ice bath for 10 minutes. The cold MEK is poured onto the filter. This is repeated with two additional 25 mL washes of MEK. When the last portion of MEK has completely flowed through the filter, the vacuum is shut off and the collection flask is replaced with a clean one. The circulating cold water bath is shut off. The volumetric flask is rinsed with toluene to remove any wax crystals adhering to the glass, and the toluene is poured onto the filter. This dissolves the waxes and causes the wax solution to flow through the filter plate. Vacuum can be applied and the toluene can be warmed to expedite the process. Toluene is added until the filtrate from the filter is clear. The wax and dewaxed solutions are transferred to labeled and weighed 20 mL containers (the volume of the solutions is reduced via rotary evaporation, if necessary). The samples are placed on a nitrogen evaporator overnight. The samples are then completely divested of solvent via rotary evaporation. First the samples are placed on a rotary evaporation equipped with a boiling water bath (100°C [212°F]) at full vacuum for 1 hour. The samples are then transferred to a rotary evaporator equipped with a hot oil bath (130°C [266°F]) at full vacuum for 1 hour. The samples are cooled and weighed. The percent recovery, percent waxes, and percentage of dewaxed material can then be determined.

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[1] This experiment has been carefully designed so that the equipment called for can accurately and precisely handle weights of up to 5 grams of starting material. The procedure could be scaled up but it would require reworking of all equipment specifications.

[2] If using less than 4 grams of starting material, add proportionally less than 10 mL of toluene.

Data Calculation and Precision

Only weights of waxes and dewaxed materials are recorded. The procedure is preparative, not quantitative.

SUMMARY

A method for isolating waxes from IEC neutral fractions was developed. The neutral fractions are dissolved in toluene, and the solution is treated with methylethyl ketone. This mixture is chilled, and the precipitated waxes are recovered by filtration. The waxes are sufficiently pure for studies of thermal and rheological properties.

METHOD 13. A PENETRATION TESTER FOR ASPHALT MASTICS

ABSTRACT

An asphalt mastic is a mixture of an asphalt binder and an aggregate filler. However, mastics have widely variable chemistry and hence it is logical to assume that variations in filler composition with any given asphalt or variations in asphalt composition with any given filler will result in variability in the physical properties of the mastic. Fine fillers have large surface areas compared with larger aggregates, so the interactions between asphalt and mineral (filler) will be large. The purpose of this study is to determine the magnitude of variability of physical properties among mastics that are prepared from aggregates and asphalts of the same grade but that have very different compositions. The adhesion of asphalt to filler develops mechanical strength by chemically interacting at the interface, but is likely to vary with composition of both the filler and the asphalt. To understand the roles of a binder and a fine filler in a mastic, the interfacial adhesion strength must be related to the chemistry of the two materials. Determination of the variability necessitates measurement of overall interfacial strength in the mastic. For this purpose, a penetration method was devised to measure the global mechanical strengths of mastics.

INTRODUCTION AND APPLICABILITY

A measure of the stress required to maintain a constant rate of penetration with a tool and sample of fixed geometry was selected as the method to differentiate among mastics. Further, all comparable data sets had constant asphalt to aggregate weight ratios, the same filler size (by screen), and were acquired at one temperature.

When one considers pavement deformation under tire pressure, the loading mechanism involves compression in the pavement section directly underneath the tire, tension at some distance from the tire and at the bottom of the pavement, and a confinement effect from the remainder. The penetration method to evaluate stress at small displacement levels simulates compression, tension, and confinement simultaneously.

PROCEDURE

Equipment

The penetration tool and the specimen mold are attached to an Instron Dynamic Testing Instrument (Model 8511) with an environmental chamber. A schematic diagram of the test set-up is shown in figure 13-1.

Sample Preparation

a. The specific size of a given aggregate fine filler is prepared by grinding (if necessary) and sieving.

b. The fine filler is dried in the oven at 170°C (338°F) for at least 4 hours.

c. A quart can of an asphalt binder is also heated in the oven at 170°C (338°F) for 1 hour.

d. The proper amount of the dried filler and the heated binder are weighed and poured into the mixing container maintained at 160°C (320°F).

e. Mixing is performed for 30 minutes to make a well-dispersed, consolidated mixture. The mixer used in this study is a double planetary type (Ross Co., USA; LDM-2 model; 2-gallon capacity) with the top open to the air.

During the mixing at 160°C (320°F) the following mixing properties are observed. Initially, very fine spherical granules are formed, then the size of the granules increases with mixing time, and finally, all the spherical particles coalesce together to form a consolidated mixture. A consolidated mix without any air void is highly desirable in studying asphalt-filler interfacial effects because it does not need compaction and minimizes the confounding effects of large aggregates and variation in compaction. However, the mixing time required to reach the consolidated mix depends on many factors. The observed factors are filler shape, size, content, chemistry of filler, freshness of fractured face, asphalt binder viscosity, asphalt composition, amount of mixing material in the mixer, and mixing temperature. For very high filler to asphalt ratios, the consolidated mix state is never attained because of too little binder. On the other hand, mixtures with the higher binder to filler ratio form a consolidated mix immediately without going through the spherical granulation. Different mixing times at 160°C (320°F) will alter the aging characteristics of the mixed material. Hence, the mixing time is usually fixed to be 30 minutes, unless it is specifically stated otherwise. Most of the mix consolidation is completed in 30 minutes.

f. After mixing, 700 grams of the asphalt-filler sample are weighed and placed into the specimen container (a stainless steel cylindrical container of 10.16 cm in diameter and 10.16 cm in height as shown in figure 13-1). Remaining air voids are removed by compacting the specimen with a hand-operated, hydraulic compactor (a stainless steel cylinder 9.525 cm in diameter and 2.54 cm in thickness attached to a 15 cm steel rod whose diameter is 2.54 cm).

g. The sample in the mold is cooled to room temperature overnight for testing.

Testing Procedure

a. The prepared sample in the mold is placed above the supporting iron rod that is seated above the load cell of the Instron 8511, all located in the environmental chamber.

b. The desired test temperature is set on the temperature controller. The temperature is monitored by the sensor and controlled by the heater located inside the chamber. A sufficient amount of time (usually 1½ hours) is provided to allow the sample to come to thermal equilibrium.

c. The test is performed by causing the tool to penetrate the specimen at a constant rate of 0.0254 cm/s (0.01 inch/s). The ramp wave form in the position control mode is set to penetrate the specimen 2.54 cm (1 inch) or less from the top surface at the indicated rate.

d. The depth and the stress required for penetration during the entire test period are detected by the position sensor and the load cell. These values are stored in the computer for data handling and analysis.

Precision

The reproducibility of this test was studied by preparing five identical mastics consisting of a mixture of 16 mass percent of asphalt AAM-1 and 84 mass percent RD filler (all < #200). The 30 minutes of mixing was enough to produce the consolidated mastic specimens. The penetration tests were performed at 40°C (104°F) and the rate of 0.0254 cm/s. The test results are shown in figure 13-2. Good reproducibility was observed for the five mastic samples. Each experiment shows some variation, but the results are acceptable. As expected, experience has shown that temperature equilibration of the specimen (10.16 cm [4 inches] diameter × 6.35 cm [2 ½ inches] height) before testing is very important to reduce variation in results.

Discussion

This method was developed for the study of "Interfacial Adhesion Strength at Interface" reported in chapter 5 of Volume I. A display of representative data and a discussion of the results are found there.

SUMMARY

The method described here is a straightforward way to compare properties of asphalts in the form of mastic, i.e., an environment for asphalt that is more realistic relative to roadways than asphalt alone. The results suggest the need for the invention of a simple device to evaluate the effects of aggregate on the physical properties of asphalt as part of a purchase specification.

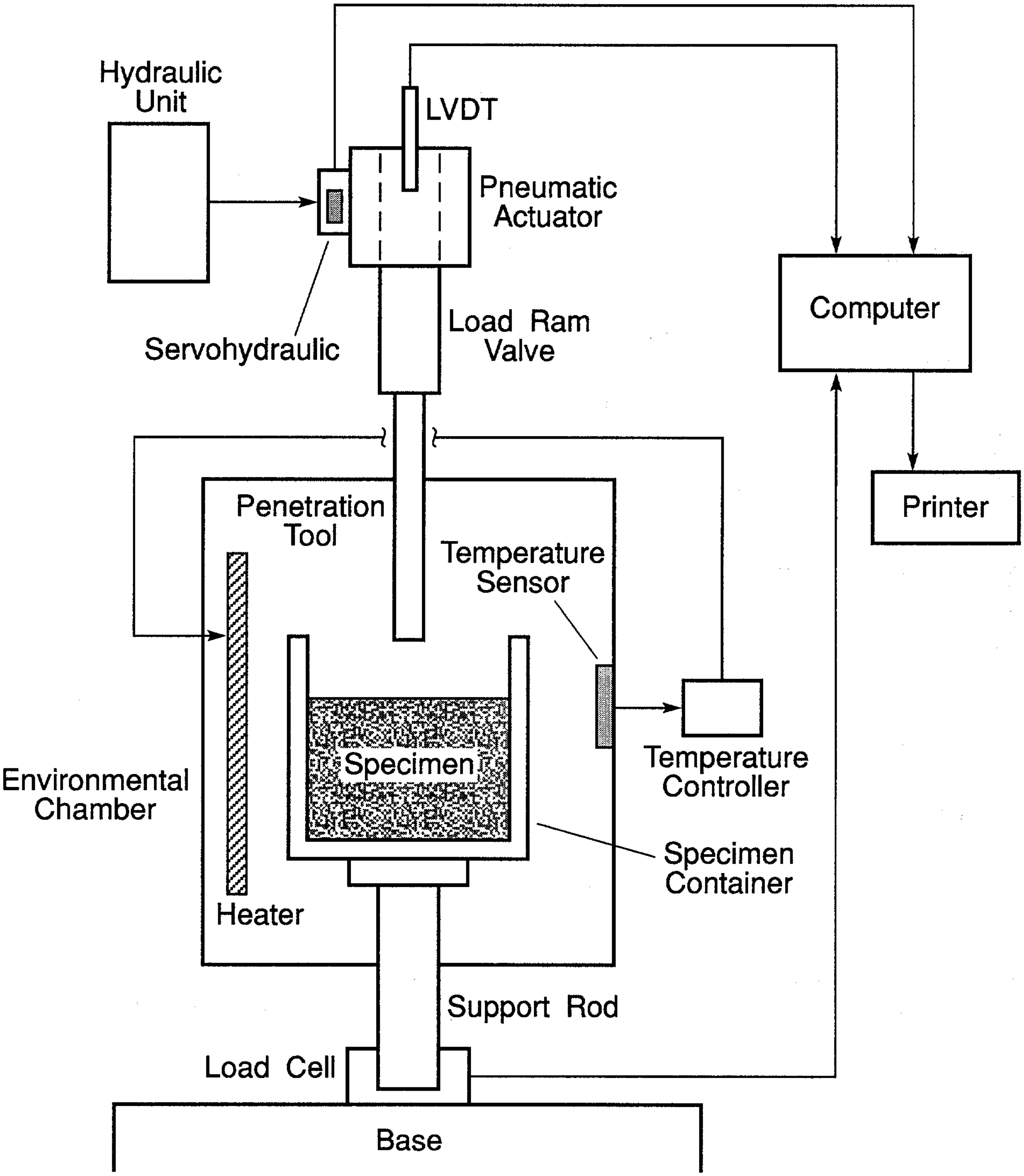


Figure 13-1. Schematic diagram of penetration tester for stress measurement.

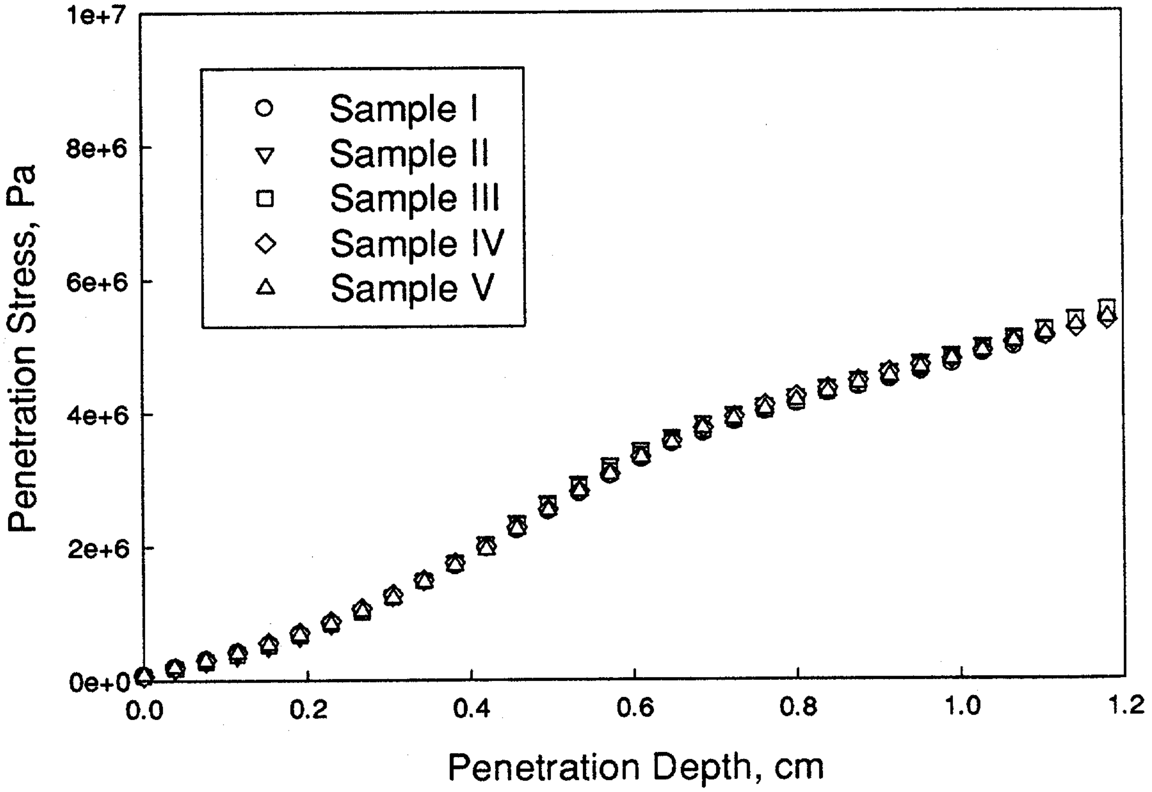


Figure 13-2. Reproducibility test results at 40°C for the mastics made of 16 mass % of AAM-1 binder and 84 mass % of RD-filler (all < #200) by the penetration method.

METHOD 14. PREDICTION OF PAVEMENT DURABILITY BY INVERSE GAS-LIQUID CHROMATOGRAPHY (IGLC)

Previous inverse gas-liquid chromatography (IGLC) work with petroleum asphalts has demonstrated a good correlation between IGLC data after aging with the tendency to form cracks in both Weather-Ometer [Davis and Petersen 1966] and road tests [Davis and Petersen 1967]. The IGLC technique was revisited because of its strong potential as a research tool for studying the durability of asphalt (pavement performance prediction), and asphalt polarity or functionality. The objectives of this task were (1) to develop a fast reliable IGLC procedure, (2) to evaluate the durability of asphalts using the IGLC technique and compare the results with their field performance, e.g., from Long Term Pavement Performance (LTPP) studies, and (3) to identify the effects of the relative polarity of asphalts determined by IGLC.

Comparison of results from conventional (packed column) IGLC with infrared (IR) functional group analysis, relative polarity from ion exchange chromatography (IEC) separations, and heteroatom content were studied. Details of IGLC procedures and conditions are reported by Kim et al. [1997]. The packed column IGLC also provided a standard for development of a fast IGLC procedure using a capillary column gas chromatography (GC) method. The use of capillary columns enables the use of a thinner asphalt coating and will substantially reduce the time required for preparation and aging.

The relationship of IGLC interaction coefficients with aging and chemical functionality parameters determined during SHRP was examined. These parameters are: aging index defined by the ratio of viscosities at 60°C (140°F) before and after thin film oven/pressure aging vessel (TFO/PAV) aging at 80°C (176°F) for 144 hr; chemical composition; IEC results; and non-aqueous potentiometric titration (NAPT) results. The aging index is believed to be a function of overall chemical composition, microstructural state, and initial rheological state. In this analysis of data, no significant correlation between aging indices and IGLC interaction coefficients was found. For unaged asphalts the interaction coefficient of 1-methylpyrolidine (I_{1MPD}) increases as the concentration of carboxylic acid functionality increases. The strongly basic 1-methylpyrrolidine appears to interact with this strong acidic functionality. The I_{1MPD} is positively related with the amount of IEC strong acid fraction in asphalt. Good correlations between butanol and phenol interaction coefficients and the non-aqueous potentiometric base titration results were found. The phenol interaction coefficient of the 6-hr aged sample is also strongly related with concentration of sulfoxide in TFO/PAV (80°C [176°F], 144 hr) residue.

METHOD 15. SIZE EXCLUSION CHROMATOGRAPHY SEPARATION OF ASPHALT

INTRODUCTION AND APPLICABILITY

Size exclusion chromatography (SEC) can be used to separate asphalt solutions into several fractions based on molecular size. Asphalt solutions are pumped through glass columns containing swelled gel particles. The gel particles contain pores of varying sizes and are swelled with organic solvents. Large molecules, or associations of smaller molecules, are not able to enter the pores; hence, they flow rapidly through the gel bed between the gel particles and, therefore, elute from the column first. Smaller molecules enter the pores of the gel particles and are held up in the gel matrix for varying amounts of time depending on their size. The smallest of these molecules remain within the column for the longest time and elute last. The SEC separation method can be used to separate small amounts of an asphalt or as a preparative method separating several grams. A preparative method used to separate 16 gram samples of neat or aged asphalt is described below.

PROCEDURE

Apparatus (for a single column separation)

Most of the items listed below may be obtained from a large number of vendors. Some specialized items are not widely available, and so the vendor is listed in these cases.

Equipment

One Lab Crest™ column (Andrews Glass Co.), 5.0 cm I.D. x 100 cm long, with a water jacket and end fittings with stopcocks
Two coarse porosity sintered glass discs (Ace Glass Co., P. O. Box 688, Vineland, NJ 08360) seated into the end fittings of the columns
Bio-Beads® S-X1 (200-400 mesh) gel (Bio-Rad Laboratories, 2000 Alfred Nobel Drive, Hercules, CA 94547)
One laboratory pump, FMI model RPG-50, 0.25 inch (0.635 cm) piston (Fluid Metering Inc., 5 Aerial Way, Suite 500, Syosset, NY 11791)
One pulse dampener, FMI model PD-60LF (Fluid Metering Inc.)
Teflon® spaghetti tubing, 0.0625 inch (0.15875 cm) diameter with suitable connectors. Approximately 4-5 meters of tubing is required for a typical setup.
Tygon® tubing, approximately 4-5 meters
One circulating water bath with temperature control
One 500 mL wide-mouth Erlenmeyer flask
One 1,000 mL Erlenmeyer flask
Four to nine 500 mL graduated cylinders
One 10 mL graduated cylinder
One large beaker (at least 3 L)

One laboratory trip scale, weighing to ± 0.1 g
One analytical balance, weighing to ± 0.001 g
One heat lamp
One spatula (or screwdriver)
One stirring rod
One Pasteur pipette
One 10 mL syringe with long needle
One ultraviolet lamp, emitting radiation at approximately 350 nm
One rotary evaporation apparatus with water bath
One rotary evaporation apparatus with oil bath
One nitrogen evaporator with water bath
One 1,000 mL pear-shaped heavy walled flask
Two 125 mL amber bottles with adapter
Six or seven 35 mL glass vials with adapter
Differential refractometer

Reagents

Chart recorder and paper
Toluene (EM Sciences) spectral grade, degassed, approximately 4.0 L initially
Methanol (less than 100 mL), EM Sciences
Dichloromethane (less than 100 mL), EM Sciences
Various molecular weight standards
Aluminum foil

Setup, Sample Preparation, and Procedure

A schematic diagram of the apparatus used for preparative SEC of asphalts is shown in figure 15-1. Separation of an asphalt solution takes place in a water-jacketed glass column filled with a suspension of swelled gel particles in toluene. The sample is introduced into the bottom of the column and separation is effected by pumping solvent into the bottom of the column until all of the asphalt has been eluted from the top of the column. Teflon® tubing connects the bottom of the column to a pulse dampener, which suppresses the magnitude of the pressure pulses generated by the pump. The pulse dampener is connected to a pump by more Teflon® tubing, and the pump is connected to the sample container or solvent reservoir by another length of Teflon® tubing. At the top of the column, Teflon® tubing leads to graduated cylinders in which eluates are collected. The sample passes through the gel column from the bottom to the top to minimize channeling, which would occur if the separation were performed in the reverse direction. Teflon® tubing is used because of its chemical inertness. Asphalts contain waxes and highly polar components, which may form deposits on the inner surfaces of other tubing materials.

The column is packed with a slurry of Bio-Beads® S-X1 (200-400 mesh) dry gel in toluene. The amount of dry gel required (330-340 g) is determined by the volume of the column, which is approximately 2 L. When mixed with toluene, the gel swells to a volume of 7.9 mL per gram of gel. Therefore, the mixing of the gel with toluene is performed in a large beaker (the gel and toluene are stirred with a stirring rod to expel air bubbles) and not in the column. If toluene is added to dry gel in the column, the swelling of the gel could break the expensive column. The gel-toluene slurry is prepared in a fume hood.

The column, water jacket, and bottom stopcock fitting are assembled and one of the fritted glass discs is nested inside the bottom fitting. The column assembly then is vertically mounted and toluene is poured into the column to about one-fourth the column height. The gel slurry is added to the column from the top in several increments. While this is being done, the stopcock at the bottom of the column is opened and solvent drains out slowly by gravity. After all of the slurry is added, the column appears to be fully packed and the top stopcock fitting, fritted disc, etc., is put in place. However, pumping will compress the gel bed somewhat so that a gap will appear at the bottom of the gel over time. To correct this, the pumping direction is reversed (pumping from top to bottom) and a few mL methanol is pumped onto the top of the gel bed causing it to shrink. The volume of the gap at the bottom of the gel bed is calculated from its height and the diameter of the column (5.0 cm). The weight of dry gel necessary to fill the gap is then calculated from the expansion factor of the gel (7.9 mL/g) and the compressibility factor (0.75). The top stopcock fitting is then removed and the calculated amount of dry gel is added to the top of the gel bed. The top stopcock fitting is then reattached to the column and the pumping direction is again reversed, i.e., now pumping from bottom to top again. Toluene is again pumped into the bottom of the column and the methanol is gradually displaced, causing the gel (both that which had originally filled the column and the added dry gel) to expand and fill the column. The calculation of needed dry gel is not perfect so the process of adding more dry gel may have to be repeated once or twice more.

Before samples are introduced into the column, the water jacket of the column assembly is connected to the circulating water bath using Tygon® tubing. For the separations described in this report, the bath temperature was adjusted so that the column temperature was 40°C (104°F). At this warmer than ambient temperature, the gel bed volume is slightly larger than immediately after the column was filled. The flow rate of toluene is established by collecting effluent from the column in a graduated cylinder and adjusting the pump control to give a flow rate of 3.5 mL per minute. Once established, the flow rate should maintain itself from run to run, seldom requiring further adjustment.

The toluene is contained in a 1,000 mL Erlenmeyer flask solvent reservoir into which a Teflon® tube connected to the pump is immersed. Proper ventilation is necessary during the operation of the column.

The column may be calibrated using solutions of compounds of known molecular weight. Polystyrenes of various molecular weights are available from several vendors. Colored compounds such as metallophthalocyanines and porphyrins also are available. Many of these colored compounds are of moderate (500-1,000 daltons) molecular weight and are soluble in toluene. Their progress through a gel bed may be observed visually.

The first step in the separation of an asphalt is sample preparation. A 500 mL wide-mouth Erlenmeyer flask is tared on a scale and approximately 16 g of asphalt is warmed by a heat lamp and poured into the flask. A screw driver or spatula may be used to facilitate the transfer.

Heating of the asphalt is necessary to make the transfer to the flask possible but should be minimized to avoid oxidation. The flask and contents are weighed on the scale and the mass of the asphalt is recorded. In the separations described in this report, samples are normally weighed and toluene (150 mL) added late in the afternoon. The flask is then sealed with aluminum foil and stored in a dark place overnight. The next morning, the separation is begun. Long storage of asphalt solutions may result in oxidation so the sample should be run within 24 hours of dissolution.

The asphalt solution is introduced into the bottom of the column after 1 hour of pumping with pure solvent. The pulse dampener is taken out of the solvent stream at this time to prevent hold up of sample. After the solution of asphalt has been injected into the column, small amounts of toluene are pipetted into the flask to rinse the small amount of sample that inevitably adheres to the flask. Then the entry tube is transferred to the solvent reservoir. During sample injection, the pump setting is not changed, even if the flow rate slows down.

After the sample has been completely injected, the pulse dampener is replaced in the injection stream between the pump and the bottom of the column. This may be accomplished by stopping the pump and inserting the pulse dampener into the stream or by having it in a parallel stream and switching between the two. During the course of the separation, the dial on the gauge of the pulse dampener should not exceed 10 psi. If the dial exceeds this value, the pump setting is altered or the pump is shut off for a time to relieve some of the pressure. Experience has shown that column back pressure greater than 10 psi can lead to fracturing of one or both of the fritted glass discs, most likely the top disc located at the top and bottom of the column.

Solutions of asphalts are much more viscous than toluene. Consequently, the flow rate of fluids through the column during the separation will vary from the initially established rate of 3.5 mL per minute established for the solvent toluene.

Because solutions of asphalts are black, the progress of the sample through the column is easily observed. When color is observed in the tube at the top of the column, the graduated cylinder used to collect eluate is changed. The amount of solvent collected between sample injection and the observation of colored material in the eluate is the breakthrough volume, and this volume is recorded.

In most separations of asphalts described in this report, the first cutpoint after breakthrough is based on the onset of fluorescence to 350 nm radiation. When the initially eluted portion of the sample is irradiated by the ultraviolet (UV) lamp, little fluorescence is observed. After approximately 250-315 mL of eluate has been collected, distinct fluorescence of the eluate is noted. This observation applies to the entire set of SHRP asphalts, and not just the set of core asphalts, mentioned below. For some asphalts, the onset of fluorescence is abrupt, while for others this is not the case and operator judgment is required. After the initial non-fluorescent eluate has been collected, the tube exiting the top of the column is transferred to another graduated cylinder. Subsequent eluate may be collected as one fraction or as seven or more 200 mL subfractions.

In determining the onset of fluorescence, a white paper is placed behind the collecting cylinder. Room light is turned off, and the UV lamp is placed 10 cm from the cylinder. If necessary, the collecting cylinder may be filled with some quantity of fluorescent eluates. After standing an hour or so, there may be several layers of eluate of gradually increasing fluorescence. The dividing line between non-fluorescent and fluorescent eluate has been chosen to be when fluorescence becomes uniformly bright and no more layering occurs. The uppermost uniformly fluorescent eluate may be removed from the cylinder with a pipette or syringe and added to the next fraction (or subfraction) that is collected in another cylinder. For the eight SHRP core asphalts, the amount of eluate collected that is non-fluorescent ranges from 270 to 315 mL depending on the asphalt.

The initial non-fluorescent eluate is SEC Fraction-I. The volume of solvent between breakthrough and onset of fluorescence is recorded. This solution is transferred to a pear-shaped flask and most of the toluene is removed on a rotary evaporator. The remaining material may be redissolved in a more volatile solvent such as dichloromethane or, more usually, redissolved in toluene. The new solution is transferred to a tared amber bottle, and the bottle is placed in the bath of a nitrogen evaporator. A stream of dry nitrogen is introduced into the neck of the bottle while it is warmed in the bath. The vial is then dried on an oil bath under vacuum. The temperature of the oil bath should not exceed 125°C (257°F), and drying should not take more than 1 hour.

SEC Fraction-I materials are the largest molecular size components of asphalts. They are believed to consist of extensive molecular associations. These associations suppress fluorescence, which is why 350 nm radiation can be used in the detection of SEC Fraction-I materials. This initial fraction, after drying, is a black, friable solid, resembling asphaltenes.

All subsequently eluted materials are referred to as SEC Fraction-II or its subfractions (SEC Fraction II-1; II-2; etc.). After solvent removal, these materials appear to be semi-solids or viscous liquids. The subfractions are transferred to tared small glass vials for final drying.

It is occasionally observed that eluate collected toward the end of SEC separations of asphalts are red in color. This is due to the presence of metalloporphyrins, which are found in substantial amounts in some asphalts, particularly asphalts AAD-1 and AAK-1. These compounds are characterized by molecular weights of 500-700 daltons. They are among the smallest molecules present in asphalts and, therefore, elute toward the end of the separation.

The SEC fractions are usually reported as mass percents of original sample. Mass percents are calculated as the mass of the fraction (or subfraction) multiplied by 100, and this product is divided by the mass of the whole asphalt sample that was separated. Chromatograms may be constructed in which mass fractions are plotted versus elution volumes. Elution volumes are the amount of solvent collected after the beginning of sample introduction, which is zero volume. About 21 percent of the total volume of eluate will be collected before breakthrough of the initial asphalt fraction. The separation should be complete after an amount of solvent equivalent to the column volume has been collected. Elution volumes may be reported as percentages of total column (bed) volume. In the work described in this report, the elution volume that corresponds to a particular fraction or subfraction is that percentage of bed volume at which the material begins to be collected. If only two fractions are collected, chromatograms are not usually constructed. If SEC Fraction-II is collected as seven or more 200 mL subfractions, the masses of these subfractions will be observed to vary, depending on the asphalt. So will the masses of the SEC Fraction-I components. If eight or more SEC fractions and subfractions are collected, distinctive chromatograms may be constructed for each asphalt.

The SEC Fraction-I materials also may be divided into subfractions. This may be done during the initial separation or in a subsequent separation. In the work described in this report, both methods were used. In the first case, a differential refractometer (refractive index detector) attached to a chart recorder was inserted into the effluent line. As the SEC Fraction-I materials leave the column, two peaks are observed by differential refractometry. The SEC Fraction-I materials thus can be separated into two subfractions. The cutpoint is made at the lowest part of the trace on the chart recorder between the two peaks. In this separation, two SEC Fraction-I subfractions are collected, in addition to SEC Fraction-II and its subfractions. These latter are collected in the usual manner, without using any information provided by the refractive index detector.

If SEC Fraction-I of any asphalt is to be refractionated, it should be recalled that its solutions are highly viscous. The solutions of whole asphalts in toluene, when introduced to the column, are approximately 10 percent asphalt. Such a concentration of SEC Fraction-I in toluene would be too viscous to be pumped easily into the column. Solutions of SEC Fraction-I materials in toluene are, therefore, made up to be approximately 2.5 mass percent, and these more dilute solutions are introduced onto the column. After breakthrough, three subfractions of equal eluate volume are collected, based on the eluates collected in the initial separation. As an example, the elution volume after breakthrough and before onset of fluorescence of SEC Fraction-I of AAF-1 was 283 mL. This number is divided by three. Therefore, in the refractionation of SEC Fraction-I of AAF-1, three 94 mL subfractions will be collected after breakthrough. A fourth subfraction, which includes all of the rest of the colored eluate and elutes after onset of fluorescence, also is collected.

Preparative SEC separations require about 1½ workdays to perform. They are usually begun as early in a working day as possible. By the end of a normal working day, SEC Fraction-I and most of the SEC Fraction-II will have been collected. The column may be shut down overnight and the separation completed the next day. Separations completed without shutting down the column gave the same results as those separations that were shut down overnight.

Those SEC fractions that consist of more than 2 grams are dried and stored in 125 mL amber bottles. These bottles may be connected to rotary evaporators by adapters. Smaller subfractions are dried and stored in 35 mL glass vials. These vials also may be attached to rotary evaporators for drying purposes.

Recoveries in the preparative SEC of asphalts are nearly 100 percent. After much use, however, some small amount of polar material irreversibly adsorbs and accumulates on the gel. Some of these contaminants may be desorbed by pumping a mixture of 90 percent toluene and 10 percent methanol through the column. In extreme cases, the gel may be removed from the column and may be collapsed with methanol. The gel may then be treated with strong solvents such as pyridine to further clean the gel. This procedure must be performed in a good fume hood. After cleaning, the gel is suitable for reuse.

A large amount of toluene is utilized in this separation. However, the used toluene typically is distilled and used again in subsequent separations.

Data Calculation and Precision

Masses of the collected fractions are recorded. The precision of the method depends on the sharpness of the onset of fluorescence in the SEC Fraction-II eluates. For some asphalts, the onset is abrupt, but is less so for other asphalts. However, precision is very good when the same asphalt dependent cutpoint for SEC Fraction-I is used for each run.

SUMMARY

Some applications of preparative SEC separation are described. Three of these applications involve the separation of neat or aged asphalts into two or more fractions and or subfractions. Sample sizes are large enough (16 g) so that the fractions obtained after the separations are complete may be subjected to methods of analysis requiring substantial amounts of materials. In a fourth application, a fraction obtained in an initial SEC separation is refractionated. All SEC separations of asphalts provide fractions or subfractions that vary according to molecular size. If seven or eight fractions or subfractions are collected, distinctive chromatograms describing molecular size distributions of asphalts may be constructed.

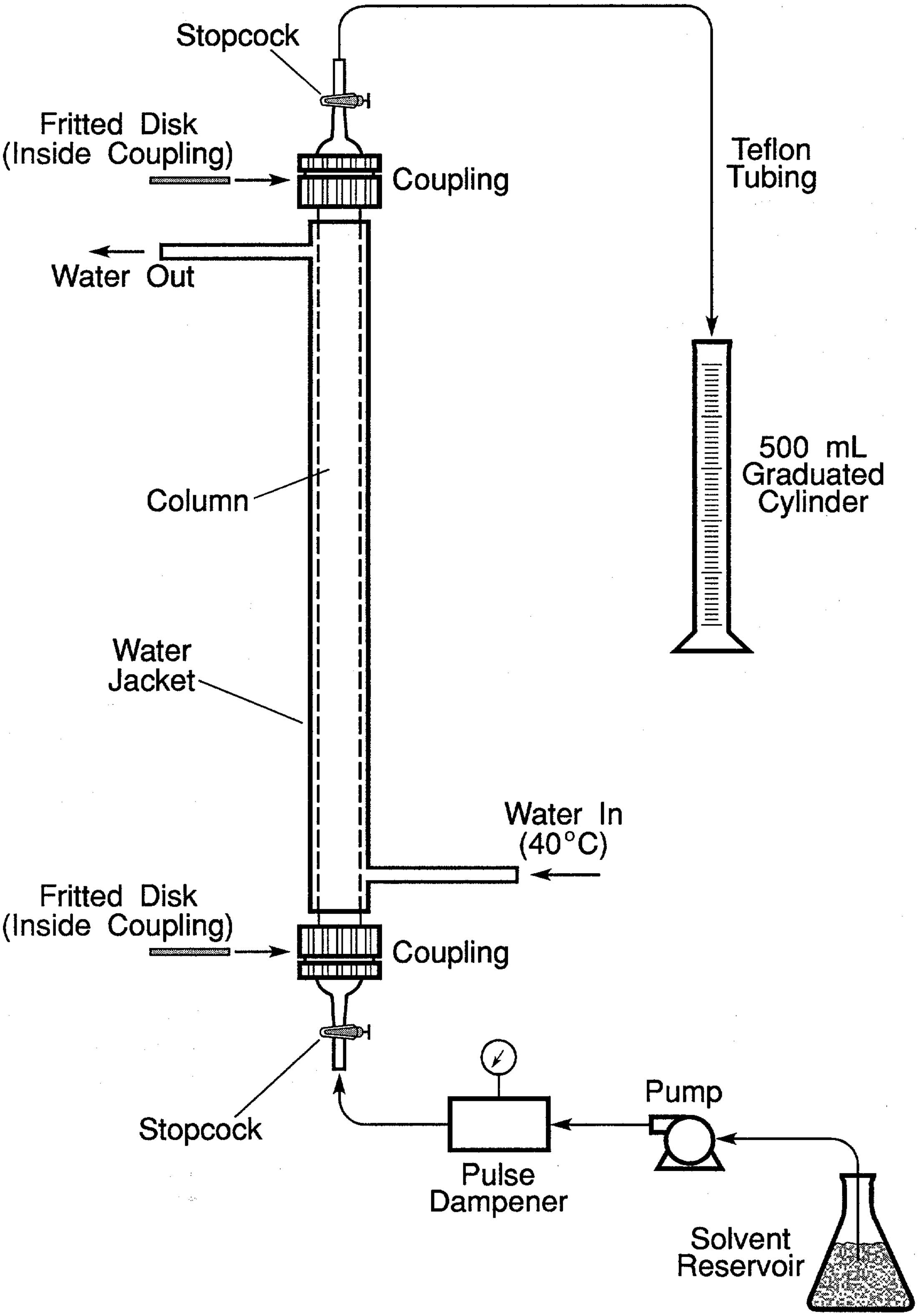


Figure 15-1. Apparatus used for preparative size exclusion chromatography separations.

METHOD 16. SLIDING PLATE MICROVISCOMETRY WITH MACHINED AGGREGATE PLATES

ABSTRACT

Measurement of the interaction between asphalt and aggregate surfaces at various film thicknesses has been accomplished using sliding plate geometry with standard Pyrex glass plates and machined aggregate plates. Significant differences in the behavior of asphalts in contact with aggregate plates have been observed, especially at low shear rates. Studies of film thickness effects on the rheological properties of asphalt binders and aggregate mixtures show that thin films of asphalt on aggregate surfaces have substantially different rheological properties than the bulk asphalt. In addition, statistical analysis has indicated that sliding plate microviscometry with both glass plates and machined aggregate plates yields less than 12 percent variance.

INTRODUCTION AND APPLICABILITY

Many tests exist for the determination of asphalt viscosity. These tests give information concerning the strengths of asphalts but do not measure what happens when the asphalt interacts with aggregate(s). The purpose of sliding plate microviscometry using machined aggregate plates is to investigate the effects of aggregate-surface-induced structure on the rheological properties of asphalt binders. This method may be used to better understand the interactions between asphalt and aggregate in situ. Long-distance aggregate shipment is not cost effective, resulting in utilization of on-site aggregate, which may be sub-ideal. Sliding plate microviscometry could be used to determine which asphalt is most compatible with locally used aggregates.

PROCEDURE

The instrument used to measure thin films of asphalts on glass and aggregate plates is a sliding plate microviscometer manufactured by Hallikainin Instruments, Berkeley, CA, under license from Shell Development Design, patent no. 2,865,197. A constant temperature bath (Cannon Instrument Co., Box 812, Boalsburg, PA) and a chart recorder (Soltec model 1242) also are required.

The other equipment and reagents described below may be categorized as general supplies in any chemical laboratory and may be obtained from any of several vendors.

Sample Preparation

The first step is to clean the plates that are going to be used in the experiment. The procedure is the same for glass or aggregate plates. The plates are washed with deionized water, followed by a rinse with acetone. The plates are then allowed to dry in air at ambient temperature. The dried plates then are marked on edges to match specific edges to one another.

The plates then are aligned on top of each other. A micrometer is used to measure the thickness of the corners of each pair of plates. These measurements are recorded.

A hot plate is turned on and the control is adjusted so that the surface warms to approximately 100°C (212°F). The plates are placed on the hot plate. Glass plates are heated for 10 minutes, and aggregate plates are heated for 40 minutes.

Next, a small quantity of asphalt is transferred to a 5 mL beaker using a clean spatula or screwdriver. A heat lamp may be used to facilitate transfer of the asphalt into the beaker. The beaker is then placed on the hotplate to liquefy the asphalt. Approximately 15 drops of hot asphalt are transferred to the top surface of one of the plates. The plate should then rest on the hot plate for 20 seconds, after which it is placed on a Styrofoam work surface (asphalt side up!). The second plate then is removed from the hot plate using a forceps. It is placed on top of the first plate, contacting an edge first. The second plate then is gently lowered so as not to trap air bubbles in the asphalt. The second plate is moved back and forth slightly lengthwise with gentle pressure to evenly distribute the asphalt.

Excess asphalt is removed from the sandwiched plates using a razor blade. Slicing should be performed perpendicular to the plane of the plates to avoid pulling asphalt from between the plates. The specimen then is grasped horizontally. A tissue soaked with a few drops of toluene is used to wipe any asphalt from the edges of the plates. This operation should be performed using gloves and in a fume hood. Holding the specimen horizontally prevents toluene from penetrating the asphalt in the specimen.

After cleaning, the micrometer is used to measure the thickness of the specimen at each corner. The four measurements are averaged.

A layer of sand is poured into a 250 mL beaker and a piece of Styrofoam is placed on top of the sand. The specimen(s) are placed on the Styrofoam. The beaker and contents is partially immersed in a water bath maintained at 25°C (77°F) for 2 hours. The water bath should be brought to the 25°C (77°F) temperature prior to the beaker being placed in it. Care should be taken to keep the specimen(s) dry.

Testing Procedure

The specimen is then properly seated in the specimen holder, which is then inserted into the microviscometer apparatus. The microviscometer is mounted in the water bath. The specimen is allowed to equilibrate thermally with the apparatus for 5 minutes. A stopwatch should be used. During the equilibration period, use the manual position control of the microviscometer to adjust the micrometer of the microviscometer so that it just touches the contact surface of the specimen holder. This is the zero point for the test.

After the 5 minute equilibration period, testing is begun by placing the first load on the weight hanger of the apparatus. The chart recorder movement switch is turned on, the stopwatch is started again, and the position on the micrometer is recorded on the data sheet. Then, the stopwatch is stopped at a predetermined position of the micrometer. The time elapsed and the stop position are recorded on the data sheet. These steps are repeated with each successive load. After the last loading cycle is completed, stop the chart recorder. The data may be analyzed in concert with the time-deformation data on the chart recorder to calculate viscosities. The viscosity can be calculated from the following formula:

$$\eta = \frac{s}{\dot{\gamma}} = \frac{s}{dv/dr}$$

where:

η = viscosity, poises

s = shear stress, dyne/cm^2

$= \dfrac{\text{Load in grams} \times 980}{\text{Area of plate in cm}^2}$

$\dot{\gamma}$ = shear rate, sec^{-1}

$= \dfrac{\text{Chart divisions} \times \text{cm per division} \times \text{chart speed in inches/sec}}{\text{Chart movement in inches} \times \text{film thickness in microns} \times 10^{-4}}$

Comments on Temperature Control

The temperature during sample preparation needs to be controlled because changes occur in asphalt as it cools. The cooling rate was kept as constant as possible by using a hot plate to heat asphalt and aggregate. Samples are prepared on an insulating Styrofoam surface. This keeps the cooling rate constant because it removes the variability of bench top temperature (which would consequently alter the cooling rate) by virtue of physical separation. The time of post-preparation hardening was fixed at 2 hours during which time samples were held in a dry beaker inside a 25°C (77°F) water bath.

All samples were sheared while immersed in a 25°C (77°F) water bath. Prior to testing, samples were allowed to sit in the water bath for 5 minutes for temperature equilibration. The water temperature was maintained by a thermostat-actuated heating coil.

After testing, samples were stored in an oven at 25°C (77°F).

Calibration

To calibrate the chart recorder with the micrometer of the microviscometer, the chart position was set to zero by manipulating the manual control switch on the microviscometer. The micrometer of the microviscometer was read and recorded. The manual position switch of the microviscometer was then manipulated to move the micrometer to an arbitrary number some distance away from the starting position. The chart was then read and the pen position was recorded. The micrometer numbers yielded a figure of microns moved while the chart recorder gave the numbers of divisions covered. The number of microns moved was divided by the number of divisions and multiplied by 10,000 to give the centimeters per division. The target value is 0.00049 cm/division and the chart recorder was adjusted until the target value was given three consecutive times.

Precision

The precision of the testing is checked by making duplicates of each sample. For each experiment two duplicate samples were made and the results of testing for each were compared to determine a percentage of deviation. The results of statistical analysis using ANOVA on the measured viscosity at 25°C (77°F) for both glass plates and aggregate plates should be within a 15 percent range of repeatability.

SUMMARY

The sliding plate microviscometer has demonstrated that there is a quantifiable effect on the rheological properties of asphalt binders in the presence of aggregate surfaces. The sliding plate microviscometer allows the researcher to simulate in situ conditions of roadways while minimizing the effects of other variables.

ADDITIONAL TEST RESULTS

A. FURTHER STUDIES OF ASPHALT SIZE EXCLUSION CHROMATOGRAPHY FRACTIONS

MODEL COMPOUND STUDIES

In chapter 3 of Volume I, the use of preparative size exclusion chromatography (SEC) as a separation method for asphalts was described. Experimental details of the procedure are described in Method 15 of this volume. The fractionation of asphalts into components according to molecular size was shown to support the model of asphalt structure outlined in several places in Volume I. Different molecular size fractions have different influences on different physical properties. In the interests of presenting a concise discussion of SEC results, not all of the data obtained using this technique was presented in Volume I. These additional data are presented below.

During the Strategic Highway Research Program (SHRP), the effect of model compounds on asphalt rheological properties was studied. Modifiers often are blended with asphalts, to confer benefits on pavement mixtures such as resistance to stripping, and the effects of these additives on rheological properties of asphalts must be known. The SHRP studies [SHRP 1993a] showed that long-chain aliphatic diamines cause significant reductions in viscosities when they are mixed with most asphalts in small (1.0-2.0 mass percent) amounts. Long-chain dicarboxylic acids and long-chain α, ω-amino acids, on the other hand, are viscosity builders. Difunctional compounds such as these are common components of antistrip agents. How they act to modify asphalt rheological properties is not known. The mechanism by which they modify adhesive properties also is not known.

One possible explanation of the effect of modifiers on asphalt rheological properties is that model compounds containing polar functional groups will alter asphalt molecular weight distributions by interacting with indigenous compounds in asphalts that have a tendency to engage in associations. The associations might be either broken up or augmented, depending on the nature of the model compounds and the polar materials native to the asphalts.

In addition to modifiers such as relatively low molecular weight amines and acids, binders are combined with polymeric substances such as polystyrene and polyethylene, and mixtures of polymers and low molecular weight materials such as rubbers. Although the latter materials consist largely of polyisoprene and carbon black, some plasticizers and antioxidants also are present. When rubber and asphalt are mixed, low molecular weight components of rubber are likely to be dissolved in asphalt.

Molecular weight distributions in asphalts can be determined by fractionation of asphalt solutions into several fractions by SEC. The molecular weights of the various fractions then can be measured [SHRP 1993a]. The SEC separation employed for this purpose is identical to that used to separate solutions of asphalts into SEC-I and SEC-II fractions, except that the SEC Fraction-II is subdivided into eight subfractions consisting of equal volumes of eluate. It should be recalled that solutions of asphalts subjected to SEC are separated into fractions according to molecular size. The largest entities are eluted earliest in an SEC separation. The smallest molecules in an asphalt are found in the fractions eluted latest. Depending on the nature of the asphalt (and assuming identical separation conditions for each asphalt), masses of materials are distributed differently among the SEC Fraction-I materials and eight SEC Fraction-II subfractions. The last two subfractions eluted in the preparative SEC separation contain very small amounts of material because asphalts have only small amounts of low molecular weight components.

Two amines were chosen as additives. They are 1,12 diaminododecane (molecular weight = 200) and N,N dimethylnonylamine (molecular weight = 171). Formulas for these compounds are illustrated in figure A-1. Both compounds are moderately strong organic bases and should interact with acidic species in asphalts. The 1,12 diaminododecane is difunctional and can engage in multiple interactions, particularly with acidic molecules. N,N dimethylnonylamine is monofunctional and can only cap off acidic functional groups when interacting with acids. Multiple interactions are not possible. The two amines were added to asphalt AAB-1 at the 2 mass percent level. Asphalt AAB-1 was chosen as the test asphalt because it was observed that the viscosity of this asphalt is reduced more than any of the core asphalts when 1,12 diaminododecane is added [SHRP 1993a]. The toluene solutions of these mixtures then were separated into nine fractions using preparative SEC.

Each of the fractions was collected, dried, and weighed. SEC Fraction-I was collected intact, and SEC Fraction-II was subdivided into eight subfractions, as mentioned above. The first six subfractions of SEC Fraction-II were analyzed for bases by non-aqueous potentiometric titration (NAPT) using a method developed during SHRP. The last two subfractions were not titrated because not enough material was collected. Results are reported in tables A-1 to A-3. In this titration method, bases are classified as moderately strong bases or weak bases. The moderately strong bases correspond to those bases titrated up to 500 mv. Weak bases are titrated from 500-800 mv. If titrated alone in solution, model compounds 1,12 diaminododecane and N,N dimethylnonylamine would be moderately strong bases. In the base titrations, voltages reported are positive, unlike NAPT of acids in which voltages are negative (Method 7, this volume).

Table A-1 lists the masses of the SEC subfractions collected during the preparative SEC separation of a toluene solution of AAB-1. This result is similar to results previously reported [SHRP 1993a]. Both moderately strong and weak bases are distributed fairly evenly among the six SEC Fraction-II subfractions that were titrated by NAPT. There appears to be a somewhat larger concentration of moderately strong bases in subfractions II-5 and II-6 than in the other subfractions. Materials collected in these subfractions have number-average molecular weights of 550 and 430 daltons, respectively [SHRP 1993a].

The data in tables A-1 to A-3 show that adding 2 mass percent of bases does not affect significantly the mass distribution of AAB-1 in SEC separations. Masses of each of the SEC fractions and subfractions essentially are identical whether or not bases are added. Most importantly, bases do not break up the strongly associated SEC Fraction-I components into smaller components to any significant degree. Also, the added bases appear to be entirely concentrated in subfractions II-5 and II-6 for 1,12 diaminododecane (table A-2) and in subfraction II-5 for N,N dimethylnonylamine (table A-3). They are not distributed among the higher molecular weight SEC Fraction-II subfractions. Titratable base concentrations in SEC Fraction-II subfractions 1-4 are similar whether or not bases are added to AAB-1. The concentration of added bases in SEC Fraction-II subfraction-5 was observed visually as well as by NAPT. During solvent removal, some 1,12 diaminododecane sublimed, and white crystals of this substance were detected on the mouth of the glass vial containing the subfraction. Presumably some N,N dimethylnonylamine is also volatilized. This is probably why the base concentrations in the various fractions do not account for the sum of all the bases indigenous to AAB-1 plus added base. The loss of some of the additive during the solvent removal step precludes any meaningful discussion of statistical error for these experiments. Results are qualitative. It is not known why 1,12 diaminododecane titrates as a weak base in the presence of asphalt AAB-1 SEC subfractions II-5 and II-6. As mentioned previously, if it were titrated alone in solution, it would be expected to behave as a moderately strong base. N,N dimethyl nonylamine titrates as a moderately strong base (table A-3) in the presence of AAB-1 SEC subfraction II-5.

The model compounds added are of lower molecular size than most materials found in SEC Fraction-II subfraction-5. Based on this factor alone, they should have been the last compounds eluted. Therefore, there must be some association between low molecular weight materials in SEC Fraction-II of AAB-1 with the bases. It is speculated that the effect of the added bases on rheology is to lower the viscosity of the asphalt solvent moiety. There is no alteration of sizes of the larger molecular associations or any discernable reaction with them.

Possibly, antistrip agents in asphalts will behave similarly. These results indicate that the combination of SEC and NAPT may allow for their ready identification in forensic studies of cores. However, if antistrip agents react chemically with asphalts so that their identities are lost, their detection will prove to be difficult.

Asphalt AAB-1 also was mixed with two other model compounds at the 2 mass percent level. These compounds are lithium stearate and 1,3,5 cyclohexanetricarboxylic acid (figure A-1). The two compounds are highly surface active. They were each mixed with asphalt AAB-1 in dichloromethane solution, and then the dichloromethane was removed by evaporation. Upon inspection, it was evident that neither compound was completely miscible with AAB-1 as crystals of both model compounds were observed. Therefore, SEC separations were not performed. Rheological data were obtained and compared with rheological properties of a control sample of AAB-1 treated similarly with dichloromethane. The mixtures containing the model compounds are lower in viscosity than the control, indicating that there is an effect on rheological properties even with partial dissolution (table A-4).

The compound zinc tetraphenyl porphine (figure A-1) is known to associate fairly strongly with aromatic molecules. Some of the molecular associations in asphalts are believed to involve aromatic molecules, so it is possible that the associations might be broken up by adding zinc tetraphenyl porphine. Accordingly, a mixture of this compound (5 mass percent) and asphalt AAB-1 (95 mass percent) was prepared in dichloromethane. When the solvent was removed, it was noted that the model compound and asphalt appeared to be miscible. Rheological properties of the mixture were measured (table A-4). Obviously, addition of zinc tetraphenyl porphine causes an increase in the viscosity of asphalt AAB-1. The model compound is a high melting solid of substantial molecular weight, and thus might be expected to enhance viscosity and elasticity.

The AAB-1 mixture with zinc tetraphenyl porphine was dissolved in toluene and the solution was separated into two fractions by preparative SEC. Yields of SEC Fraction-I and SEC Fraction-II were the same as a control sample of AAB-1. Obviously the model compound did not break up the SEC Fraction-I molecular associations. When the SEC Fraction-I of the mixture was analyzed for zinc metal a small amount of zinc was detected (approximately 0.5 percent of the model compound added to the mixture). The model compound (molecular weight = 678) should not be detected in this fraction (which contains the largest molecules in asphalts and the largest molecular associations) unless it has become involved in associations with aromatic components of asphalt. In the absence of molecular associations, zinc tetraphenyl porphine would be among the latest eluates in an SEC separation of the mixture. The detection of Zn, even in small amounts, in the SEC Fraction-I of the separated mixture is direct evidence of molecular associations involving aromatic interactions in asphalts.

In chapter 3 of Volume I, results of experiments with four subfractions of SEC Fraction-I of SHRP asphalts were reported. The four subfractions varied greatly in molecular weight, ranging from 2,000 daltons to 40,000 daltons. The four subfractions of SEC Fraction-I of AAD-1 were mixed with SEC Fraction-II of AAD-1 at levels ranging from 5 mass percent of each subfraction to 20 mass percent. Rheological properties of the mixtures were found to be strongly influenced by the amount and molecular weight of the subfraction. Mixtures containing the largest molecular size subfractions are more viscous than mixtures containing smaller molecular size subfractions, particularly at higher concentrations. Such a result is a consequence of the model of asphalt structure described in Volume I. Accordingly, it was attempted to obtain similar results using polymeric materials instead of SEC Fraction-I subfractions in mixtures. The advantage of using the polymeric materials is that the chemical composition and molecular weight values of the polymers are known. Rheological properties of mixtures that include them can be related to compositional properties more accurately. It would be expected that, for a given amount of polymer added to an asphalt, a higher molecular weight polymer would cause greater increases in viscosity and $|G^*|$ in the mixture compared with a lower molecular weight polymer.

Polystyrene is one of the best known polymeric materials. It is available in a wide range of molecular weights (figure A-1). Five different polystyrenes were obtained, having peak molecular weights of 2,727 daltons, 3,700 daltons, 12,600 daltons, 18,700 daltons, and 45,730 daltons. This molecular weight range is similar to that of the four SEC Fraction-I subfractions of AAD-1. The polystyrenes were mixed with SEC Fraction-II of AAD-1 by dissolving both materials in dichloromethane, mixing the solutions, and removing the solvent. It was observed that the polystyrenes of molecular weight 18,700 and 45,730 daltons were not miscible with SEC Fraction-II of AAD-1 at ambient temperatures. These polymers appeared to swell, but individual particles were observed that did not dissolve in the AAD-1 SEC-Fraction-II even after heating. The other three polystyrenes are miscible so rheological properties of their mixtures with SEC Fraction-II of AAD-1 at various polymer concentrations were measured. These data are listed in table A-5. It is noted that all the mixtures containing polystyrenes of molecular weight 2,727, 3,700, and 12,600 at the 5 mass percent level or lower have similar viscosities. These viscosities range from 411 to 827 Pa·s. In some cases, viscosities of mixtures containing more polystyrene are slightly less viscous than mixtures having less polystyrene. Also, some mixtures of higher molecular weight polystyrene are lower in viscosity than mixtures containing equal concentrations of lower molecular weight polystyrene. These differences are not large and thus may be the result of experimental error, such as slight variations in loss of light ends during solvent removal. Furthermore, the viscosities are at most slightly more than twice that of the solvent, SEC Fraction-II of AAD-1. At the 5 percent level, polystyrenes of up to 12,600 daltons in molecular weight are effectively solvated by SEC Fraction-II of AAD-1, which does not discriminate among the three polystyrenes.

At the 10 mass percent level, viscosities of the mixtures are somewhat higher (table A-5). The viscosity of the mixture containing 10 mass percent of the 12,600 dalton polystyrene is very high. However, crystals of the polystyrene were observed to have formed in this mixture. Obviously, the solubility limit had been reached. Values of phase angles (δ) for these 10 mass percent mixtures are nearly 90°, indicating absence of elastic properties.

At the 15 mass percent level, only the two polystyrenes of lowest molecular weight were miscible with SEC Fraction-II of AAD-1. The viscosities of these mixtures are higher than viscosities of mixtures containing these polystyrenes at lower concentrations, as would be expected. Phase angles (δ) are nearly 90° (table A-5), indicating a lack of interaction among these low molecular weight polystyrenes in the AAD-1 SEC Fraction-II matrix. This is probably because the SEC Fraction-II materials are a poor solvent for polystyrenes, causing them to form spheres and not inducing uncoiling to form interacting chains.

The above experiments demonstrate that rheological properties of mixtures of AAD-1 SEC Fraction-II with low molecular weight (< 3,700 daltons) polystyrenes are a function of the mass percent of model compound, but that there is little response to changes in molecular weight at low (<5 percent) mass levels. Many asphalts contain approximately 15 mass percent SEC Fraction-I, the polar, aromatic component that is responsible for elastic properties and is the viscosity-enhancing fraction, and AAD-1 is one such asphalt (24 percent SEC Fraction-I). Asphalt AAD-1 is much more viscous than the 15 mass percent polystyrene mixtures and has pronounced elastic properties. If a comparison between the polystyrene mixtures and neat asphalt AAD-1 is valid, it may be concluded that the SEC Fraction-I materials of AAD-1 have effective molecular weights much larger than 3,700 daltons in asphalt matrices.

MONITORING SEC SEPARATIONS BY REFRACTIVE INDEX

Preparative SEC separations of toluene solutions of asphalts into various fractions have been based on the fluorescent response of eluates to 350 nm radiation. Initial eluates are non-fluorescent and are collected as SEC Fraction-I. Succeeding eluates are fluorescent, and in most asphalts, the cutpoint is fairly sharp, involving only a few mL of eluate. The first observation of this cutpoint was made by Dr. George Wu during the SEC separation of Boscan Crude Oil in 1965. This work was part of American Petroleum Institute Project 60. The non-fluorescent fraction contains the most polar and aromatic components of an asphalt, which would be expected to be individually fluorescent. The fluorescence of these molecules presumably is suppressed by their association, so it is valid to assume that molecular associations of these molecules exist in toluene solution. Whether or not such molecular associations are identical to or resemble those in native asphalts is not known with certainty. It has been assumed that there is a resemblance and that dissolving asphalts in toluene does not break up the stronger molecular associations. The cutpoint between SEC Fraction-I and II is based on a fundamental chemical property difference and is not arbitrary.

Preparative SEC separations also may be monitored by refractive index. Unlike fluorescence, which responds to aromatic molecules, and not aliphatics, refractive index monitors aliphatic and aromatic structures. However, the aromatic response of asphalts is canceled out by the solvent, toluene. It is of interest to measure the distribution of aliphatic materials through an SEC separation, so the SHRP core asphalts were fractionated by preparative SEC using a refractive index (RI) detector to monitor the separations. The RI traces for six of the asphalts are illustrated in figures A-2 to A-7. In all these figures, the initial response corresponds to that of solvent alone. The portions of the chromatograms designated F1 over double arrows serve to identify SEC Fraction-I.

In all six figures, an initial RI peak is observed, corresponding to high apparent molecular weight components containing considerable amounts of non-aromatic functionalities. A second peak also is observed in the RI traces. The apex of this second peak corresponds roughly with the fluorescence cutpoint referred to earlier. There follows a broad third peak, which then tapers off. The molecules in the latest eluates therefore are not highly aliphatic. They are, by definition, the smallest molecules in an asphalt. These conclusions had been tentatively reached by other studies (Volume I, chapter 3), and are confirmed by the RI data. The RI data also suggest that SEC Fraction-I consists of two fundamentally different kinds of components, at least with respect to aliphatic structural features. There are insufficient data at present to speculate on what these differences might be.

To measure material distributions corresponding to the RI peaks, SEC separations of three asphalts were performed in which asphalts were fractionated into three fractions. The initial cutpoint corresponded to the valley between the first two RI peaks. The second cutpoint was the onset of fluorescence, usually corresponding to the apex or shoulder of the second RI peak. Thus, compared with conventional preparative SEC separation into two fractions, the separations involving RI detection produce SEC Fraction-II as usual, but separate SEC Fraction-I into two subfractions, Ia and Ib. Results of the mass distributions for three asphalts are listed in table A-6. The Ia subfraction is larger than the Ib subfraction for all three asphalts. However, AAG-1 has relatively more Ib (compared with Ia) than AAD-1 or AAB-1. This is probably because AAG-1 contains relatively small amounts of strongly polar aromatic components, which form extended molecular associations. It is assumed that the SEC Ia subfraction would contain stronger molecular associations than SEC Ib subfractions.

SEC Fraction-I subfractions a and b were not further characterized. It is likely that subfraction Ia corresponds roughly to subfractions I-1 and I-2 reported in Volume I, chapter 3, and subfraction Ib corresponds to I-3. These subfractions were prepared by refractionations of SEC Fraction-I of the SHRP core asphalts by preparative SEC. In that chapter, it was noted that the properties of subfractions I-1 and I-2 are similar, but differ from I-3. As an example, I-1 and I-2 have much higher apparent molecular weights and are more aromatic than I-3 and I-4. It appears that this difference may be detectable by refractive index in the initial SEC fractionation of an asphalt.

STUDIES OF SEC FRACTIONS OF AGED ASPHALTS

Much effort has been expended in this program to elucidate the mechanism of asphalt oxidative aging. Results to date show that there is an initial, rapid oxidation, referred to as the "initial spurt" by J. C. Petersen, followed by a longer period of slower oxidation (Volume I, chapter 4). The "initial spurt" is characterized by oxidation of sulfur atoms in thioethers to form sulfoxides, along with a steep rise in asphalt viscosity. It is not known that the sulfoxide buildup causes the viscosity increase.

In support of this effort, several of the SHRP core asphalts were oxidatively aged by means of the thin film oven (TFO) procedure followed by pressure aging vessel (PAV) treatment at 60°C (140°F) for 96 hours. This time period coincides with the "initial spurt." The aged samples then were separated by preparative SEC into seven fractions. The first of these is SEC Fraction-I. After the onset of fluorescence, six more fractions were collected. Thus SEC Fraction-II is divided into six subfractions in this procedure, instead of eight. This is a variation from the usual procedure. The three latest eluting subfractions, II-6, II-7, and II-8, are combined in this modified method and are collectively designated as II-6. This was done because the small quantities of subfractions II-7 and II-8 preclude measurements of their properties. Weights of the materials were recorded after drying, and infrared (IR) spectra were obtained. The mass fraction data are listed in table A-7. Compared with mass fraction data for unaged asphalts separated into equivalent fractions by SEC, the SEC Fraction-I component is significantly larger for the aged materials, with the exception of AAB-1. The II-5 and II-6 subfractions also are smaller for the aged materials. Thus one result of oxidative aging appears to be the buildup of molecular associations and a reduction in the amount of smaller entities.

The IR spectra of the aged asphalt SEC fractions and subfractions were obtained in carbon disulfide solution. These spectra (with the exception of figure A-8) are not shown here. The features of interest are the peaks at 1,030 cm^{-1} (corresponding to the sulfoxide functional group) and at 1,700 cm^{-1} (corresponding to the carbonyl group), which are qualitatively described in the following discussion. These spectra show that, at the end of the initial spurt, most oxidation has occurred on sulfur functional groups to form sulfoxides. Sulfoxides are observed in all SEC fractions and subfractions of the aged asphalts. There appears to be no particularly large concentration of sulfoxides in any one SEC fraction or subfraction. They are prominent in the most associated materials and in the least associated materials, the initial and latest eluates. This is hardly surprising because sulfur-containing molecules that can form sulfoxides are transformed from non-polar to polar molecules as a result of the oxidation of a sulfur atom to a sulfoxide. The most polar components in asphalts tend to occur in the strongest molecular associations (SEC Fraction-I) and, somewhat surprisingly, in the lowest molecular size fraction. Adding one atom of oxygen (16 daltons) to an asphalt molecule containing one sulfur atom should not affect partitioning behavior in SEC unless the molecule becomes part of molecular associations that the original molecule was not a part of. Even the smallest molecules of asphalts are large enough that adding 16 daltons will not, by itself, alter SEC partitioning.

Of great interest is the sharpness of peaks in IR spectra of the II-5 and II-6 subfractions of all the aged asphalts. Part of the IR spectrum of subfraction II-6 of oxidatively aged AAF-1 is shown in figure A-8. In these subfractions, the sulfoxide region is almost a double peak, with a maximum at 1,030 cm^{-1} and a distinct shoulder at 1,055 cm^{-1}. The 1,055 cm^{-1} shoulder is ascribed to aromatic sulfoxides. The sulfoxide peaks of most aged asphalts and asphalt fractions usually are not sharp enough to permit distinction between aliphatic and aromatic sulfoxides. The distinction is not evident in the IR spectra of the other SEC fractions and subfractions of the aged asphalts.

Very prominent peaks at 750 cm^{-1}, 810 cm^{-1}, and 870 cm^{-1} are observed in the IR spectra of the SEC-II-6 subfractions of all seven aged asphalts. These peaks correspond to aromatic carbon-hydrogen vibrations and demonstrate that relatively unsubstituted one and two ring aromatic compounds are present in these subfractions. Such aromatic compounds most likely would be of low molecular weight and would be found in the last eluates of SEC separations. They would be less likely to engage in molecular associations than aromatic compounds having more than two rings.

The II-6 subfractions also are characterized by very large 3,485 cm^{-1} peaks, corresponding to hydrogen atoms bonded to nitrogen in pyrroles, indoles, and carbazoles.

Ketone concentrations of the SEC fractions and subfractions of the seven lightly aged asphalts are listed in table A-8. In most of the materials, ketone concentrations are not large because sulfur compounds mostly are oxidized during the "initial spurt." In four aged asphalts (AAA-1, AAB-1, AAD-1, AAK-1) most of the ketones formed are observed in the SEC-II subfractions. Few ketones are observed in the SEC Fraction-I materials. These four asphalts are the least compatible (most associated) of the SHRP core asphalts, measured by Heithaus titrations, relative viscosities, and other methods. They contain substantial amounts of SEC Fraction-I materials before oxidative aging. It is speculated that molecules involved in molecular associations may be somewhat less susceptible to oxidation compared with molecules not involved in associations. This is because oxidation occurs at only certain reactive functional groups in a molecule. Being part of a molecular association may protect the reactive functional groups from oxygen attack. The presence of sulfoxides in SEC Fraction-I materials may result from conversion of non-polar, non-associating sulfides to polar sulfoxides. That is, sulfoxides in SEC Fraction-I materials of aged asphalts may not be from molecules in original molecular associations of the unaged asphalts. The above ideas are speculative, and there is no direct evidence to support them.

The ketones in the SEC Fraction-II subfractions of aged asphalts AAA-1, AAB-1, AAD-1, and AAK-1 are slightly concentrated in the subfractions (SEC II-4 to II-6) of lower or intermediate molecular weight, indicating that oxidation at carbon atoms to form ketones occurs mainly in the asphalt solvent moiety during the initial spurt in these asphalts. Asphalts AAC-1, AAF-1, and AAG-1 are relatively compatible asphalts. They do not contain as large amounts of SEC Fraction-I as the other four asphalts. Oxidative aging increases the amount of this fraction. The SEC Fraction-I of aged AAC-1 and AAF-1 contain significant amounts of ketones. The lower molecular weight SEC-II subfractions of aged AAC-1 and AAG-1 contain large amounts of ketones. Thus, in these three asphalts (AAC-1, AAF-1, AAG-1), carbon oxidation is more pronounced during the "initial spurt." This is because these three asphalts contain less sulfur and smaller amounts of associating materials. The participation in molecular associations in less compatible asphalts may protect the components of the associations from mild oxidation.

The above results support suggestions about the mechanism of asphalt oxidation proposed by J. C. Petersen. Oxidation at sulfur and possibly aromatization of low molecular weight species are the earliest events when asphalts are exposed to oxygen at moderate temperatures and pressures. Few ketones are formed because reactive benzylic compounds are part of molecular associations in less compatible asphalts. As oxidation proceeds and reactive sulfur containing molecules are converted to sulfoxides, unprotected benzylic carbon-containing carbons react with oxygen. This process occurs sooner in compatible, low sulfur asphalts. In any event, the products formed in the early stages of oxidation cause large increases in viscosities of asphalts. As oxidation proceeds and sulfur compounds are used up, reaction with activated carbon groups to form ketones becomes more important, but formation of these compounds does not appear to cause such great viscosity changes as the initially formed oxidation products.

If asphalts are viewed as dispersions of associated molecules in a bulk solvent, oxidative aging results in the formation of more associated material at the expense of solvent. The nature of the solvent also is transformed, becoming more polar. This, in turn, solubilizes the additional associated materials.

CROSSBLENDS OF SEC FRACTIONS OF AGED AND UNAGED ASPHALT AAB-1

Samples of asphalts oxidatively aged by an initial thin film oven (TFO) procedure followed by pressure aging vessel (PAV) treatment at 100°C (212°F) for 20 hours were separated into two fractions by SEC. As usual, onset of fluorescence was used as the cutpoint between the two fractions. The cutpoint was observed to occur at nearly the same elution volume in the aged asphalts as in the unaged parent asphalts, although yields of SEC Fraction-I materials in the aged asphalts are greater.

Crossblends of SEC fractions of oxidatively aged asphalt AAB-1 with complementary SEC fractions of the unaged parent asphalt have been prepared. The crossblends consist of SEC Fraction-I of aged AAB-1 with SEC Fraction-II of the unaged parent asphalt, and SEC Fraction-I of the unaged parent asphalt with SEC Fraction-II of oxidatively aged AAB-1. Natural abundance levels of the crossblend is that of the unaged parent asphalt. Rheological properties of the crossblends were determined on the dynamic shear rheometer. Viscosities and tan δ values at 25°C (77°F) are listed in table A-9. Also listed in table A-9 are data for a control sample, in which the two SEC fractions of unaged AAB-1 are mixed together at natural abundance level, 20.8 percent SEC Fraction-I and 79.2 percent SEC Fraction-II. To prepare the crossblends, each of the two SEC fractions was mixed together in dichloromethane solution, and then the solvent was removed. Some light ends are lost in this procedure, so that the rheological properties of the original asphalt are not exactly reproduced.

The data in table A-9 show that the mixtures containing oxidatively aged components are somewhat more viscous than the control sample. However, neither is as viscous as a sample of

AAB-1 oxidatively aged under the same conditions. Since there is not a large buildup of SEC Fraction-I in the oxidation of AAB-1 (this is the rationale for selecting AAB-1 for this study – see table A-7), it would seem that for this asphalt interactions between the two SEC fractions in the aged asphalt enhance viscosity. It is possible that the SEC Fraction-II component of the aged asphalt has a much higher viscosity than the unaged asphalt. Unfortunately, the viscosity of aged SEC Fraction-II was not measured. The results of this experiment indicate that aging affects rheological properties throughout an asphalt and does not just affect one component. This conclusion is based on the comparison of the rheological properties of aged AAB-1 with rheological properties of the crossblends.

SEC FRACTIONATION OF IEC NEUTRAL FRACTIONS

The neutral fractions of asphalts obtained by the technique of ion exchange chromatography (IEC) contain the least polar components of asphalts. Properties of these materials have been published for the SHRP core asphalts [Branthaver et al. 1993]. Work done in this program involving these materials is described in Volume I, chapter 3 of this report. The IEC neutral fractions contain non-polar aliphatic hydrocarbons, sulfur-containing compounds, and weakly polar aromatic compounds. In particular, waxes comprise much of the IEC neutral fractions in some asphalts. Waxes in asphalts have been subjects of much investigation because of their great influence on low temperature physical properties.

Number-average molecular weight values of IEC neutral fractions are lower than those of whole asphalts, as would be expected. The ranges of molecular weights in IEC neutral fractions of asphalts have not been determined. The molecular weight distributions of organic mixtures influence their physical properties, so it is desirable to know what the molecular weight ranges are for asphalt IEC neutral fractions.

Neutral fractions of asphalt AAB-1 were generated using Method 11, described earlier in this volume. An amount of 16.0 g of the IEC neutrals of AAB-1 was dissolved in toluene and the solutions were separated into nine fractions by size exclusion chromatography (SEC). Cutpoints were identical to those that would have been used had the original asphalts been separated by SEC. Thus, an SEC Fraction-I component was collected, followed by various SEC Fraction-II subfractions. All the materials were dried and molecular weights were measured by vapor phase osmometry (VPO) in toluene at 60°C (140°F). There was not enough material in the two last eluted subfractions to obtain molecular weights, so they were not measured. Table A-10 lists the VPO molecular weight values and mass fractions of these SEC fractions and subfractions. Surprisingly, there is a substantial amount of SEC Fraction-I material (5 mass percent) and it has a high molecular weight. Because of the nature of the materials, this value is a true molecular weight, and not a result of molecular association. Some of the SEC Fraction-II subfractions also are quite large, but the majority of the material is below 700 daltons. A weight average molecular weight ($\sum = 847$) was calculated. This is much higher than the VPO number-average molecular weight value of the AAB-1 IEC neutral fraction of 660 daltons.

In summary, the IEC neutral fraction of AAB-1 was found to contain substantial amounts of fairly high molecular weight material. This result is somewhat unexpected. The high molecular weight component, if fully saturated, would average about 200 carbon numbers. Large molecules such as this would be poor solvents and would disproportionately influence rheological properties of asphalts. Their presence may explain the surprisingly low solubility parameter values reported for the IEC neutral fractions in Volume I, chapter 3 of this report.

Table A-1. Base concentrations of AAB-1 SEC Fraction-II subfractions.

SEC fraction and subfraction	Mass % of SEC fraction and subfraction[1]	Moderately strong bases in SEC subfraction (meq/g)[2]	Weak bases in SEC subfraction (meq/g)[2]
I	20.0	-	-
II-1	11.3	0.11	0.11
II-2	19.4	0.085	0.08
II-3	23.0	0.08	0.08
II-4	17.2	0.11	0.08
II-5	7.2	0.14	0.08
II-6	1.8	0.13	0.08
Total	99.9	0.079	0.067

[1] Masses normalized to 100%.

[2] Averages of two determinations.

Table A-2. Base concentrations of SEC Fraction-II subfractions of AAB-1 (98%) mixed with 1,12 diaminododecane (2%).[1]

SEC fraction and subfraction	Mass % of SEC fraction and subfraction		Moderately strong bases in SEC subfraction (meq/g)		Weak bases in SEC subfraction (meq/g)	
	run 1	run 2	run 1	run 2	run 1	run 2
I	20.6	20.6	-	-	-	-
II-1	11.1	11.3	0.12	0.12	0.12	0.12
II-2	17.7	18.4	0.09	0.095	0.08	0.095
II-3	24.1	23.9	0.08	0.085	0.08	0.08
II-4	17.9	16.4	0.11	0.10	0.08	0.12
II-5	6.9	7.6	0.10	0.10	1.19	1.00
II-6	1.5	1.7	0.08	0.10	0.33	0.47
Totals	99.8	99.9	0.076	0.077	0.148	0.154

[1] 2% 1,12 diaminododecane adds 0.2 meq/g of base to mixture.

Table A-3. Base concentrations of SEC Fraction-II subfractions of AAB-1 (98%) mixed with N,N dimethylnonylamine (2%).[1]

SEC fraction and subfraction	Mass % of SEC fraction and subfraction		Moderately strong bases in SEC subfraction (meq/g)		Weak bases in SEC subfraction (meq/g)	
	run 1	run 2	run 1	run 2	run 1	run 2
I	20.0	19.8	-	-	-	-
II-1	11.0	11.3	0.12	0.12	0.10	0.10
II-2	18.3	19.0	0.09	0.09	0.065	0.065
II-3	22.7	22.9	0.09	0.09	0.06	0.07
II-4	18.9	17.3	0.035	0.07	0.095	0.08
II-5	7.2	7.7	0.9	0.65	0.04	0.07
II-6	1.7	1.9	0.05	0.09	0.11	0.08
Totals	99.8	99.9	0.122	0.115	0.59	0.60

[1] 2% N,N dimethylnonylamine adds 0.117 meq/g of base to mixture.

Table A-4. Rheological properties of mixtures of AAB-1 with three model compounds.

Model compound in mixture and mass %	Temp., °C	ω, rad/s	G′, Pa	G″, Pa	Viscosity, η*, Pa·s[1]	Tan δ
Zinc tetraphenyl-porphine, 5%	25	0.1	8,243	33,705	346,990	4.1
		1.0	77,722	213,110	226,850	2.7
		10.0	532,940	1,119,200	123,980	2.1
	60	0.1	-	35	351	-
		1.0	7.	331	331	-
		10.0	4 239	3,038	305	12.7
Lithium stearate, 2%	25	0.1	2,709	14,095	143,530	5.2
		1.0	30,058	96,890	101,450	3.2
		10.0	235,520	558,940	60,666	2.4
	60	0.1	-	19	186	-
		1.0	-	188	188	-
		10.0	113	1,776	179	16
1,3,5 cyclohexane-tricarboxylic acid, 2%	25	0.1	2,567	12,828	130,810	6.1
		1.0	27,823	85,940	90,340	3.1
		10.0	209,990	482,620	52,644	2.3
	60	0.1	-	19	194	-
		1.0	-	189	181	-
		10.0	118	1,703	170	14.4

[1] The viscosity of AAB-1 worked up in the same manner as the above samples was observed to be 176,300 Pa·s at 25°C and 1.0 rad/s, and 229 Pa·s at 60°C and 1.0 rad/s. The viscosity of neat AAB-1 was observed to be 95,000 Pa·s at 25°C and 1.0 rad/s, and 160 Pa·s at 60°C and 1.0 rad/s.

Table A-5. Viscosities, 25°C, 1.0 rad/s, of mixtures of AAD-1 SEC Fraction-II[1] with polystyrenes of various molecular weights.

Molecular weight of polystyrene, daltons	Concentration of polystyrene in mixture, mass %	Viscosity, Pa·s	δ, deg
2,727	2	434	-
2,727	4	668	-
2,727	5	640	-
2,727	10	1,560	88.9
2,727	15	2,235	88.8
3,700	2	537	-
3,700	4	661	-
3,700	5	827	-
3,700	10	1,700	87.7
3,700	15	2,915	88.8
12,600	2	462	-
12,600	4	411	-
12,600	5	822	-
12,600	10	96,330	88.0

[1] SEC Fraction-II of AAD-1 has a viscosity of 360 Pa·s at 25°C and 1.0 rad/s.

Table A-6. SEC separation of three asphalts into three fractions using cutpoints based on refractive index and fluorescence detection.

Asphalt	Yield of SEC fraction, mass %			Total
	Fraction-Ia	Fraction-1b	Fraction-II	
AAB-1	15.7	5.0	78.9	
AAB-1	16.6	6.0	77.4	
AAB-1	15.7	5.0	78.9	
Average, AAB-1	16.0	5.3	78.4	99.7
AAD-1	18.7	4.8	77.0	
AAD-1	18.2	4.2	78.0	
AAD-1	18.2	5.3	77.0	
AAD-1	18.8	3.7	77.4	
Average, AAD-1	18.5	4.5	77.4	100.4
AAG-1	6.6	3.4	89.3	
AAG-1	7.2	4.4	88.1	
Average, AAG-1	6.9	3.9	88.7	99.5

Table A-7. Mass fractions of SEC fractions and subfractions of unaged asphalts and TFO/PAV (60°C; 96 hours) aged asphalts.

Asphalt	SEC fraction or subfraction, mass % [1]						
	I	II-1	II-2	II-3	II-4	II-5	II-6
AAA-1	21.6	10.4	14.0	21.3	21.1	9.3	2.1
AAA-1 aged	27.4	10.1	14.4	21.7	18.5	6.5	1.3
AAB-1	20.9	10.7	18.0	25.0	16.7	7.2	1.9
AAB-1 aged	20.9	11.0	19.1	23.9	16.7	6.8	1.6
AAC-1	13.6	12.0	25.6	29.1	13.8	4.7	1.2
AAC-1 aged	19.3	12.2	23.9	25.1	12.8	4.6	2.2
AAD-1	23.4	9.4	11.2	17.6	22.3	12.3	3.0
AAD-1 aged	27.8	9.2	10.8	16.4	21.5	12.1	2.2
AAF-1	13.9	11.8	19.9	27.0	18.2	7.6	2.0
AAF-1 aged	18.8	12.6	20.1	24.9	15.8	6.4	1.5
AAG-1	11.9	8.8	17.4	27.0	22.0	10.4	2.8
AAG-1 aged	14.1	9.3	16.8	24.9	21.0	10.5	3.4
AAK-1	25.8	11.5	14.3	19.2	18.3	8.7	3.0
AAK-1 aged	30.0	10.9	14.0	18.8	17.7	6.7	1.8

[1] Normalized to 100%.

Table A-8. Ketone concentrations of SEC fractions and subfractions of TFO/PAV aged asphalts.

Asphalt	SEC fraction or subfraction, ketone concentration, mol/L							Total ketone concentration, mol/L
	I	II-1	II-2	II-3	II-4	II-5	II-6	
AAA-1	0.06	0.10	0.12	0.09	0.11	0.12	0.17	0.09
AAB-1	0.06	0.08	0.07	0.07	0.08	0.11	0.13	0.07
AAC-1	0.13	0.12	0.08	0.10	0.13	0.19	0.17	0.11
AAD-1	<0.05	0.10	0.13	0.13	0.11	0.08	0.08	0.09
AAF-1	0.09	0.11	0.08	0.09	0.11	0.14	0.15	0.10
AAG-1	0.05	0.13	0.12	0.12	0.12	0.20	0.25	0.12
AAK-1	trace	0.09	0.12	0.14	0.11	0.11	0.12	0.08

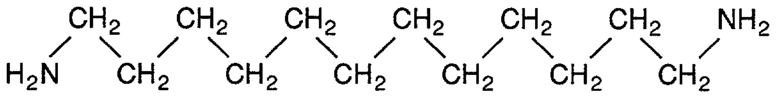
Table A-9. Viscosities of crossblends of aged and unaged SEC Fractions of AAB-1.

Composition of mixture	Viscosity, η, at 25°C and 1.0 rad/s, Pa·s	Tan δ at 25°C and 1.0 rad/s
SEC Fraction-I of unaged AAB-1 and SEC Fraction-II of TFO/PAV aged AAB-1	235,640	2.3
SEC Fraction-I of TFO/PAV aged AAB-1 and SEC Fraction-II of unaged AAB-1	194,320	2.2
SEC Fraction-I and SEC Fraction-II of unaged AAB-1	152,410	2.4
AAB-1, aged at 100°C for 24 hours	910,000	1.4

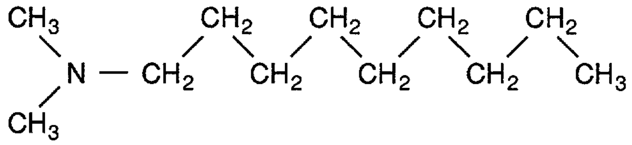
Table A-10. SEC fractionation of IEC neutral fraction of AAB-1.

SEC subfraction	Mass % of IEC fraction	Molecular weight (daltons)	Molecular weight (column 2) multiplied by mass % (column 3)
I	5.1	2,760	140.8
II-1	10.5	1,360	142.8
II-2	21.2	900	190.8
II-3	30.5	680	207.4
II-4	22.8	540	123.1
II-5	8.3	430	35.7
II-6	1.7	340	5.8 $\sum = 847$[1]

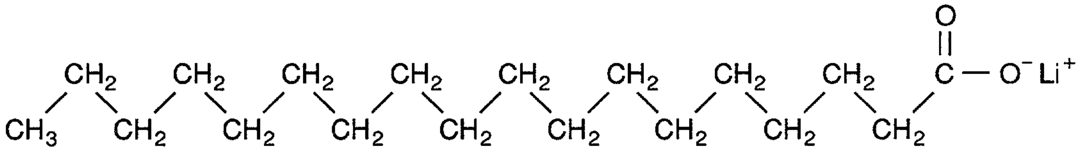
[1] This $\sum$ value is equivalent to the weight average molecular weight of the IEC neutral fraction of AAB-1.



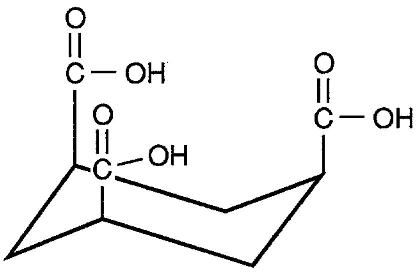
1,12 diaminododecane, MW = 200, MP = 68-70°C



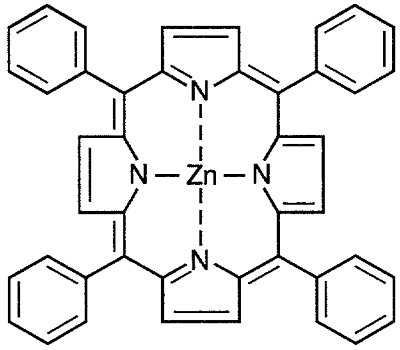
N,N dimethylnonylamine, MW = 171



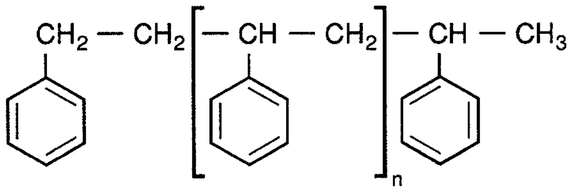
lithium stearate, MW = 290, MP = 220°C



1,3,5 cyclohexane tricarboxylic acid, MW = 216, MP = 215°C



zinc tetraphenyl porphine, MW = 678



polystyrene, n = 24, 36, 119, MW = 2,727, 3,700, 12,600

Figure A-1. Structures of model compounds added to asphalts and asphalt fractions.

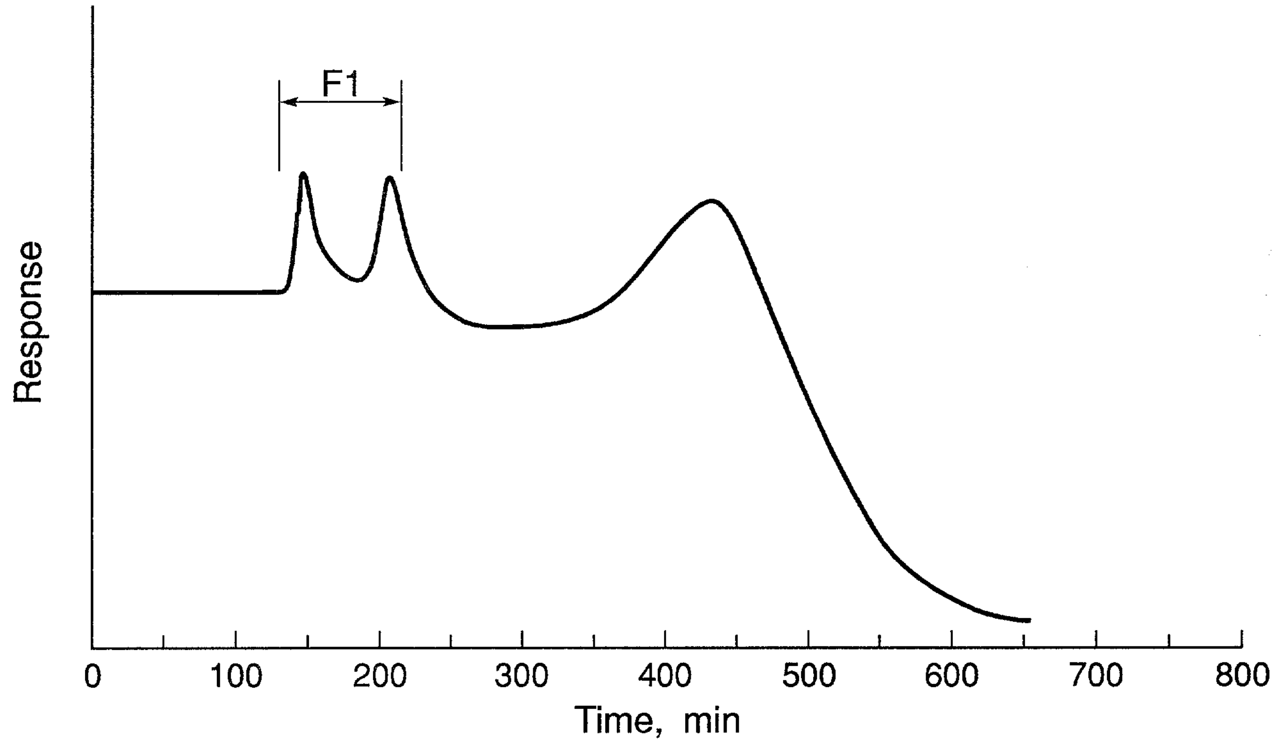


Figure A-2. RI trace of preparative SEC chromatogram of AAA-1.

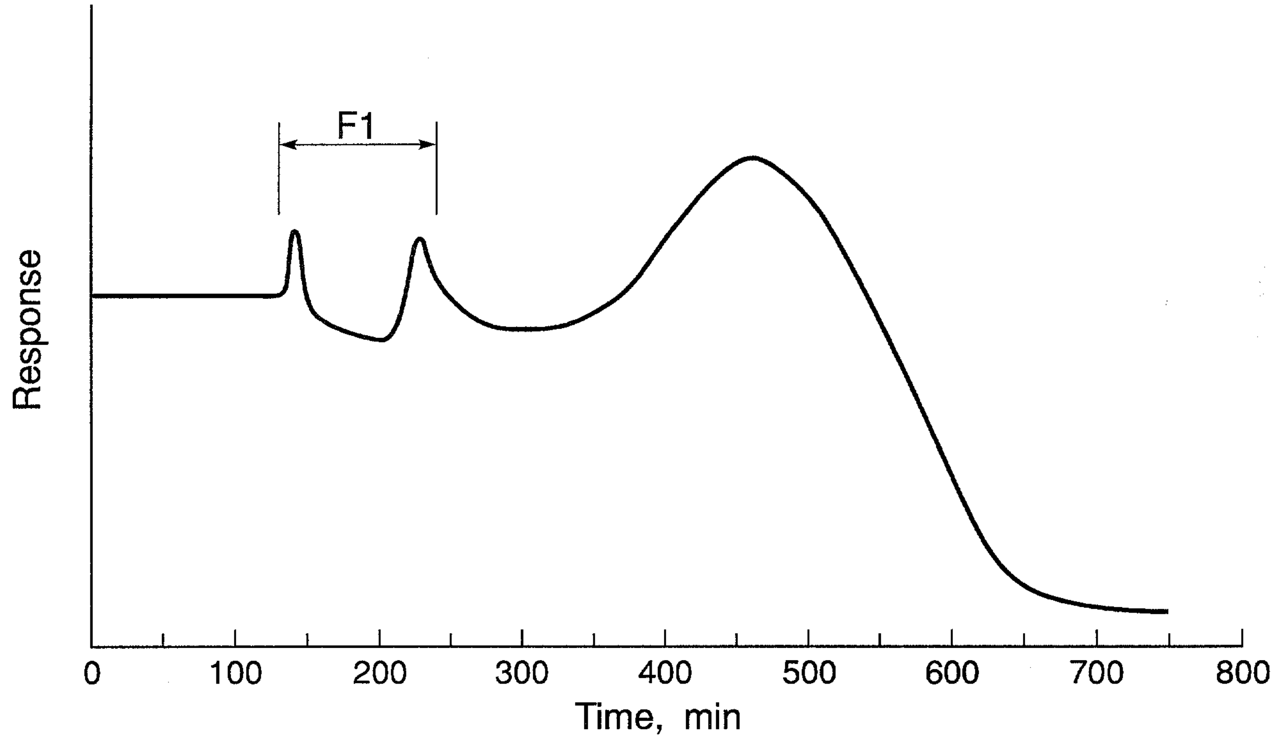


Figure A-3. RI trace of preparative SEC chromatogram of AAB-1.

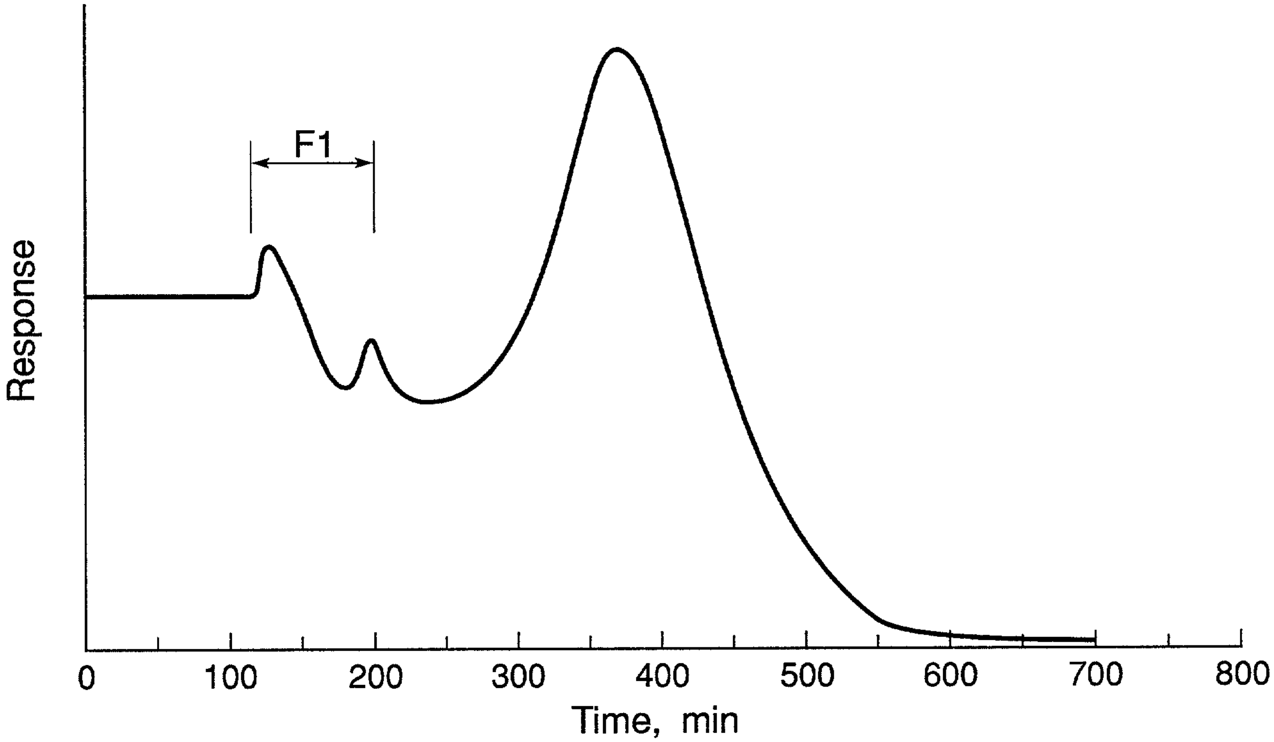


Figure A-4. RI trace of preparative SEC chromatogram of AAC-1.

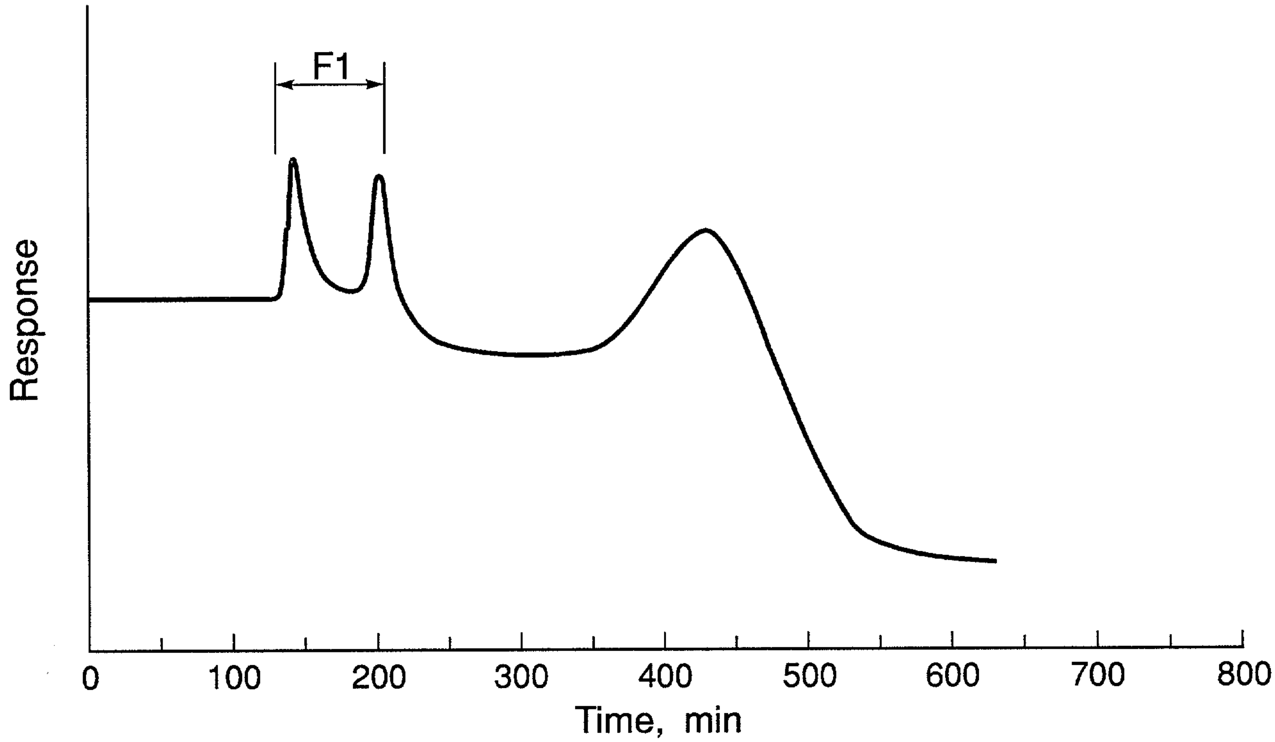


Figure A-5. RI trace of preparative SEC chromatogram of AAD-1.

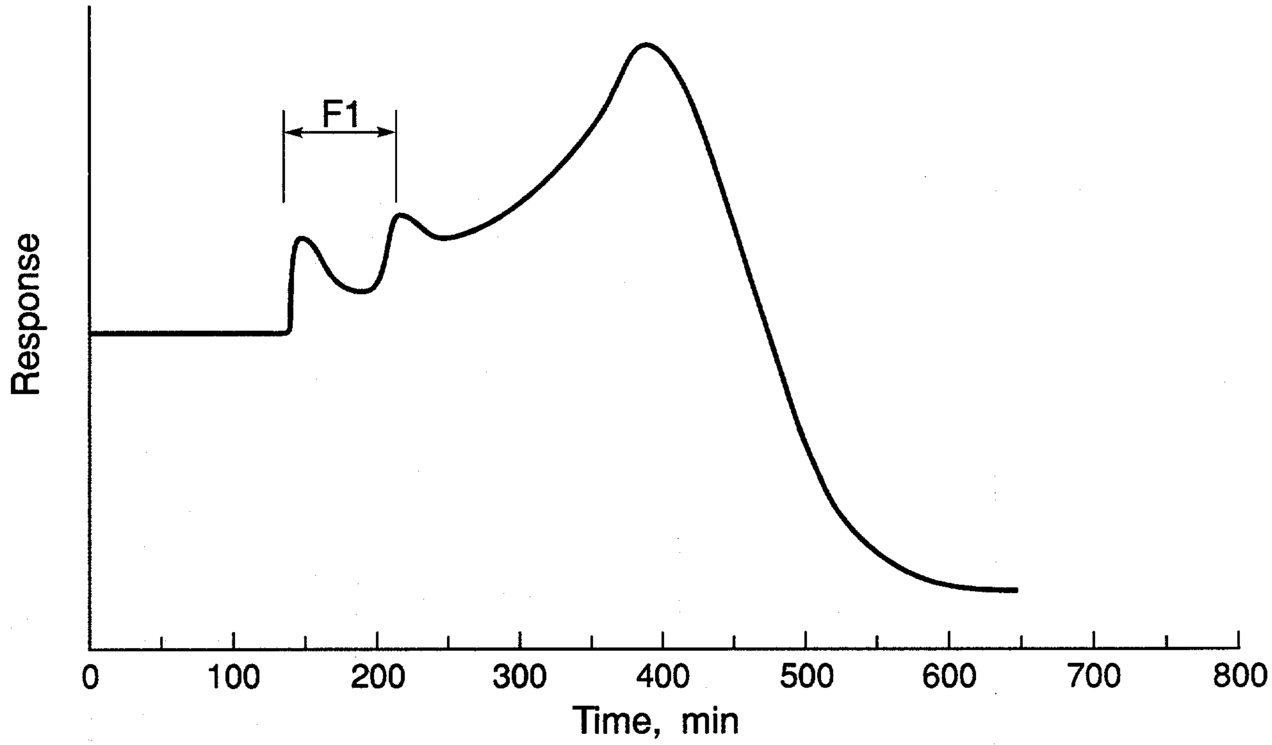


Figure A-6. RI trace of preparative SEC chromatogram of AAF-1.

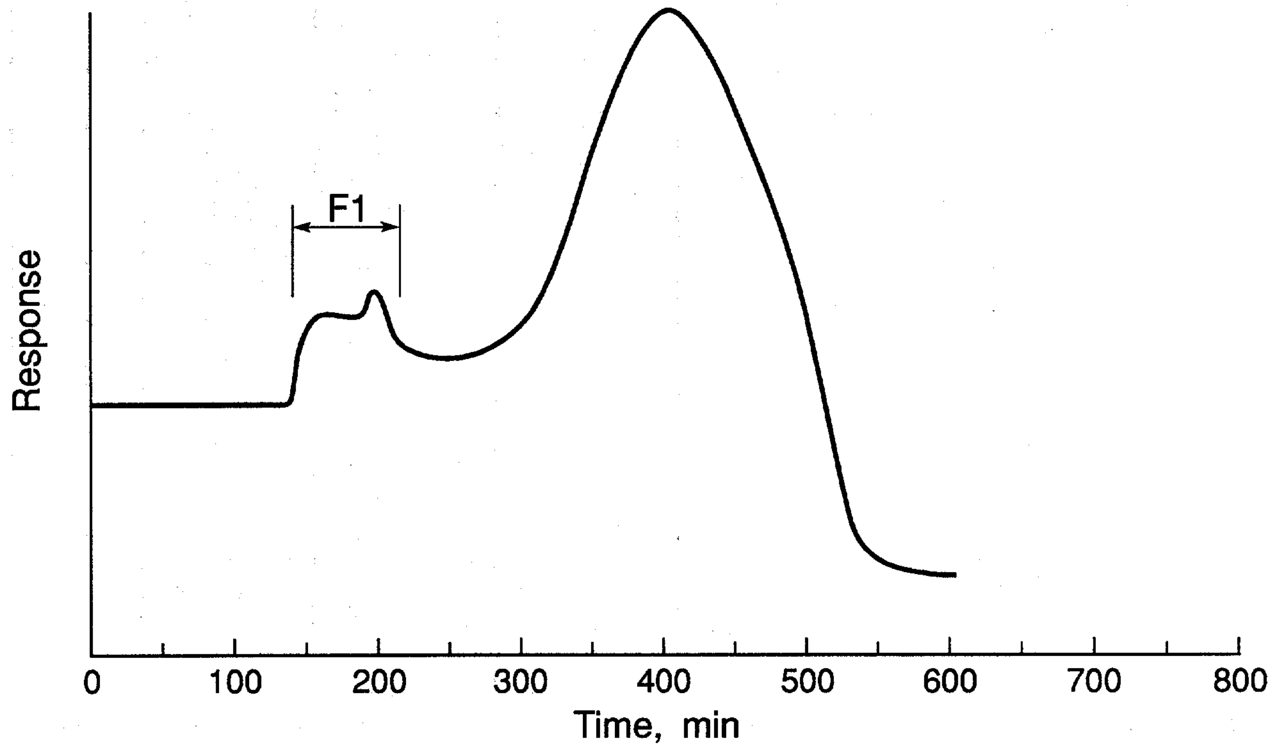


Figure A-7. RI trace of preparative SEC chromatogram of AAG-1.

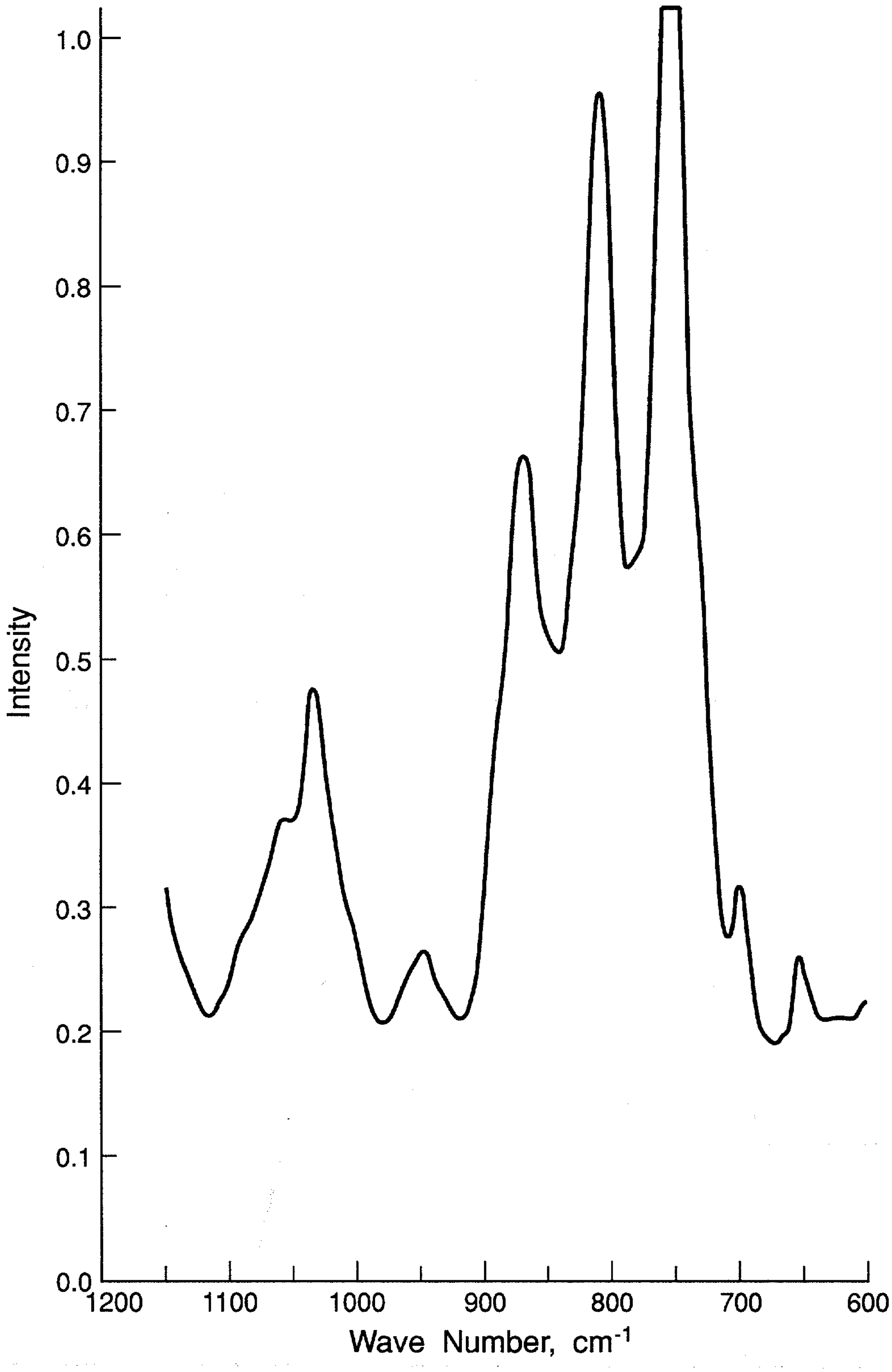


Figure A-8. Partial infrared spectrum of SEC Fraction II-6 of oxidatively aged AAF-1.

B. PYRIDINE TEST

ABSTRACT

This section of Volume II contains the sample preparation techniques and experimental procedures for the development of the pyridine test. The interpretation of results is in chapter 5 of Volume I.

INTRODUCTION AND APPLICABILITY

This work was designed to investigate the thermal desorption of pyridine from aggregates as a possible fast test for predicting the water-stripping characteristics of aggregates. The research investigated the hypothesis that pyridine forms bonds of different strengths with various aggregates and is displaced from aggregates by water according to the bond strength. The stronger the bond strength, the more difficult the displacement of pyridine from aggregate by water. In a pyridine test for moisture sensitivity, thermal desorption of the pyridine from various aggregates would occur at different temperatures, the highest temperatures being required to desorb pyridine most tightly bound to an aggregate. By measuring quantitatively the amount of pyridine desorbed from different aggregates over selected temperature ranges, it would be possible to rank aggregates according to relative pyridine bond strength and develop a fast, predictive, moisture sensitivity test for aggregates.

The intent of the test development was to replace the relatively slow Lottman TSR (tensile strength ratio) and WRI pedestal tests with a fast, simple, water-stripping prediction test. Pyridine desorption data from the earlier studies on Lottman aggregate samples [Petersen et al. 1982] were plotted against the Lottman TSR data for Idaho, Montana, Virginia, Colorado, Arizona, and Georgia. The modest correlation between the desorption data and the Lottman data for this small sample set indicated that additional research was needed to determine if a correlation between pyridine thermal desorption data and Lottman TSR data could be found. At the conclusion of this work, the r-squared values for all correlations were too low to be of interest.

STANDARD PROCEDURES

Sample Preparation

This is the procedure used to prepare aggregate samples for pyridine desorption experiments and additional pyridine water-wash experiments. The aggregate samples were the same materials obtained from Lottman and used by Petersen et al. [1982] in the earlier experiments. Steps 1 through 6 below are the procedures used by H. Plancher published in Petersen et al. [1982]. This procedure was used to replicate previous experiments.

Additional aggregates were obtained from the Materials Reference Library and from industrial sources. The aggregates were sized (60-80 mesh) using a disk pulverizer and the samples were screened to the mesh size required for the experiments. The sized materials were washed with distilled water, deionized water, or tap water to remove dust and were dried at 150°C (302°F) for several days. No differences in desorption results were observed among the uses of distilled water, deionized water, or tap water.

Procedure

1. Save about 1.0 g of the washed and dried aggregate for blank nitrogen desorption experiments.

2. Place about 1.0 g of aggregate in an open container and submerge the aggregate in about 5 mL of pyridine (neat, reagent grade). Immediately place the container, open to the atmosphere, in a hood and allow the pyridine to evaporate until the sample of aggregate appears dry.

3. Continue to dry the sample in an oven (with circulation of air) for at least 48 hours at 115°C (239°F).

4. Place about 0.5 g of the pyridine-treated aggregate, accurately weighed, on a fritted-glass filter and wash with 50 mL of distilled water in 10 mL increments.

5. Dry the water-washed aggregate on the filter using air at ambient temperature.

6. Place recovered, pyridine-treated, water-washed aggregate in crucible covers and dry overnight in a 60°C (140°F) oven.

Calibration

An Antek 7000 instrument, which measures trace quantities of nitrogen as it is desorbed during a programmed temperature rise, was operated under the same conditions of detector sensitivity and gas flows for all of the work described in the project. These were: detector sensitivity setting no. 1, ozone flow 1.5 mL/min, pyro flow 3.5 mL/min, inlet no. 1 flow 0.5 mL/min, inlet no. 2 flow 3.5 mL/min. The nitrogen detector was calibrated using the calibration software program of the instrument and two solid calibration standards provided by Antek. For calibration, weights of standard samples are entered as milligrams, and the data readout is reported in parts per million. The relative standard deviation for calibration standards was about 5 percent. The pyrotube was temperature calibrated using a data logger having type K thermocouples and a National Institute of Standards and Testing (NIST) traceable thermometer. A note of caution: because the internal temperature of a pyrotube is variable along the length of the tube, temperatures of the sample boat must be measured by an internal thermocouple.

Temperature Programming

Temperature program no. 1, which was used for the data reported in Volume I, is designed to heat samples between 260°C (500°F) and 818°C (1,504.4°F) in six increments over a period of 30 minutes with a hold time of 2 minutes per increment. To conduct an experiment, a sample of aggregate (60-80 mesh, nominally 100 mg) accurately weighed to five (5) decimals in a quartz boat, was carefully positioned in the heating zone of the pyrotube set for 260°C (500°F). The temperature program was started immediately. The instrument was programmed to hold at 260°C (500°F) for 2 minutes and then ramp to temperatures of 353, 446, 539, 632, 725, and 818°C (667.4, 834.8, 1,002.2, 1,169.6, 1,337, and 1,504.4°F) with ramp times of 2 minutes and hold times of 2 minutes. The pyrotube of the instrument was temperature-calibrated using a multi-channel digital thermometer having type K thermocouples calibrated to plus or minus 2°C (3.6°F).

Temperature program no. 2 used for the Lottman samples described in Volume I mimicked the early experiments of Petersen and Plancher [Petersen et al. 1982] and is designed to heat samples from 260°C (500°F) to 650°C (1,202°F) in three increments over a period of 30 minutes with hold times of 6, 4, and 7 minutes. In these experiments the same loading procedure was followed. The boat was carefully positioned in the heating zone at 260°C (500°F) and held at that temperature for 5 minutes. The first ramp was performed in 1 minute and raised the temperature to 330°C (626°F) with a hold time of 6 minutes. The second ramp was performed in 4 minutes and raised the temperature to 470°C (878°F) with a hold time of 4 minutes. The third and final ramp was performed in 7 minutes and raised the temperature to 650°C (1,202°F) with a hold time of 4 minutes. This temperature program produced nitrogen desorption profiles that very closely duplicated the earlier nitrogen desorption profiles.

Testing

Three thermal desorption experiments were performed on each aggregate. First, washed raw aggregate was tested to determine the indigenous nitrogen content of each aggregate and the temperature range over which the indigenous nitrogen was thermally removed. Second, pyridine coated aggregate was tested to determine the amount of pyridine adsorbed by the aggregate and the temperature range over which pyridine desorbed from the aggregate. The amounts of pyridine desorbing at temperature of 260, 330, 470, and 650°C for the various aggregates were compared. Third, pyridine-treated aggregate was washed with water and dried as described above. Thermal tests then showed the amount of pyridine remaining on the aggregate after the water wash and the temperature range over which the pyridine thermally desorbed. The aggregates were then ranked with respect to each other according to the amount of pyridine desorbed above 300°C. The aggregates having the largest amounts of pyridine desorbed above 300°C were thought to be aggregates least susceptible to water stripping because pyridine was tightly bound to the aggregate and not displaced by water.

Reaction of Model Carboxylic Acid With Aggregates

The model acid compound used to mimic the carboxylic acids occurring in asphalts was indole-3-acetic acid. This carboxylic acid, like the carboxylic acids in asphalts, reacts with aggregates to form soluble or insoluble metal salts that coat the aggregate surface at the aggregate-asphalt interface. This model acid also contains one nitrogen per molecule, which is the material detected by the Antek 7000 instrument. The reaction was used to rank the aggregates according to the degree of chemical reactivity with the acid.

The following procedure was used to measure the amount of indole-3-acetic acid that reacted with each aggregate over a period of 48 hours. Five grams of aggregate (60-80 or 80-100 mesh) was placed in a glass vial to which was added 20 mL of 0.01 M solution of indole-3-acetic acid (reagent grade) dissolved in methanol (95 percent)/water (5 percent). A 0.01 M solution of indole-3-acetic acid (molecular weight = 174.2) contains 1.742 g of the acid per liter of solution. The reaction of carboxylic acid and aggregate was allowed to continue at 60°C (140°F) for 48 hours. The reaction solution was removed with a syringe, filtered through a 0.2 micron syringe filter, and a portion was saved for x-ray fluorescence analysis and atomic absorption analysis of dissolved metals such as calcium and sodium. A remaining portion of the reaction solution was potentiometrically titrated with tetrabutylammonium hydroxide (TBAH, 0.01 M) dissolved in a solution of propanol, ethanol, and water (1:1:1 by volume) to measure the amount of indole-3-acetic acid that reacted with each aggregate. SHRP aggregates RA, RB, RC, RD, RE, RF, RG, RH, RJ, RK, and RL obtained from the Materials Reference Library were thus ranked according to their chemical reactivity with indole-3-acetic acid, the chemical reactivity reported as milliequivalents/gram.

Precision

Two replicate data sets were produced for the development of the predictive water-stripping test based on composition. Information concerning precision is included in the reports containing statistical calculations produced by the University of Wyoming [Seier 1997; Stoevska-Kojouharov 1997]. In general, the results of the replicate experiments were reproducible and the conclusions based on statistical analyses were the same for both experimental sets.

SUMMARY

Experiments conducted in this project showed that the development of a fast, simple test to predict the water-stripping characteristics of aggregates, based on the thermal desorption properties of pyridine from aggregates, was probably not feasible. The pyridine thermal desorption experiments demonstrated that pyridine does not selectively bind to aggregates, or is displaced from aggregates by water, to a degree that can be detected and measured by thermal desorption.

The experiments involving the reaction of carboxylic acids with aggregates demonstrated that the water-stripping characteristics of any asphalt-aggregate combination are influenced by the reaction chemistry of a few select chemical components of both the aggregate and the asphalt, in addition to nonreactive adsorption/desorption processes. Statistical analyses of the data set used in this work suggest that, based on the calcium, magnesium, and carbonate content of the aggregates and the carboxylic acid content of the asphalts, it may be possible to predict the water-stripping characteristics of any asphalt-aggregate pair. The development of a fast, predictive test for water stripping based on composition may be possible.

C. STERIC HARDENING TEST

ABSTRACT

This section of Volume II contains the sample preparation techniques and experimental procedures for the steric hardening experiments not included in Volume I or the data base. The work is in two parts. The first part describes measurements of steric (isothermal, reversible, time dependent) hardening in binders and the second part describes measurements of steric hardening in mastics.

INTRODUCTION AND APPLICABILITY

Steric hardening is the isothermal, reversible and time dependent hardening always observed in asphalts that have been heated to become a free-flowing liquid and then allowed to cool. Steric hardening is thought to occur as molecules in a randomly-oriented, complex mixture reorganize upon cooling over time to form an organized mixture of molecules in the lowest achievable thermodynamic state. In the laboratory and in the field, asphalts and asphalt pavements are usually observed to harden significantly in the first 72 hours of cooling and then continue to harden indefinitely at a lower rate. The long-term hardening results from oxidative aging and steric hardening. The steric hardening process can be reversed by heat, as accomplished in recycle processes.

Specially designed cup and cylinder cells (couettes) were used in a dynamic shear rheometer to measure, without disturbing the physical structure of the sample, the isothermal hardening and thermal restoration (softening) properties of asphalts. The magnitude of steric hardening was measured for 18 neat, rolling thin film oven (RTFO)-oxidized, and RTFO/pressure aging vessel (PAV)-oxidized asphalts. The effect of aggregate on steric hardening was measured in separate axial compression experiments using mastics. Measurements were made with an MTS Systems Corporation testing machine.

STANDARD PROCEDURES

Asphalt Binders

All rheological measurements using neat asphalts were made using a Rheometrics model RMS-605 dynamic shear rheometer. Special cup and cylinder sample cells, with removable indexing collars, were fabricated that contained 6.5 grams of asphalt. Rheological measurements were made in the dynamic oscillatory mode. This sampling and measurement technique allowed asphalt samples to be repetitively heat treated and/or stored over time without mechanically disturbing the sample. The hardening properties of the sample over time due to molecular structuring were thus measurable. The rheological parameters measured included dynamic viscosity, G', G'', and G^*. The instrumental conditions under which the data were recorded and example data can be found in chapter 5 of Volume I. All of the data are stored in the database.

The procedure for the measurement of rheological properties followed a precise experimental protocol in an effort to obtain reproducible data. In this work the properties being measured constantly changed as a function of the rate of cooling during sample preparation, storage temperature, and time. The following procedure was used for measuring the rheological properties of neat, RTFO-oxidized, and RTFO/PAV-oxidized asphalts. Couettes are first filled with asphalt weighed to four decimal places (usually 6.5000 g) and the cylinder is mounted in the cup with care being taken not to trap an air bubble under the cylinder. The couette is carefully mounted in the rheometer to maximize correct alignment.

1. The sample cell (couette) is annealed in the rheometer at 150°C (302°F) for 2 hours to melt the asphalt in the couette and produce an unstructured, uniformly positioned liquid.

2. The couette is cooled to 25°C (77°F) over a period of 1 hour.

3. The rheological properties of the sample are measured at 25°C (77°F) using selected instrumental parameters.

4. The undisturbed couette is removed from the rheometer and stored at 25°C (77°F) for the appropriate length of time in a constant temperature (± 2°C) oven: 24, 72, 168, 672, or 2,016 hours.

5. The stored sample is removed from the oven, remounted in the rheometer, and the rheological properties measured again at 25°C (77°F) using the original instrumental parameters to measure the amount of steric (isothermal hardening, intermolecular structuring) hardening that occurs during the period.

6. The couette is then heat-treated again in the rheometer, at 150°C (302°F) for 2 hours, to melt the sample and eliminate molecular structuring that has occurred.

7. The couette is returned to 25°C (77°F) over a period of 1 hour and the rheology measured again at 25°C (77°F) using the same instrumental parameters. In this manner the amount of steric hardening retained after the heat treatment is measured.

Asphalt Mastic

The objective of this test series is to measure the magnitude of steric hardening (isothermal hardening) of various mastics over an 8-month time period. A total of 9 different asphalt-aggregate mastic combinations, each in an unoxidized and an oxidized form, for a total of 18 different material types, were tested. Two replicates were tested at 5 different times for a total of 180 individual test specimens.

To ensure the hardening times and hardening conditions for specimens of the same material were identical, all specimens of a particular material type were molded simultaneously. This was accomplished by concurrent molding of 12 (2 extra) specimens in a specially designed and constructed 4-cavity mold. Specimens are 1.5 inch (3.81 cm) diameter cylinders, using 45 g of material for each test specimen, resulting in specimens nominally 0.75 inches (1.91 cm) tall. The arrangement of components from bottom to top in each cylindrical mold cavity consisted of: a ½-inch (1.27-cm) steel bottom spacer, an asphalt specimen, a 1-inch steel spacer, an asphalt specimen, a 1-inch steel spacer, an asphalt specimen, and a 2-1/2-inch (6.35-cm) long steel punch. The tops of the punches were machined to hemispherical shapes, and a series of rocker arms was used to apply equal loads (thus equal pressures) to the four cavities. Four 750-watt rod heaters were installed in the mold; temperature was monitored using a thermocouple probe. Temperature control was maintained by use of an analog temperature controller. Molding was carried out in a 30-ton hydraulic press.

Molding procedures consisted of loading the mold with asphalt specimens and placing it into the hydraulic press. A pressure of 4,000 psi (27,586 kPa) was applied while the specimens were heated to and maintained at 150°C (302°F) for 1 hour. Specimens were then cooled to room temperature over at least 2 hours. The mold was reheated to 45°C (113°F) to facilitate removal of the specimens. Specimens were stored in a convection oven at 27°C (80.6°F).

These cylindrical specimens were tested in compression by loading between two flat platens using a 5,000 pound (2,286 kg) capacity MTS Systems Corporation servohydraulic testing machine. A load is applied to the two flat faces of the specimens (axial compression) to maintain a relatively uniform compression stress state. A controlled displacement was applied at 0.05 inches/minute (0.127 cm/min). The tests are stopped when failure load has been achieved. Typical tests take between 2 and 5 minutes to complete. Both axial and diametrical dimension changes are measured using LVDT (linear variable differential transducer) displacement sensors. A full load-deflection data set was acquired for each test. Tests were performed at 3 days, 30 days, 60 days, 120 days, and 240 days after molding. The primary information obtained was failure load (stress) as a function of aging time. Data were obtained to examine stress-strain response for each specimen, thus permitting comparisons among the aged specimens.

Discussion

All rheological data recorded from this work can be found in chapter 5, Volume I and in the database. Statistical analyses were performed at WRI by Dr. Sang-Soo Kim. Analysis of variance for the percent of steric (isothermal hardening) showed a pooled standard deviation of 7.53. Analysis of variance for the percent of reversible hardening (softening by heat treatment at 150°C; 302°F) showed a pooled standard deviation of 21.9. Data for the reversible hardening experiments showed more standard deviation than the isothermal hardening experiments because more physical manipulations of the samples were involved in making the measurements. The statistical analyses showed that asphalt source and cure time are the most important factors influencing hardening. All failure testing was performed at 25°C. The statistical analyses showed that oxidation does not affect the ability of asphalt to steric harden or effect the ability of the asphalt to be softened by heat. Details of discussion of this work can be found in Volume I, chapter 5.

SUMMARY

The isothermal hardening (steric hardening) characteristics of unoxidized and oxidized neat asphalts were measured using a specially designed cup and cylinder couette in a dynamic shear rheometer. The magnitude of hardening due to intermolecular structuring over time was found to vary between about 10 and 130 percent, depending on the composition of the asphalt. Also, experiments to determine the effect of aggregates on steric hardening by measuring the axial compression of mastic briquets were completed. Unaged and artificially aged asphalts were used. Hardening was shown to be asphalt dependent.

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