
Standard Method of Test for

Determination of Polymer Modifier in Asphalt

AASHTO Designation: T xxx-xx (2005)

1. SCOPE

- 1.1.** This method of test is used to determine the polymer content of an asphalt sample. This method is applicable to any asphalt binder or asphalt cement that can be dissolved in toluene.
- 1.2.** This method does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this method to establish appropriate safety and health practices and determine the application of regulatory limitations prior to use.
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2. TERMINOLOGY

2.1. Definitions:

- 2.1.1. GPC**—Gel Permeation Chromatography, a technique used to separate different materials in solution based on their molecular size.
- 2.1.1.1. discussion**—GPC is also called SEC, Size Exclusion Chromatography.
- 2.1.2. GPC Column**—A tube packed with tiny, porous, gel particles that performs a molecular size separation on materials in solution.
- 2.1.3. RID**—Refractive Index Detector, a device used to determine the presence of materials in solution, usually after they have been separated by chromatography.
- 2.1.4. Retention time**—a precise measurement of the time it takes a particular component to be separated from other materials in a chromatography column and be observed by a detector.
- 2.1.5. Chromatogram**—a two-dimensional plot of detector response vs. retention time.
- 2.1.6. MWD**—Molecular Weight Distribution, the relative amounts of different molecular weight molecules that comprise a material, usually determined by GPC separation.
- 2.1.6.1. M_n** —Number-average molecular weight, a calculation of the MWD that treats the total number of molecules present in the MWD equally.

- 2.1.6.2. M_w —Weight-average molecular weight, a weighted calculation of the MWD that emphasizes the larger molecules present in the MWD.

3. SUMMARY OF TEST METHOD

- 3.1. Mixtures of naphthalene and polystyrene standards of known molecular weight are dissolved in toluene, and the solutions are filtered to remove particulates. The filtrates are injected onto a GPC column and the eluate is monitored with RID.
- 3.2. Asphalt samples are dissolved in toluene, and the solutions are filtered to remove particulates. The filtrates are injected onto the GPC column and the eluate is monitored with RID.
- 3.3. The sample chromatograms are examined for any polymeric materials, which have significantly lower retention times than asphaltic compounds. GPC software is utilized to calculate the concentration and MWD of the polymeric material, using the naphthalene and polystyrene standards as calibrants.

4. MATERIALS AND REAGENTS

- 4.1. Toluene [C.A.S. 108-88-3], HPLC grade, Aldrich part number (P/N) 27,037-7 or equivalent.
- 4.2. Naphthalene [C.A.S. 91-20-3], 99%, Aldrich P/N 14,714-1 or equivalent.
- 4.3. Polystyrene standards kit, Waters Corporation P/N 34209 or equivalent, consisting of a minimum of the following eight polystyrene standards:
- 4.3.1. Molecular weight (M.W.) 436 or similar.
- 4.3.2. M.W. 1300 or similar.
- 4.3.3. M.W. 3000 or similar.
- 4.3.4. M.W. 10900 or similar.
- 4.3.5. M.W. 28600 or similar.
- 4.3.6. M.W. 70600 or similar.
- 4.3.7. M.W. 210000 or similar.
- 4.3.8. M.W. 629000 or similar.

5. APPARATUS

5.1. *Volumetric flasks with screw cap closures—*

5.1.1. 5-mL, Kontes P/N 297050-0005 or equivalent.

5.1.2. 10-mL, Kontes P/N 297050-0010 or equivalent.

5.1.3. PTFE-lined screw cap closures, Kimble P/N 73802-13425 or equivalent.

5.2. *Disposable syringes and filters—*

5.2.1. 10-mL syringes with Luer-Lok™ fitting, Becton Dickinson P/N 30960404 or equivalent.

5.2.2. 25-mm diameter filters with Luer-Lok™ fitting, 0.45 μm PTFE membrane, Corning P/N 431231 or equivalent.

5.3. *Autosampler with vials—*

5.3.1. High performance liquid chromatography (HPLC) autosampler, Waters Corporation Model 717 or equivalent.

5.3.2. 4-mL autosampler vials with PTFE-lined septa and screw cap closure, Waters Corporation P/N 186000838 or equivalent.

Note 1—In the absence of an autosampler, a manual injection apparatus such as a Rheodyne Model 7725i or equivalent may be used.

5.4. *GPC system hardware—*

5.4.1. HPLC pump for isocratic solvent delivery, Waters Corporation Model 515 or equivalent.

5.4.1.1. *discussion*—an isocratic system is defined as a liquid chromatography system that uses only one solvent. For the purposes of this method, toluene is the isocratic solvent, and it may be referred to as the mobile phase.

Note 2—A gradient HPLC pump, for use of more than one solvent, can be used in isocratic mode for delivery of a single solvent.

5.4.2. Mobile phase guard assembly, Phenomenex AJ0-7220 cartridge holder with Phenomenex AJ0-7223 cartridge filter, or equivalent.

5.4.3. GPC column, Phenogel 5 μm Linear (2), 300 x 7.80 mm, Phenomenex P/N 00H-3259-K0 or equivalent.

5.4.3.1. *discussion*—the porous gel material packing inside the GPC column may be referred to as the stationary phase.

5.4.4. Column heater and controller, FIAtron CH-30 with TC55, or equivalent.

5.4.5. Refractive Index Detector, Waters Model 2414 or equivalent.

5.5. *Data System*—

5.5.1. A/D converter for RID data, Chrom Perfect Tigre Instrument Interface or equivalent.

5.5.2. GPC software, for system calibration and MWD calculations, Chrom Perfect Spirit or equivalent.

5.5.3. PC, with specifications that meet requirements for A/D converter and GPC software.

Note 3—bundled GPC systems consisting of an autosampler, pump, detector, A/D converter, GPC software, and PC are commercially available from a variety of manufacturers.

6. PREPARATION OF STANDARDS AND SAMPLES

6.1. *Standards Preparation*—

6.1.1. Using an analytical balance, weigh 10 mg (± 0.5 mg) of naphthalene and polystyrene M.W. 1300, 10900, 70600, and 629000 standards into a 10-mL volumetric flask. Dilute to volume with toluene, close the screw cap, and mix until the polystyrene is dissolved. Label the flask “GPC Calibration #1 (0.1%)”.

6.1.2. Using an analytical balance, weigh 10 mg (± 0.5 mg) of polystyrene M.W. 436, 3000, 28600, and 210000 standards into a 10-mL volumetric flask. Dilute to volume with toluene, close the screw cap, and mix until the polystyrene is dissolved. Label the flask “GPC Calibration #2 (0.1%)”.

6.2. *Sample Preparation*—

- 6.2.1. Using an analytical balance, weigh 10 mg (± 0.5 mg) of asphalt sample into a 5-mL volumetric flask. Dilute to volume with toluene, close the screw cap, and mix until the asphalt is dissolved. Label the flask with the sample name and concentration (0.2%).
- 6.2.2. Using an analytical balance, weigh 250 mg (± 12.5 mg) of asphalt sample into a 5-mL volumetric flask. Dilute to volume with toluene, close the screw cap, and mix until the asphalt is dissolved. Label the flask with the sample name and concentration (5.0%).

Note 4—The dissolution of the polystyrene standards and asphalt samples in toluene can be performed quickly by placing the filled and capped volumetric flasks in an ultrasonic bath for a few minutes.

6.3. *Filtration*—

- 6.3.1. Using a disposable pasteur pipette, carefully transfer 2-3 mL of each standard and sample solution to an open syringe containing a filter. Place the filter outlet into an autosampler vial, and insert the plunger into the syringe barrel. Push the plunger slowly, and collect the filtrate in the vial. Cap and label each vial.
- 6.3.2. Place the vials in the autosampler carousel in preparation for auto-injection of the solutions onto the GPC column. In the absence of an autosampler, set the vials in a vial rack in preparation for manual injection.

7. **PROCEDURE**

- 7.1. Power up the components of the GPC system. Prime the HPLC pump according to the manufacturer's instructions, and set the toluene mobile phase flow rate to 1.0 mL/min. Examine the mobile phase flow path closely for any leaks, and tighten any fittings that are leaking. Set the GPC column heater to 40°C. Allow about 20 minutes for the components of the system to warm-up.
- 7.2. Switch the detector flow path to the reference cell to allow fresh toluene into the reference cell. After switching the flow path back to the sample cell, select an appropriate detector attenuation that is compatible with the full scale voltage of the A/D converter. Consult the manufacturer's instructions for guidance in flushing the reference cell and selecting the proper detector attenuation.
- 7.3. Set the GPC analysis runtime for 15 minutes, and inject 150 μ L of GPC Calibration #1 (0.1%). The chromatogram should contain five peaks as shown in **Figure 1**. Adjustments to the detector attenuation, injection volume, analysis runtime, and mobile phase flow rate may be necessary to produce an on-scale chromatogram with resolution between the five components. Integrate the five peaks using the GPC software to obtain a retention time for each peak.

- 7.4. Using the same settings as for Calibration #1, inject GPC Calibration #2 (0.1%). Integrate the four peaks to obtain their retention times. In the calibration section of the GPC software, assign the retention times to the molecular weights of the nine standard components, as shown in **Table 1**. A plot of retention time vs. log of the M.W. is a linear calibration (**Figure 2**) which will be used for the analysis of the asphalt samples.

Table 1—Example GPC Calibration Data

Retention Time	M.W.	Log M.W.
7.50 minutes	629000	5.798
8.11	210000	5.322
8.66	70600	4.849
9.17	28600	4.456
9.65	10900	4.037
10.22	3000	3.477
10.55	1300	3.114
10.98	436	2.640
12.02	128	2.107

- 7.4.1. *discussion*—GPC separation is based on the interaction of the molecules in the mobile phase with the porous gel of the stationary phase. Molecules with relatively small sizes and low molecular weights will penetrate the gel pores better than molecules having relatively large sizes and high molecular weights. Thus, higher molecular weight polymeric material will elute from the GPC column before the relatively lower molecular weight asphaltic material.
- 7.5. Using the same settings as for the Calibrations, inject the sample solution(s) prepared at (0.2%) concentration. The sample chromatograms should exhibit peaks with detector responses that are within the same order of magnitude as the nine standard components.
- 7.6. Using the same settings as for the Calibrations, inject the sample solution(s) prepared at (5.0%) concentration. The sample chromatograms should exhibit peaks with detector responses that are an order of magnitude higher than the nine standard components. Examine the tops of the peaks closely; peak apexes that are extremely rounded may indicate column overload, and it may be necessary to inject a smaller sample volume. Peak apexes that exhibit flat tops may indicate detector overload, and it may be necessary to change detector attenuation.

8. QA/QC

8.1. *Continuing Calibration Verification (CCV)*—

8.1.1. For every ten consecutive sample injections and at the end of each sample sequence, it is necessary to evaluate the stability of the GPC system by re-injecting the GPC Calibration standards. When re-analyzed in such fashion, Calibration #1 (0.1%) and Calibration #2 (0.1%) are called Continuing Calibration Verification (CCV) standards. Inject one CCV standard after every ten consecutive sample injections, alternating between standard #1 and #2. Bracket the end of any sample sequence with a CCV standard.

8.1.1.1. A stable GPC system will have differences of < 0.1 minute for retention times in the calibration data vs. those of a CCV. Sample analysis may proceed in ten sample intervals indefinitely with a stable GPC system.

8.1.1.2. An unstable GPC system will have differences of 0.1 minute or greater for retention times in the calibration data vs. those of the CCV. An unstable GPC system requires that corrective action be taken before any additional samples can be analyzed.

8.2. *Corrective Action*—

8.2.1. *discussion*—Subtle changes in the mobile phase flow rate are the most common cause of an unstable GPC system. Flow rate changes may be caused by particulates clogging the guard column assembly, leading to increased mobile phase backpressure. During analysis, it is prudent to monitor backpressure; higher pressures may be alleviated by changing the cartridge filter. Another common cause of an unstable GPC system is detector baseline drift. If ramped or fluctuating baselines are observed during analysis, RID temperature changes are usually at fault.

8.2.2. Consult the manufacturer's hardware guide for specific maintenance and troubleshooting instructions. Any samples that could not be bracketed by a CCV meeting the requirements of 8.1.1.1 must be re-analyzed. Proceed to Section 7.2. to begin another analysis sequence.

9. RESULTS

9.1. *Qualitative Analysis*—

9.1.1. Examine the chromatograms of the asphalt samples analyzed at the (0.2%) concentration level. Typically, the asphaltic material will elute as a smooth peak in the M.W. range of the lowest four standards (M.W. 128 – 3000).

9.1.1.1. For an asphalt sample that has not been polymer modified, the asphalt peak should be the only peak evident in the chromatogram. **Figure 3** is an example of asphalt that is not polymer modified.

9.1.1.2. *discussion*—The vertical lines in the chromatogram represent retention time variables used to calculate a peak's MWD; Cal S (start) indicates the highest M.W. calibrant, while Cal E (end) indicates the lowest. The solid line under the peak indicates how it was integrated. The software uses these parameters to calculate the MWD values M_n and M_w . Generally, asphalts that have not been polymer modified have M_n values that typically range from ~ 500 to 650, and M_w values that typically range from ~ 1000 to 1400.

Note 5— software routines may vary among manufacturers; consult the software user's guide for specific user variables and MWD calculations.

9.1.1.3. For a polymer modified asphalt, a chromatographic peak in the M.W. range of the highest four standards (M.W. 28600 - 629000) will be present. **Figure 4** is an example of polymer modified asphalt. Note the appearance of the polymeric material in the higher M.W. region of the chromatogram.

9.1.1.4. *discussion*—Polymer modified asphalts typically have M_n values that range from ~ 500 to 1000, and M_w values that range from ~ 1500 to 3500, for peaks integrated together as shown in Figure 4.

9.1.2. Examine the chromatograms of the asphalt samples analyzed at the (5.0%) concentration level. The asphalt peak may contain bumps, shoulders, or extra peaking on the high molecular weight side (lower retention time) of the primary peak. The asphaltic material will typically elute in the M.W. range of the lowest five standards (M.W. 128 – 10900).

9.1.2.1. *discussion*—Asphalt samples prepared in toluene at concentrations exceeding ~0.4% exhibit asphaltene agglomeration, which are evident in GPC chromatograms as higher molecular weight asphaltic material. Increasing concentrations of asphalt will generally produce higher MWD values. However, analysis at higher concentrations allows detection of lower concentrations of polymer, which is the primary reason for analyzing at the (5.0%) level.

Note 6—Some data suggest that higher concentrations of asphalt may be prepared in tetrahydrofuran (THF) before asphaltene agglomeration occurs. Thus, the necessity of analyzing every asphalt sample at two concentrations may be avoided by substituting THF for toluene. It is not known at this time how this method performs using THF.

9.1.2.2. For an asphalt sample that has not been polymer modified, the asphalt peak should be the only peak evident in the chromatogram. **Figure 5** is the same

asphalt shown in Figure 3, but analyzed at (5.0%). Note the shoulder inclusion in the M.W. 10900 region.

Note 7—Figure 5 is highlighted to show the M.W. regions of the calibrants, and the chromatogram is truncated at a detector output of 300 millivolts.

9.1.2.3. For a polymer modified asphalt, a chromatographic peak in the M.W. range of the highest four standards (M.W. 28600 - 629000) will be present. **Figure 6** is the same asphalt shown in Figure 4, but analyzed at (5.0%). In addition to the shoulder inclusion in the M.W. 10900 region, note the distinct presence of the polymeric material in the M.W. 70600 – 210000 region.

9.2. *Quantitative Analysis*—

9.2.1. If chromatographic peaking in the polymer region is present in any sample chromatogram, compare the chromatogram to that from the alternate concentration level.

9.2.1.1. In instances where both sets of chromatograms (0.2% and 5.0%) exhibit peaking in the polymer region, use the software to integrate the polymer and asphalt as two distinct peaks. The polymer content of the asphalt is determined by the integration results:

$$\% \text{ Polymer Modifier} = \text{Area of Polymer Peak} / (\text{Area of Polymer Peak} + \text{Area of Asphalt Peak})$$

Note 8—Consult the software user’s guide for instructions on proper integration techniques. Peaks that are relatively small and broad, or those that are not baseline resolved, require proper technique for reliable results.

9.2.1.2. For asphalts with low polymer content, the (5.0%) concentration chromatogram may be the only one that shows peaking in the polymer region. In this instance, determine the polymer content as described in 9.2.1.1.

9.2.1.3. In the event that chromatographic peaking is observed in the polymer region for the (0.2%) concentration but not for the (5.0%) concentration, sample preparation and analysis must be repeated. Proceed to Section 6.2.

9.3. *Analysis Report*—

9.3.1. If polymeric material is not present in the sample chromatograms at either concentration level, indicate that the sample is not polymer modified.

9.3.2. If polymeric material is present in the sample chromatogram for the (5.0%) concentration only, report the % polymer content as described in 9.2.1.1. Report the MWD data calculated by the software for the polymer peak only, and indicate that the MWD data were obtained using polystyrene calibration.

9.3.3. If polymeric material is present in the sample chromatograms for both concentrations, report the % polymer modifier as described in 9.2.1.1. for both concentrations. Report the MWD data calculated by the software for the polymer peak for both concentrations, and indicate that the MWD data were obtained using polystyrene calibration.

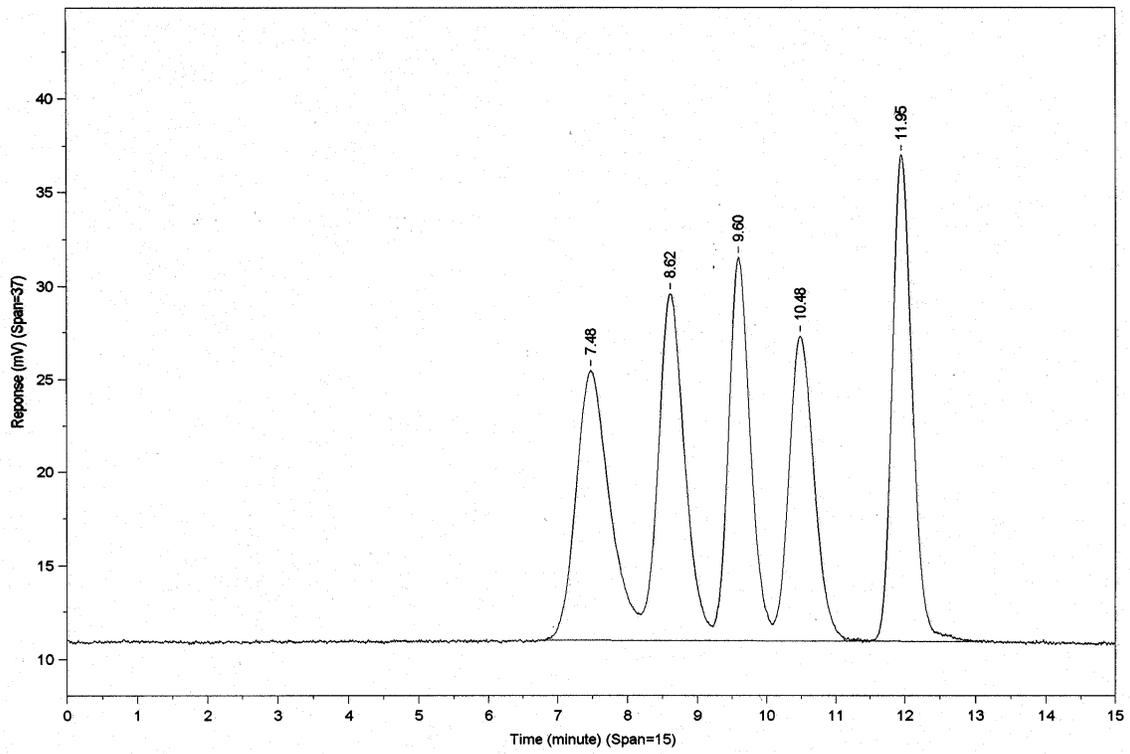


Figure 1
Calibration #1 (0.1%)

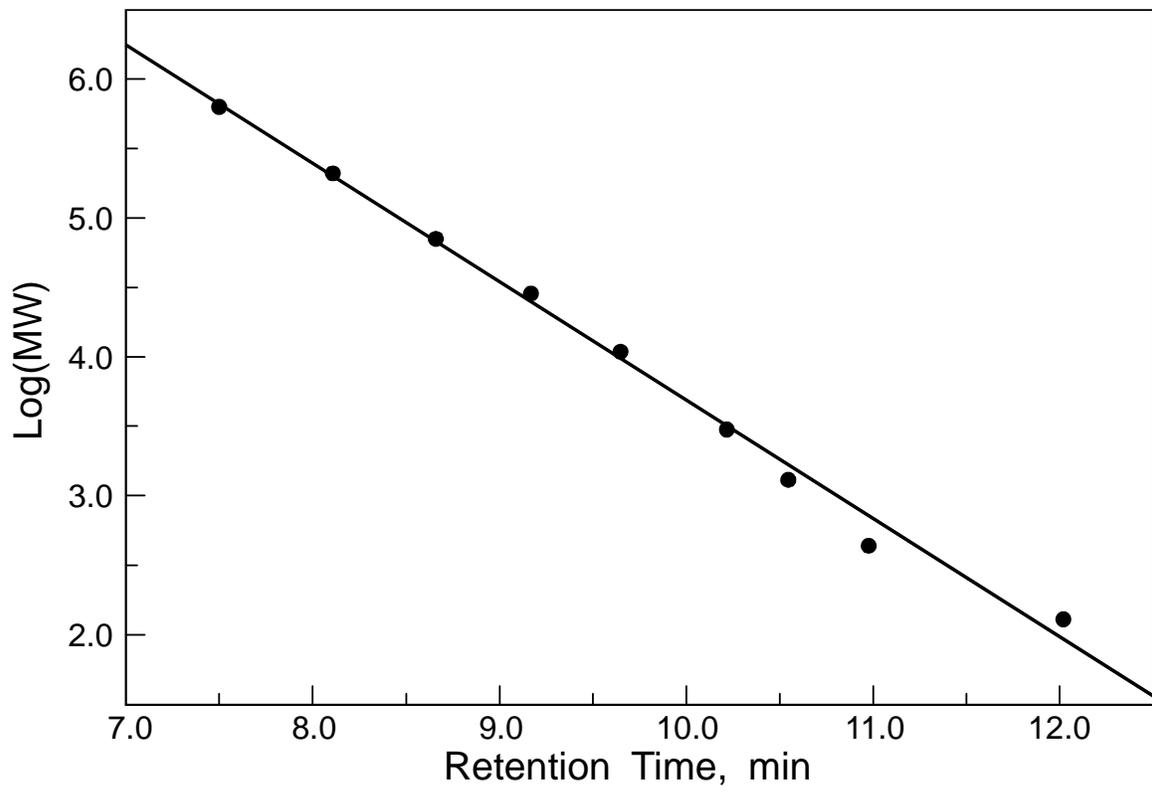


Figure 2
GPC Calibration Curve

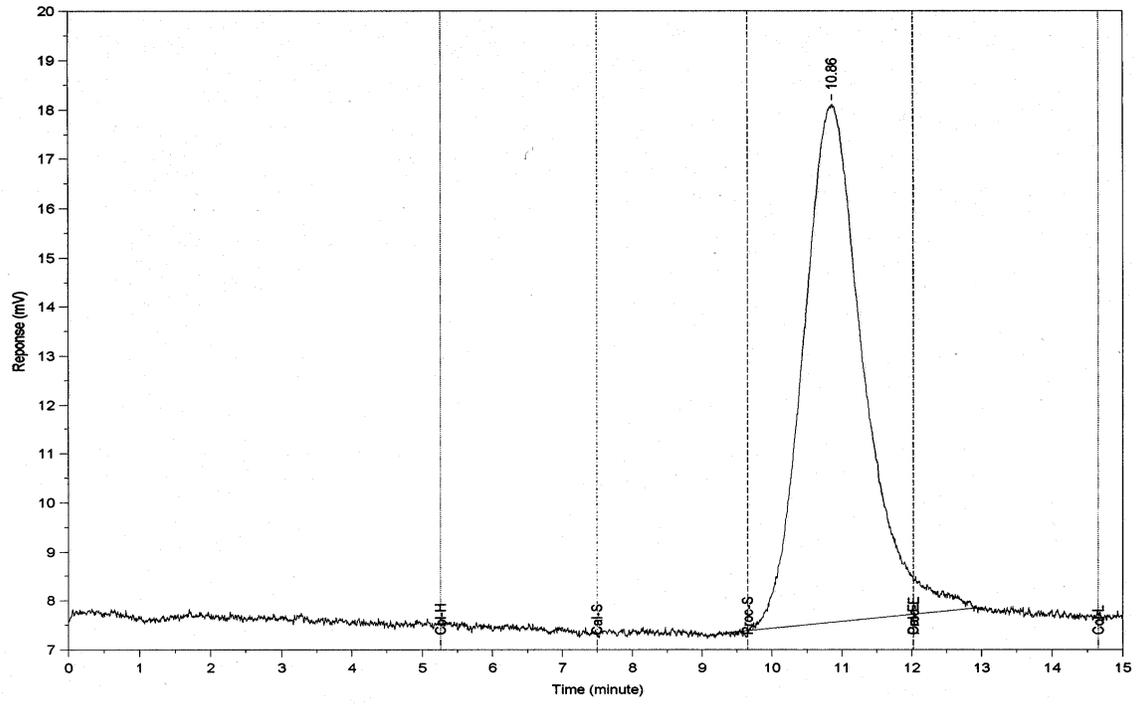


Figure 3
Example of Asphalt Without Polymer Modifier
(0.2%) Concentration

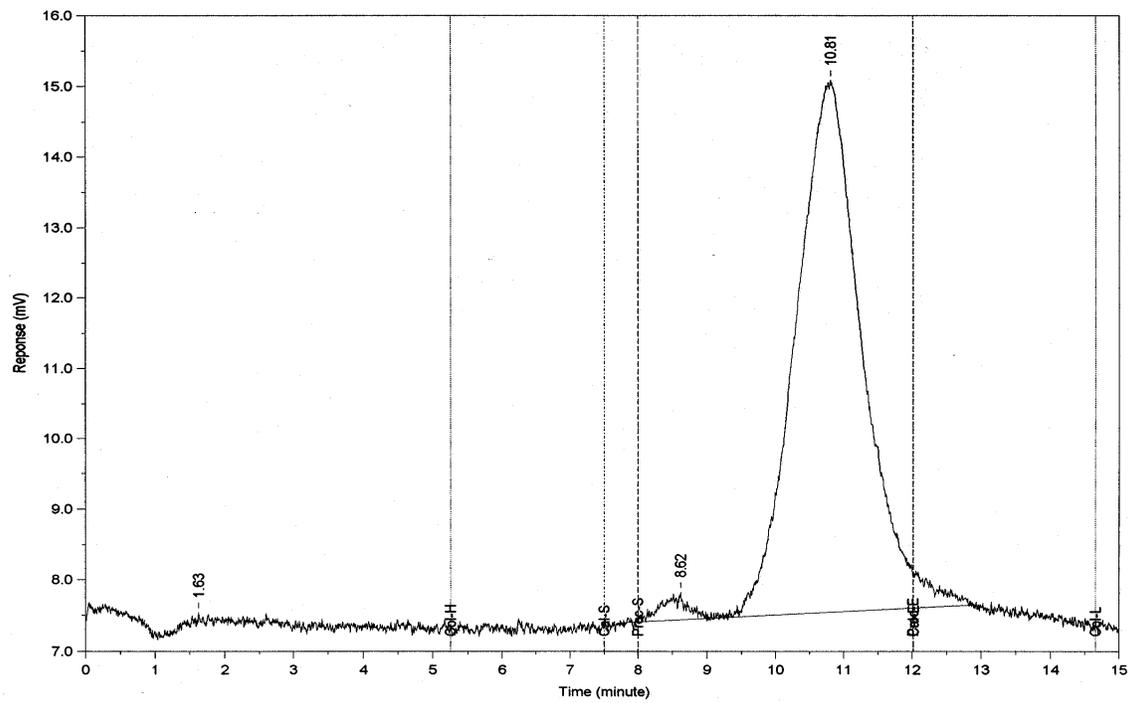


Figure 4
Example of Polymer Modified Asphalt
(0.2%) Concentration

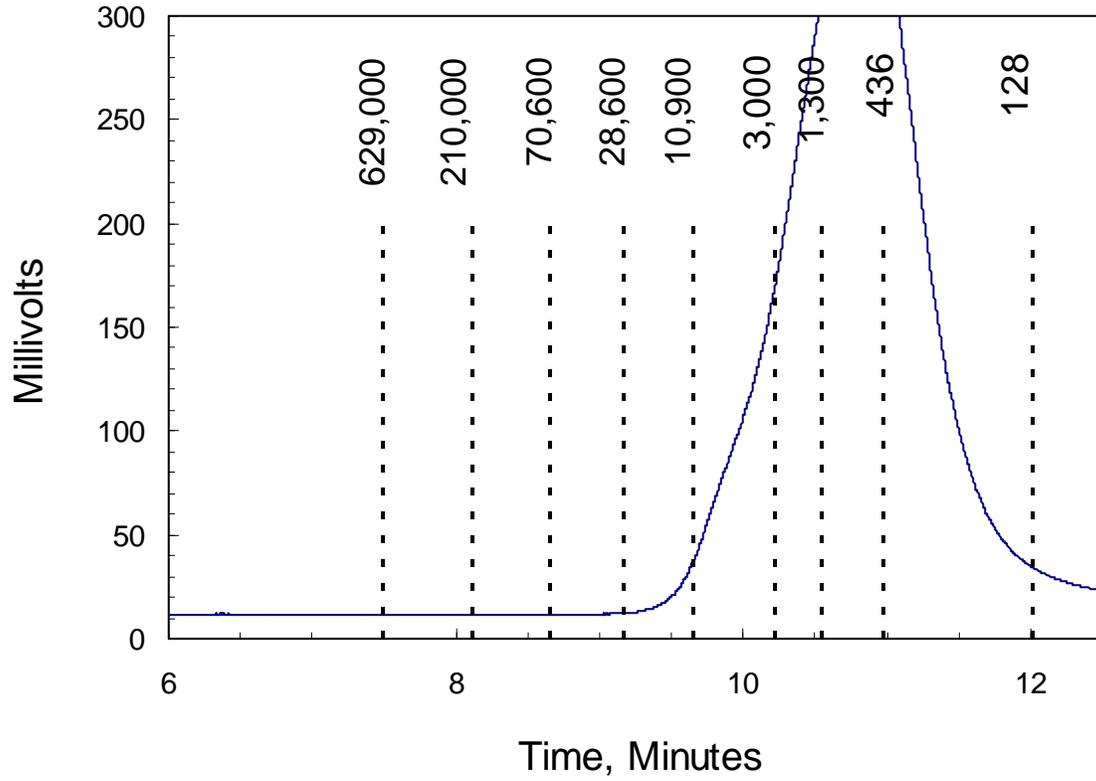


Figure 5
Example of Asphalt Without Polymer Modifier
(5.0%) Concentration

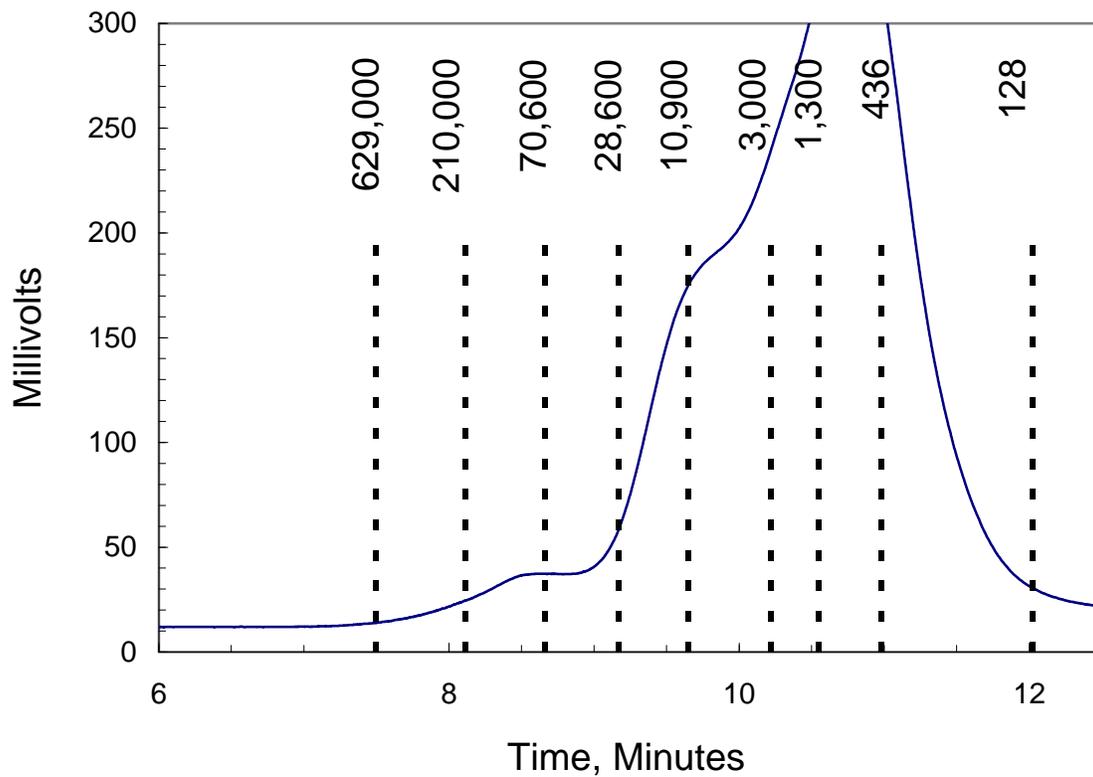


Figure 6
Example of Polymer Modified Asphalt
(5.0%) Concentration