Technical White Paper

Adaptation of Existing Analytical Scale Size Exclusion Chromatography Methods

Fundamental Properties of Asphalts and Modified Asphalts III Product: FP 22

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INTRODUCTION

The microstructure and colloidal models of asphalt structuring have gained general acceptance in recent years due to a preponderance of data (Lesueur 2009, Le Guern et al. 2010). Size exclusion chromatography separations (SEC) performed at WRI that separated asphalt into one fraction of associated components and a second fraction of non-associating components were among early evidence supporting these models (Branthaver et al. 1993). Several permutations of SEC separations of asphalt involving a variety of separation conditions exist in the literature (Altgelt and Hirsch 1970; Haley 1975; Brûlé and Migliori 1983, Pribanic et al. 1989, Jennings et al. 1992, Kim 1993; Bishara and McReynolds 1992; Schabron et al. 2001; Wahhab et al. 1999), including methods for quantification of polymer and monitoring polymer degradation with oxidative aging (McCann et al. 2008, Dreessen et al. 2010). These methods either rely on the manual collection and weighing of the elution material at designated times or a detector, typically differential refractive index (RI), to correlate specific asphalt material with hydrodynamic volume and, consequently, molecular weight. The former method is typically used if further analysis of the material is needed. The latter type of separation, often referred to as analytical scale SEC, is more rapid for higher throughput and is generally more precise.

A major drawback in using an RI detector for quantification of asphalt molecular weights from SEC separations is that different types of molecules give different changes in RI for a particular solvent. For example, waxes within a binder show a negative ΔRI, and more polar asphaltene type molecules give a very positive ΔRI. Aromatics and weakly polar molecules are somewhere in the middle of this polarity spectrum and show a moderately positive ΔRI. As an alternative, an evaporative light scattering (ELS) detector can be used that responds more uniformly across sample types (Carbognani 1997).

EXPERIMENTAL

The assembled SEC system utilizes a Waters Acquity pump, autosampler, 2424 evaporative light scattering detector and RI detector. Two 300 x 7.8 mm i.d. 5 µm Phenogel columns with 50 Å and 1000 Å pore sizes, respectively, connected in series and thermostated to 30°C precede either the RI detector or the ELS detector. The ELSD is set to 35 psi nitrogen flow and 60°C drift tube temperature. Because of the destructive nature of the ELSD and the large void volume of the RI which causes too much peak broadening downstream, the two detectors were unable to be used simultaneously, and two injections were required for complete data acquisition. Toluene was the carrier solvent at a flow rate of 0.5 ml/min. Polystyrene standards of molecular weight 70600, 10900, 3000, 1920, 1300, 890, 370 and 266 Da respectively were used for calibrating molecular weights of binders and gave a calibration curve with an R^2 of > 0.999 in all instances. For comparison of molecular aggregation, 4 µL, and 40 µL of 10% wt/vol asphalt in toluene solutions were separated. Waters EmPower software was used for data acquisition and analysis.

RESULTS AND DISCUSSION

Tables 1 and 2 list five neat and aged binders and their respective calculated ELSD and RI molecular weights after SEC separation of 4 mg and 0.4 mg sample mass. The aging conditions were 70°C for 12 weeks with 150 µm binder film thickness in a forced draft oven. Number average (M_n), weight average (M_w) and peak molecular weights (M_p) were calculated based on polystyrene equivalents. The 4 mg separations show greater molecular weights than the 0.4 mg separations indicating more aggregation in these solutions. The RI detector always shows a greater polydispersity (M_w/M_n) than the ELS detector. While the ELSD does not detect molecules smaller than ~C_{22} due to volatility of the compounds, this is not an issue in asphalt as molecules of this size do not exist (Carbognani 1997). There are no clear trends in the SEC profiles with aging as some samples yield lower and some higher apparent molecular weights when aged. This is contrary to reports in the literature (Le Guern et al. 2010; Brûlé and Migliori 1983). It is believed that our separation conditions and detector setup are not sensitive to binder oxidative aging changes. However, the system may be quickly refigured to obtain similar results described in the literature.

Table 1. Results from the ELSD and RI detectors after SEC separation of 40 µL of 10% asphalt solutions listing the number average molecular weight, weight average molecular weight, and molecular weight of the peak, M_n, M_w, and M_p, respectively, in daltons.

ELSD	Amount Injected	M_n	M_w	M_p	M_w/M_n
Sample					
AAB-1 aged	40 µL 10%	851	1450	1264	1.70
AAB-1 Neat	40 µL 10%	893	1628	1265	1.82
AAC-1 aged	40 µL 10%	929	1464	1407	1.58
AAC-1 neat	40 µL 10%	916	1644	1372	1.79
AAD-1 aged	40 µL 10%	691	1144	866	1.66
AAD-1 neat	40 µL 10%	748	1482	889	1.98
AAM-1 aged	40 µL 10%	1607	4230	3215	2.63
AAM-1 neat	40 µL 10%	1530	3688	2925	2.41
ABD-1 aged	40 µL 10%	705	1143	990	1.62
ABD-1 neat	40 µL 10%	713	1179	1017	1.65

RI	Amount Injected	M_n	M_w	M_p	M_w/M_n
Sample					
AAB-1 aged	40 µL 10%	660	1474	727	2.23
AAB-1 Neat	40 µL 10%	739	1855	790	2.51
AAC-1 aged	40 µL 10%	665	1441	830	2.17
AAC-1 neat	40 µL 10%	670	1372	850	2.05
AAD-1 aged	40 µL 10%	592	1255	494	2.12
AAD-1 neat	40 µL 10%	680	1669	486	2.45
AAM-1 aged	40 µL 10%	1149	4635	6002	4.03
AAM-1 neat	40 µL 10%	1084	3832	1408	3.54
ABD-1 aged	40 µL 10%	601	1200	631	2.00
ABD-1 neat	40 µL 10%	612	1189	661	1.94

Table 2. Results from the ELSD and RI detectors after SEC separation of 4 µL of 10% asphalt solutions listing the number average molecular weight, weight average molecular weight, and molecular weight of the peak, M_n, M_w, and M_p respectively.

ELSD	Amount Injected	M_n	M_w	M_p	M_w/M_n
Sample					
AAB-1 aged	4 µL 10%	860	1297	1183	1.51
AAB-1 Neat	4 µL 10%	900	1468	1372	1.63
AAC-1 aged	4 µL 10%	947	1384	1352	1.46
AAC-1 neat	4 µL 10%	958	1410	1445	1.47
AAD-1 aged	4 µL 10%	697	1030	947	1.48
AAD-1 neat	4 µL 10%	757	1344	903	1.78
AAM-1 aged	4 µL 10%	1542	3773	1634	2.45
AAM-1 neat	4 µL 10%	1534	3299	2575	2.15
ABD-1 aged	4 µL 10%	723	1053	1027	1.46
ABD-1 neat	4 µL 10%	728	1102	1003	1.51

RI	Amount Injected	M_n	M_w	M_p	M_w/M_n
Sample					
AAB-1 aged	4 µL 10%	604	1255	703	2.08
AAB-1 Neat	4 µL 10%	647	1374	772	2.12
AAC-1 aged	4 µL 10%	613	1262	799	2.06
AAC-1 neat	4 µL 10%	612	1141	834	1.86
AAD-1 aged	4 µL 10%	534	961	490	1.80
AAD-1 neat	4 µL 10%	628	1394	475	2.22
AAM-1 aged	4 µL 10%	872	2706	1251	3.10
AAM-1 neat	4 µL 10%	881	2579	1308	2.93
ABD-1 aged	4 µL 10%	543	913	611	1.68
ABD-1 neat	4 µL 10%	583	1100	648	1.89

Example chromatograms in figure 1 from the ELS and RI detectors after SEC separations of AAA-1 show the RI having a wider distribution profile compared to the ELS detector. This visual result is consistent with the calculated polydispersities (M_w/M_n) in tables 1 and 2. It is also evident that binder differences due to oxidative aging would be more pronounced in the RI chromatograms compared to the ELSD. The visual differences in the RI chromatograms between neat and aged binders are presented in figures 2-6.

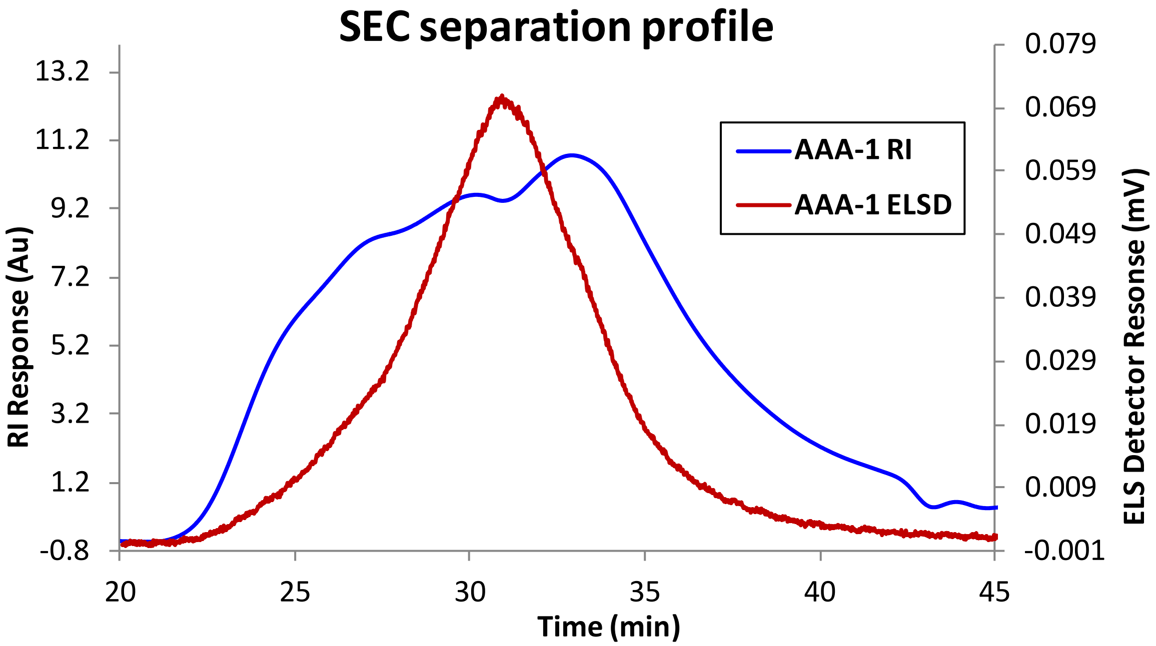

Figure 1. Example chromatograms after SEC separations of asphalt AAA-1 showing the differences between the ELS and RI detectors.

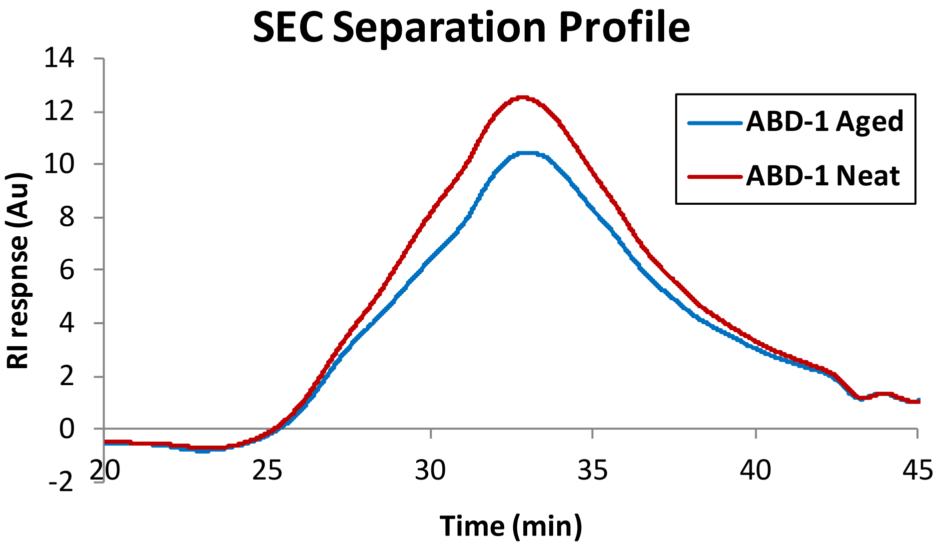

Figure 2. RI SEC separation profiles showing the changes occurring during laboratory aging.

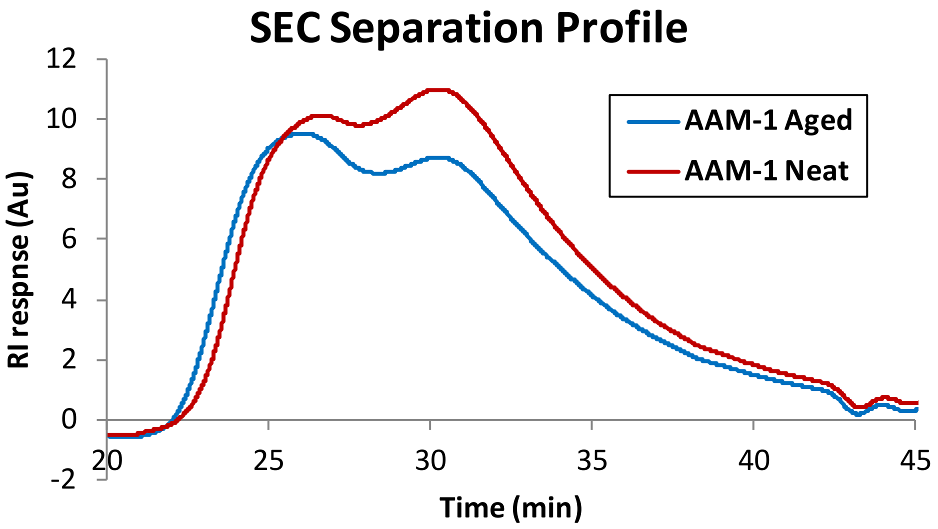

Figure 3. RI SEC separation profiles showing the changes occurring during laboratory aging.

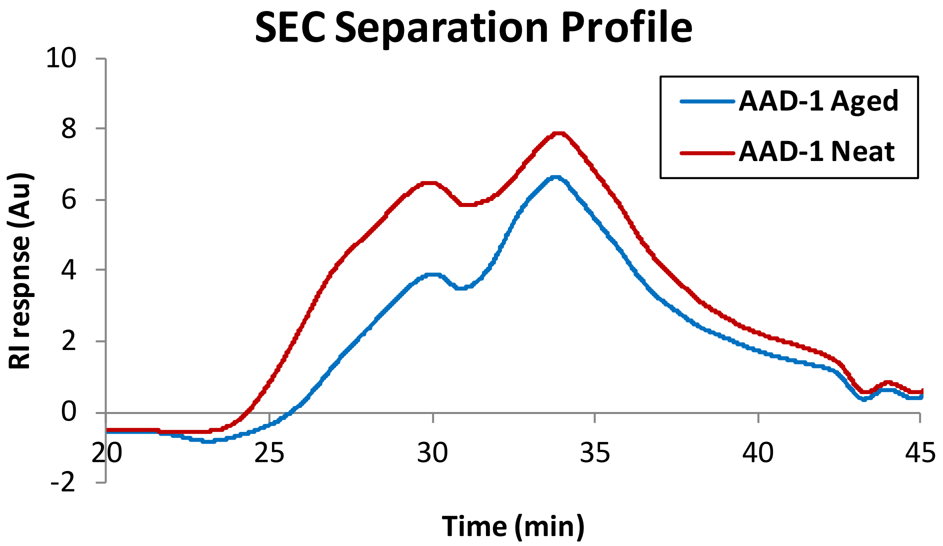

Figure 4. RI SEC separation profiles showing the changes occurring during laboratory aging.

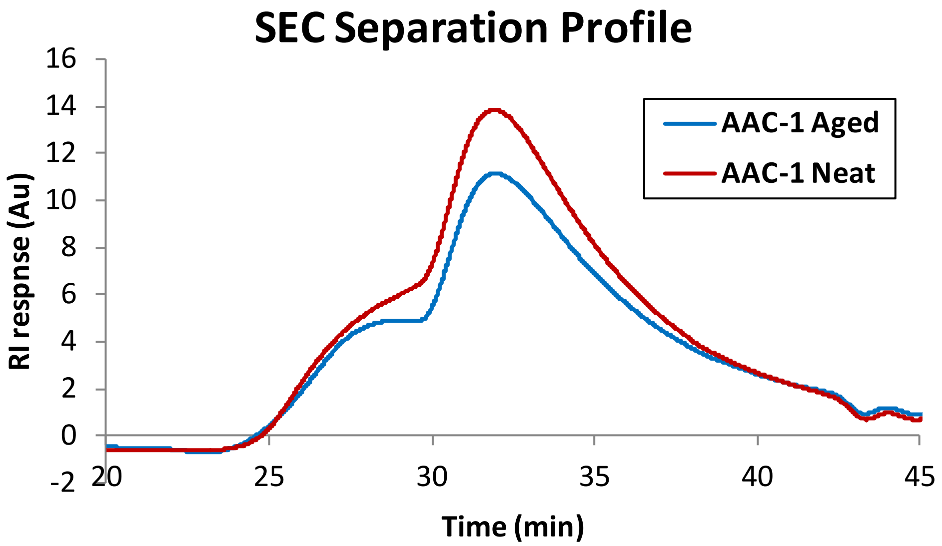

Figure 5. RI SEC separation profiles showing the changes occurring during laboratory aging.

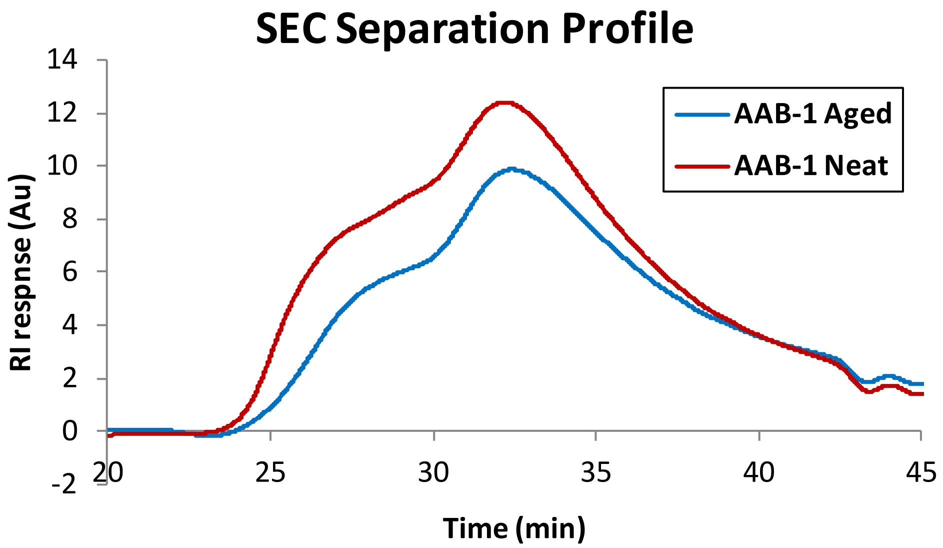

Figure 6. RI SEC separation profiles showing the changes occurring during laboratory aging.

In an effort to determine the precision of this separation method, seven separate 10% w/v solutions were prepared from the same can of asphalt AAF-1, and 40 µg were separated on the SEC system. Molecular weight averages were calculated from the resulting chromatograms using polystyrene standards and the results along with standard deviation calculations are presented in table 3. The standard deviation is a maximum of 3.7% for all of the calculated MW numbers.

Table 3. Results from 40 µL separations of seven separate 10% binder solutions prepared from the same can of AAF-1 showing the precision of the SEC separation method with both the RI and ELS detectors.

ELSD	M_n	M_w	M_p	M_w/M_n
Sample				
1	888	1417	1282	1.60
2	882	1461	1288	1.66
3	886	1416	1230	1.60
4	891	1420	1280	1.59
5	889	1334	1292	1.50
6	891	1469	1355	1.65
7	895	1499	1281	1.67
Average	889	1431	1287	1.61
St. Dev.	4.1	53.1	36.5	0.1
% St. Dev.	0.5	3.7	2.8	3.6
RI	M_n	M_w	M_p	M_w/M_n
Sample				
1	610	1334	846	2.19
2	619	1383	853	2.23
3	620	1403	848	2.26
4	625	1410	851	2.26
5	630	1441	857	2.29
6	629	1440	842	2.29
7	627	1426	853	2.27
Average	623	1405	850	2.25
St. Dev.	7.1	37.7	5.0	0.04
% St. Dev.	1.1	2.7	0.6	1.6

CONCLUSION

The assembled SEC system separates binders into molecular weights of individual molecules and aggregates ranging from 100-70,000 Da that are subsequently measured using RI and ELS detectors. Number average, weight average, and peak molecular weights may be calculated from the resulting chromatograms using polystyrene standards. ELS detectors show more uniform response with regard to differing molecular types present in asphalt as compared to RI detectors. Consequently, for molecular weight calculations, the ELS data are more quantitative than historical RI data for whole asphalts. The RI profiles give some insight into associations, but their interpretation and significance is difficult. All separations have been performed in toluene, but tetrahydrofuran or dichloromethane may be employed if less molecular aggregation is desired. Four µg and 40 µg binder separations were performed to observe the effect of sample concentration on molecular aggregation in toluene. Standard deviations were calculated to be a maximum of 3.7% by preparing and separating seven distinct samples of the same binder.

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DISCLAIMER

The contents of this report reflect the views of Western Research Institute which is responsible for the facts and the accuracy of the data presented herein. The contents do not necessarily reflect the official views of the policy of the Department of Transportation.

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