TECH**BRIEF**

Automated High-Performance Liquid Chromatography Saturate, Aromatic, Resin, and Asphaltene Separation

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Background

Dividing a material into its constituent parts is necessary to define its composition. These compositional analyses are useful in binder formulation through blending, rejuvenation, and modification, as well as prediction of physical performance. Normal phase chromatographic separation methods for oils have been around for several decades. One early version of this type of analysis divides a crude oil or asphalt into saturate, aromatic, resin, and asphaltene (SARA) fractions.(1,2)

These SARA separations mainly employ chromatography using polar stationary phases such as activated silica gel or activated aluminum oxide. Prior to the chromatography, the oils are typically divided into two solubility classes by a gravimetric separation using a low-polarity hydrocarbon solvent such as isooctane, pentane, or heptane. The soluble material is defined as the *maltene*, and the insoluble material is defined as the *asphaltene*. The gravimetric asphaltene/maltene separation typically takes 24 h. The chromatographic separation of maltenes takes another day. If the asphaltenes are to be further subdivided gravimetrically into two solubility fractions, such as cyclohexane soluble and cyclohexane insoluble, then that process takes yet another day.

Using normal-phase liquid chromatography, the maltenes are often divided into three fractions called saturates, aromatics, and resins/polars (SAR). The saturate fraction

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consists of both linear and branched fully saturated organic molecules of low polarity containing carbon and hydrogen with essentially no hetero-atoms. A molecule in the aromatics fraction contains mainly carbon and hydrogen, possibly some thiophenic sulfur, and few-to-no hetero-atoms, and it is distinct from the saturates fraction by containing one or more aromatic carbon rings. The resins and asphaltenes fractions both contain many aromatic rings, some pericondensed, with many polar substituents.

A known commercial method called Iatroscan involves conducting capillary thin-layer chromatography (TLC) with whole oils on silica or alumina rods as a stationary phase, followed by evaporating the elution solvent and then slowly passing the rods through a flame ionization detector to provide information on the relative amounts of hydrocarbon in the fractional zones on the rod.(3,4) The Iatroscan instrument typically elutes the fractions in a sequence of solvents consisting of linear alkane, cyclohexane, toluene, and dichloromethane:methanol mixtures. However, the Iatroscan method has major drawbacks, including variable response factors for the polar fractions, relatively large amounts of polar compounds retained near the spot location on the TLC rod, and aromatics grouping together to act like resins would during separation.(5,6) The separation has a large amount of error on repeat analysis, and there is a problem with the strongly adsorbed asphaltene material that does not migrate up the rod.(6)

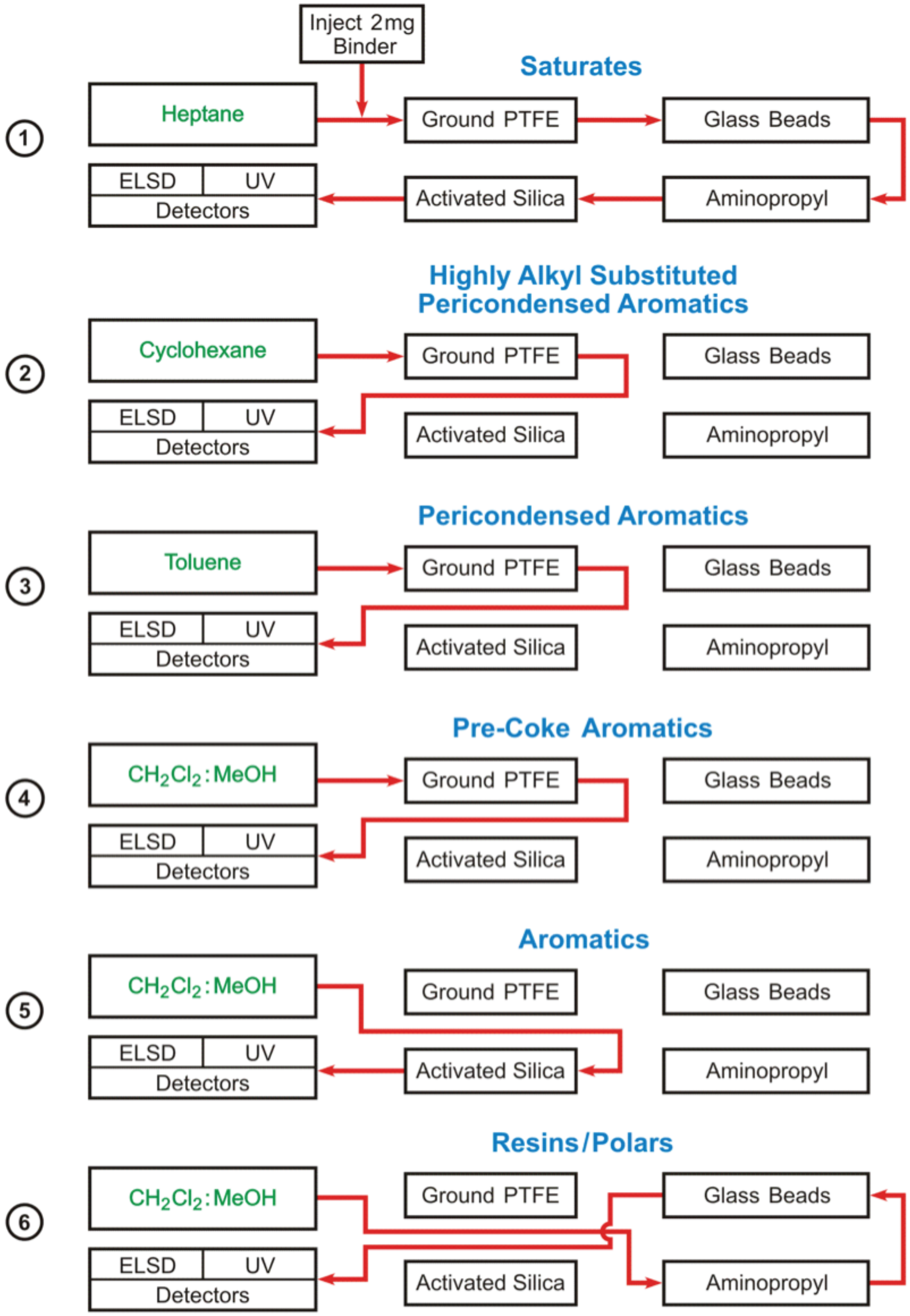
Asphaltene determinator (AD) is a novel automated high-performance liquid chromatography (HPLC)-based asphaltene separation process developed by Schabron and Rovani.(7) Following an injection of 2 mg of a petroleum oil or vacuum residuum, asphaltenes precipitate onto a polytetrafluoroethylene (PTFE)-packed column in an excess of heptane. The asphaltenes are then selectively dissolved with stronger, more polar solvents to quantitatively give three fractions of asphaltenes.(7,8) Using this system, coupled on the front end to separate the asphaltenes, the maltenes can then be separated into SAR fractions, resulting in a fully automated SARA separation. The research team is exploring separation profiles from the SAR-AD to develop indicators that correlate with binder performance.

Final Operating SAR-AD Conditions

This fully automated separation subdivides heavy oils and asphalts into chemically meaningful chromatographic and asphaltene solubility fractions using only 2-mg samples. The stationary phases are not changed between separations. To conduct the separation, a 1-g portion of oil or asphalt is diluted to a 10-mL volume with chlorobenzene to give a 10 wt/vol-percent solution. The solution is filtered with a 0.45-µm syringe filter. A 20-µL aliquot of the solution is injected into an HPLC system consisting of an optical absorbance detector set at 500 nm and an evaporative light scattering detector (ELSD).

Four columns are used for the fully automated separation, and the column switching and separation sequence is illustrated in figure 1. The saturates elute with heptane through a ground PTFE column, glass bead column, aminopropyl bonded silica column, and activated silica

Figure 1. Column switching and solvent flow scheme for automated SAR-AD separations.



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column. The asphaltenes precipitate in an excess of heptane on the PTFE column (no chromatography is occurring here), and the highest surface energy resins adsorb on the glass beads, while other resins adsorb to the aminopropyl-bonded silica column. The aromatics adsorb on the activated silica column. In steps 2 through 4, the precipitated asphaltenes on the ground PTFE column are selectively dissolved with cyclohexane, followed by toluene, and finally CH_2Cl_2:MeOH (98:2 v:v), yielding, respectively, highly alkyl substituted asphaltene components, less alkyl substituted pericondensed aromatic asphaltenes, and pre-coke pericondensed aromatic asphaltenes. Step 5 is a forward flush with toluene through the activated silica column to elute the aromatics. The final step involves backflushing the aminopropyl-bonded silica and glass bead columns with CH_2Cl_2:MeOH (98:2 v:v) to elute the resin molecules. The entire system is then regenerated with an initial toluene flush followed by heptane, leaving the system ready for the next separation without changing the stationary phases. Example chromatograms from this separation are presented in figure 2.

Example Results

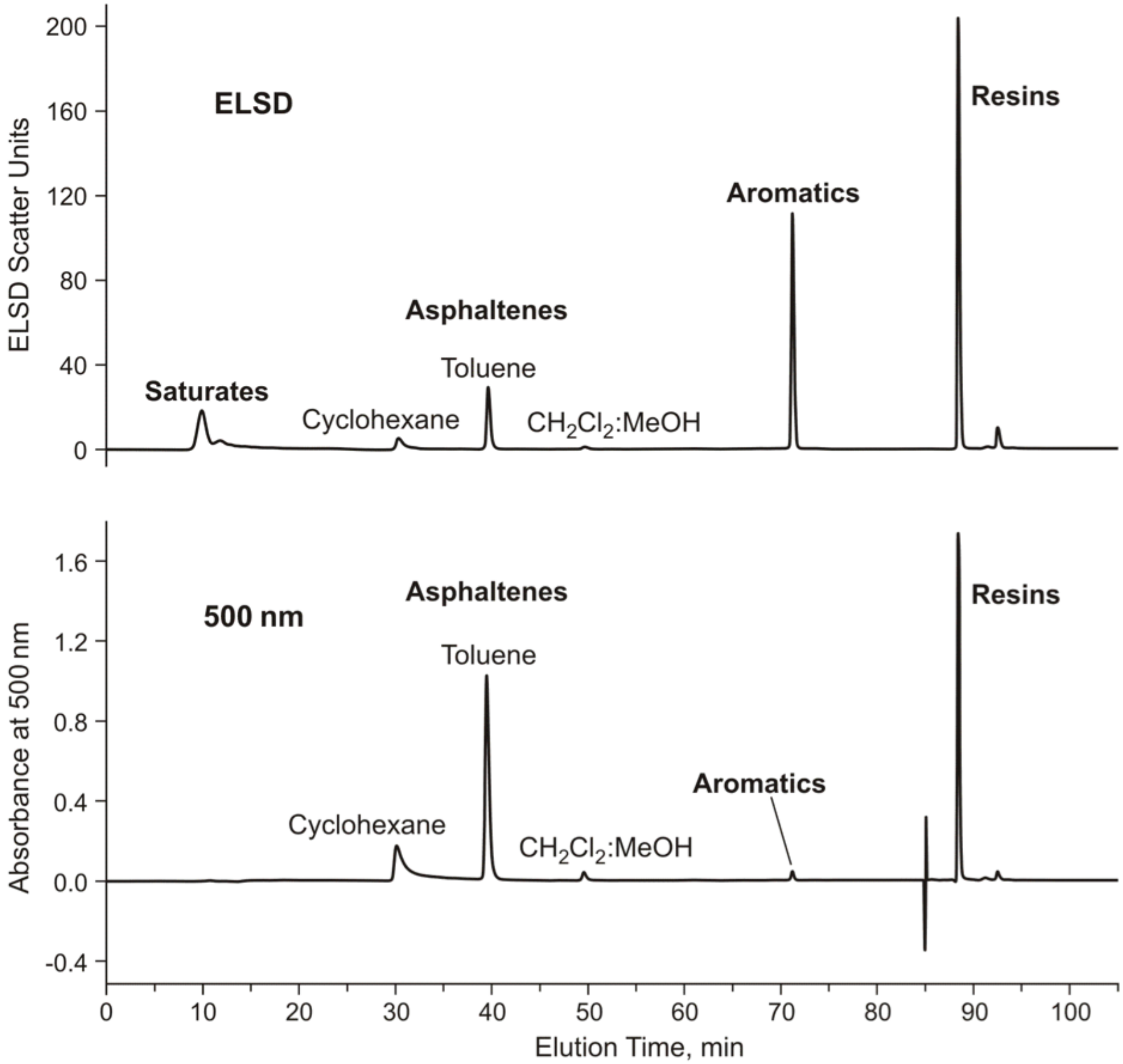
The research team is exploring separation profiles from the SAR-AD to develop indicators that correlate with binder performance. Several of these indicators already exist for the AD portion of the separation. The first of these is the absorbance aging index ratio (ADAIR), which is the ratio of the toluene soluble asphaltenes to the resins' 500-nm peak areas. Absorbance at 500 nm is due to the presence of pericondensed aromatic structures in various molecules. The material that elutes with the saturates, aromatics, and resin peaks (maltenes) represents the heptane soluble polar/alkyl-substituted naphthenic component molecules with pericondensed aromatic structures. The material that elutes with the toluene soluble asphaltene peak is representative of the pericondensed aromatic structures that typically comprise a large portion of asphaltenes with relatively few aliphatic side chains.(9)

The total pericondensed aromaticity (TPA) is the ratio of the mass of material that absorbs 500 nm of light to the total mass of the sample. To calculate this value, the 500 nm and ELSD peak areas for the sum of the three asphaltene peaks are correlated to give a 500-nm response factor specific to a particular sample. This peak area response factor is used to calculate the weight percent of 500 nm of absorbing material that elutes with the aromatics and resins fractions. The sum of weight percents from the three asphaltene, aromatics, and resins fractions that absorb at 500 nm is designated TPA for that sample.

The ELSD toluene-to-aromatics ratio is an empirical ratio that may be useful in predicting physical properties, including service life of a binder because higher TPA and toluene-to-aromatics ratios lead to embrittlement. More data and research are needed to validate the utility of these ratios and subsequent correlations.

The SAR-AD results for the Federal Highway Administration Accelerated Load

Figure 2. Automated SAR-AD separation profile for 2-mg asphalt.



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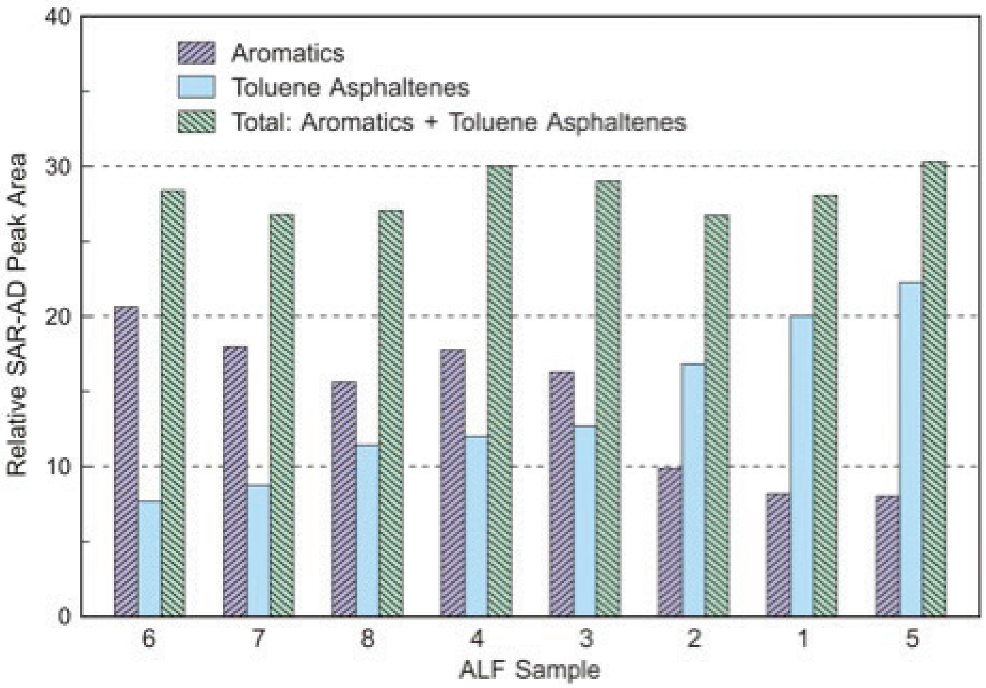
Facility (ALF) binders at varying degrees of laboratory and field aging are presented in table 1. It is clear that aging increases asphaltene content, in particular toluene asphaltenes, and decreases aromatic content. Total pericondensed aromaticity, toluene-to-aromatics ratio, and ADAIR all increase with aging severity. The quantities of resins, saturates, cyclohexane, and methylene chloride asphaltenes remain relatively unchanged with aging. Figure 3 highlights these changes with aging severity.

Table 1. Automated SAR-AD results from ALF binders. (Ambient binders are materials that were aged on the road under atmospheric conditions.)

ALF Lane 2			Maltenes			Asphaltenes				Aging Ratios		
ALF Sample #	Treatment	Detector	Saturates	Aromatics	Resins	CyC6	Toluene	CH_2Cl_2:MeOH	Total ELSD	ADAIR	Toluene/ Aromatics	TPA
6	Control	ELSD	18.0	20.7	51.6	1.9	7.7	0.2	9.7	NA	0.4	15.8
		500 nm	0.0	0.3	38.1	17.9	41.3	2.3	NA	1.1	NA	NA
7	RTFO	ELSD	16.5	18.1	54.2	2.2	8.8	0.2	11.2	NA	0.5	17.3
		500 nm	0.0	0.3	35.0	19.8	42.8	2.1	NA	1.2	NA	NA
8	RTFO PAV	ELSD	17.5	15.7	52.6	2.7	11.5	0.2	14.3	NA	0.7	20.3
		500 nm	0.0	0.2	29.6	19.4	49.2	1.6	NA	1.7	NA	NA
4	Ambient	ELSD	16.9	17.8	50.3	2.6	12.0	0.4	15.0	NA	0.7	21.0
	Fourth slice	500 nm	0.0	0.2	28.4	18.4	49.4	3.5	N[a]	1.7	NA	NA
3	Ambient	ELSD	16.6	16.4	51.3	2.6	12.7	0.4	15.7	NA	0.8	21.6
	Third slice	500 nm	0.0	0.2	27.2	18.0	50.9	3.7	NA	1.9	NA	NA
2	Ambient	ELSD	15.7	9.9	54.6	2.2	16.9	0.8	19.9	NA	1.7	25.3
	Second slice	500 nm	0.0	.02	21.3	13.7	59.2	5.7	NA	2.8	NA	NA
1	Ambient	ELSD	13.2	8.2	55.4	2.4	19.9	1.0	23.3	NA	2.4	28.9
	Top slice	500 nm	0.0	0.1	19.3	13.2	61.5	6.0	NA	3.2	NA	NA
5	Accelerated	ELSD	13.7	8.0	52.0	2.8	22.3	1.0	26.2	NA	2.8	31.6
	Top slice	500 nm	0.0	0.1	17.1	14.0	63.6	5.2	NA	3.7	NA	NA

RTFO = Rolling thin film oven aging.
RTFO PAV = RTFO plus pressure aging vessel.
NA= Not applicable.

Figure 3. Relationship of aromatics and toluene soluble asphaltenes with aging. (Aging severity increases from left to right.)



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Conclusions

The automated SAR-AD separation identifies real content differences between asphalt binders that allow correlations between chemical content and physical properties. These correlations can be useful in binder formulation through blending, rejuvenation, and modification as well as prediction of physical performance. More work is needed to further develop and validate these correlations. The columns used in the separation process can be regenerated between separations, making the system fully automated and allowing complete separation and column regeneration in 4 h.

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