

Technical White Paper

Automated HPLC SAR-AD Separation

Fundamental Properties of Asphalts and Modified Asphalts III Product: FP 01

March 2015

Prepared for
Federal Highway Administration
Contract No. DTFH61-07-D-00005

By
Ryan Boysen and John Schabron
Western Research Institute
3474 North 3rd Street
Laramie, WY 82072
www.westernresearch.org

TABLE OF CONTENTS

INTRODUCTION	1
EXPERIMENTAL	2
Development of the Automated SAR-AD Method.....	2
Final Operating SAR-AD Conditions	3
Instrumentation	3
Separation Procedure	4
RESULTS AND DISCUSSION	7
CONCLUSIONS	12
RECOMMENDATIONS	12
ACKNOWLEDGMENTS	12
DISCLAIMER	12
REFERENCES	12

LIST OF FIGURES

Figure1. Photo. The automated SAR-AD apparatus setup at WRI.....	4
Figure 2. Diagram. Column switching and solvent flow scheme for automated SAR-AD separations.....	5
Figure 3. Graph. Automated SAR-AD separation profile for 2 mg asphalt	7

LIST OF TABLES

Table 1. Automated SAR-AD results for SHRP core binders	9
Table 2. Automated SAR-AD results from ALF binders	10

AUTOMATED HPLC SAR-AD SEPARATION

INTRODUCTION

Dividing a material into its constituent parts is necessary to defining its composition. 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 (Jewel et al. 1972; Corbett 1969).

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 utilizing a low polarity hydrocarbon solvent such as isooctane, pentane, or heptane. The soluble material is by definition called the maltenes and the insoluble material is, by definition, called asphaltenes. The gravimetric asphaltenes / maltenes separation typically takes 24 hours. 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, it takes yet another day.

The maltenes are often divided into three fractions by normal-phase liquid chromatography called saturates, aromatics, and resins/polars (SAR). The saturates fraction consist 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, few to no hetero-atoms, and is distinct from the saturate fraction by containing one or more aromatic carbon rings. The resins and asphaltenes fractions both contain many aromatic rings, some being pericondensed, with many polar substituents.

The methods for SARA separation can be classified into two groups. The first method that has been widely utilized uses a technique known as thin-layer chromatography (TLC), and when combined with flame ionization detection (FID) becomes semi-automated. There is a known commercial method named Iatroscan in which capillary thin layer chromatography is conducted 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 hydrocarbon in the fractional zones on the rod (Karlsen and Larter 1991, Wan et al. 1992). The Iatroscan instrument typically elutes the fractions in a sequence of solvents consisting of a linear alkane, cyclohexane, toluene, and dichloromethane:methanol mixtures. However, the Iatroscan method has severe drawbacks including variable response factors for the polar fractions, relatively high amounts of polar compounds retained near the spot location on the TLC rod, and aromatics grouping together to act like resins during separation (Jiang et al. 2008; Masson et al. 2001). The separation has a large amount of error on repeat analysis and there is a problem with the strongly adsorbed, asphaltene material which does not migrate up the rod (Masson et al. 2001).

The second type of method requires precipitation of the asphaltenes by dissolving the sample in an excess of an alkane before further separation of the maltenes into the saturate, aromatic, and resin (SAR) fractions by liquid chromatography. Typical methods for asphaltene separations are described in ASTM D4124. Many variations of the SAR separation have been developed using amino, cyano, or alumina columns including several automated or semi-automated methods utilizing high performance liquid chromatography (HPLC) (ASTM D3279-97 1997; ASTM D4124-01 2001; Grizzle and Sablotny 1986; Fan and Buckley 2002; Aske et al. 2001; Kharrat et al. 2007; U.S. Patent 4,988,446 1991). The variations for automated separation of the maltenes typically use silica gel derivatized with aminopropyl or cyano functional groups. These generally do not provide fully resolved separations of saturates and aromatics and irreversible adsorption occurs on the columns due to resins and soluble asphaltene-type component molecules. A version of an HPLC SARA method that uses chemically bonded aminosilane stationary phase for an automated SAR separation of crude oil maltenes (Grizzle and Sablotny 1986) was evaluated at WRI. While the authors claim that it also works on bituminous material, no data were presented to support this assertion and the most polar fractions of asphalt were not desorbed from the system resulting in poor recovery and fouling of the column. Fan and Buckley (2002) developed a similar method that utilizes two aminosilane columns. While their system appears to work well for crude oils, the most polar components of the resins fraction of asphalt became irreversibly bonded to the column. It was evident that a new system was needed for asphalt that performs the SAR separation without fouling the column and that allows near full recovery of all the fractions.

Asphaltene Determinator (AD) is a novel automated HPLC based asphaltene separation developed by Schabron and Rovani. Following an injection of 2 mg of a petroleum oil or vacuum residua, asphaltenes precipitate onto a polytetrafluoroethylene (PTFE) packed column in excess of heptane. The asphaltenes are then selectively dissolved with stronger, more polar solvents to quantitatively give three fractions of asphaltenes (Schabron and Rovani 2008; Schabron et al. 2010). Using this system coupled on the front end to separate the asphaltenes, the maltenes can then be separated into SAR fractions giving a fully automated SARA separation.

EXPERIMENTAL

Development of the Automated SAR-AD Method

Several different avenues were explored in the development of the fully automated SAR-AD separation. Initially, n-heptane maltenes prepared by gravimetric isolation from AAA-1 binder were separated into saturates, aromatics and resins fractions on a HPLC system with activated silica as the stationary phase and n-heptane, toluene, and methylene chloride:methanol (98:2 v/v) as the solvents. Because methanol deactivated the silica during a separation, the column was repacked with fresh activated silica for each subsequent separation. Unacceptably large variations between repeat separations of the same sample eliminated this as a viable analytical tool.

Following the lead of Fan and Buckley (2002), an aminopropyl bonded silica column was employed using the same AAA-1 maltenes and solvents as above. Irreversible absorption of part of the resins fraction quickly fouled this column, and it did not yield complete recovery of the binder.

In a ground breaking departure from previous work, three columns were then utilized packed with glass beads, aminopropyl bonded silica, and activated silica respectively, with which the same AAA-1 maltenes were separated. The primary concept was that some of the resins adhere to the glass beads, the remaining resins and some aromatics adhere to the aminopropyl bonded silica, and the remaining aromatics elute through all three columns with n-heptane as the mobile phase. Toluene was then used to backflush the activated silica and aminopropyl bonded silica columns to elute the aromatics, and methylene chloride:methanol (98:2 v/v) eluted the polars from the amino and glass bead columns. It became evident that the toluene backflush of the amino column was also eluting resins from this column, and once the less polar resins were removed from the amino column, the more polar resins were irreversibly bound to the column.

In an effort to allow all aromatics to elute through to the activated silica column, the aminopropyl bonded silica was replaced with deactivated silica. Additionally, the PTFE column was added to the front end of the system to precipitate out the asphaltenes from whole asphalts as described by Schabron et al. (2010). While all the aromatics eluted through the deactivated silica with n-heptane, so did some of the resins and the activated silica column quickly fouled.

The final necessary step taken to obtain a quality SARA separation involved replacing the deactivated silica with aminopropyl bonded silica to remove all the resins from the n-heptane prior to the activated silica column. In doing this, the resins are defined as all the maltene material adhering to either the glass beads or aminopropyl bonded silica columns with n-heptane as the solvent. Consequently, it is possible that some species traditionally thought of as aromatic compounds become trapped in the resin fraction and thus, this separation generally yields a smaller quantity of aromatics relative to the traditional ASTM D4124 SARA separations using only active silica or alumina as the stationary phase. Many other small changes were evaluated during the development of this method and are not included in this report.

Final Operating SAR-AD Conditions

Instrumentation

Waters brand HPLC equipment automate the SAR-AD separation including a model 600 pump, 2707 autosampler, 2489 variable wavelength absorbance detector set at 500 nm and 700 nm, and 2424 evaporative light scattering detector (ELSD). Figure 1 is a picture of the setup. The 2707 autosampler is set to 20 μ L injections containing partial loop in needle overflow mode. The 2424 ELSD has 35 psi nitrogen flow, 60°C drift tube, and the nebulizer is set to cooling (about 12°C).



Figure 1. Photo. The automated SAR-AD apparatus setup at WRI.

The separation is performed with four 250 mm X 7 mm i.d. columns packed with ground 40-60 mesh polytetrafluoroethylene (PTFE), 150-212 μm glass beads, 15-35 μm 9 mm pore size aminopropyl bonded silica gel, and 37-70 μm 150 Å silica gel activated at 120°C overnight respectively. All columns are thermostatted to 30°C. Automated 4 and 6 port electronic actuated Valco switching valves control the flow path of the solvents and these switches are activated by the pump and UV detector. Step gradient solvent changes are heptane, cyclohexane, toluene, methylene chloride:methanol (98:2 v:v), all at 2 mL/min. The cyclohexane is HPLC grade and all other solvents are reagent grade or better.

Separation Procedure

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 1.0 gram portion of oil or asphalt is diluted to 10 mL volume with chlorobenzene to give a 10 wt/vol % solution. The solution is filtered with a 0.45 μm syringe filter. A 20 μL aliquot of the solution is injected into a HPLC system with an optical absorbance detector set at 500 nm and 700 nm and an ELSD.

The column switching and separation sequence is illustrated in figure 2. The saturates elute with heptane through a ground polytetrafluoroethylene (PTFE) column, glass bead column, aminopropyl bonded silica column, and activated silica column. The asphaltenes precipitate in 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 2-4 the precipitated asphaltenes on the ground PTFE column are selectively dissolved with cyclohexane, followed by toluene, and finally $\text{CH}_2\text{Cl}_2\text{:MeOH}$ (98:2 v:v) yielding highly alkyl substituted asphaltene components, less alkyl substituted pericondensed aromatic asphaltenes, and pre-coke pericondensed aromatic asphaltenes respectively. Step 5 is a forward flush with toluene through

the activated silica column to elute the aromatics. The final step involves back flushing the aminopropyl bonded silica and glass bead columns with $\text{CH}_2\text{Cl}_2:\text{MeOH}$ (98:2 v:v) to elute the resin molecules. The entire system is then regenerated with an initial toluene flush followed by heptane.

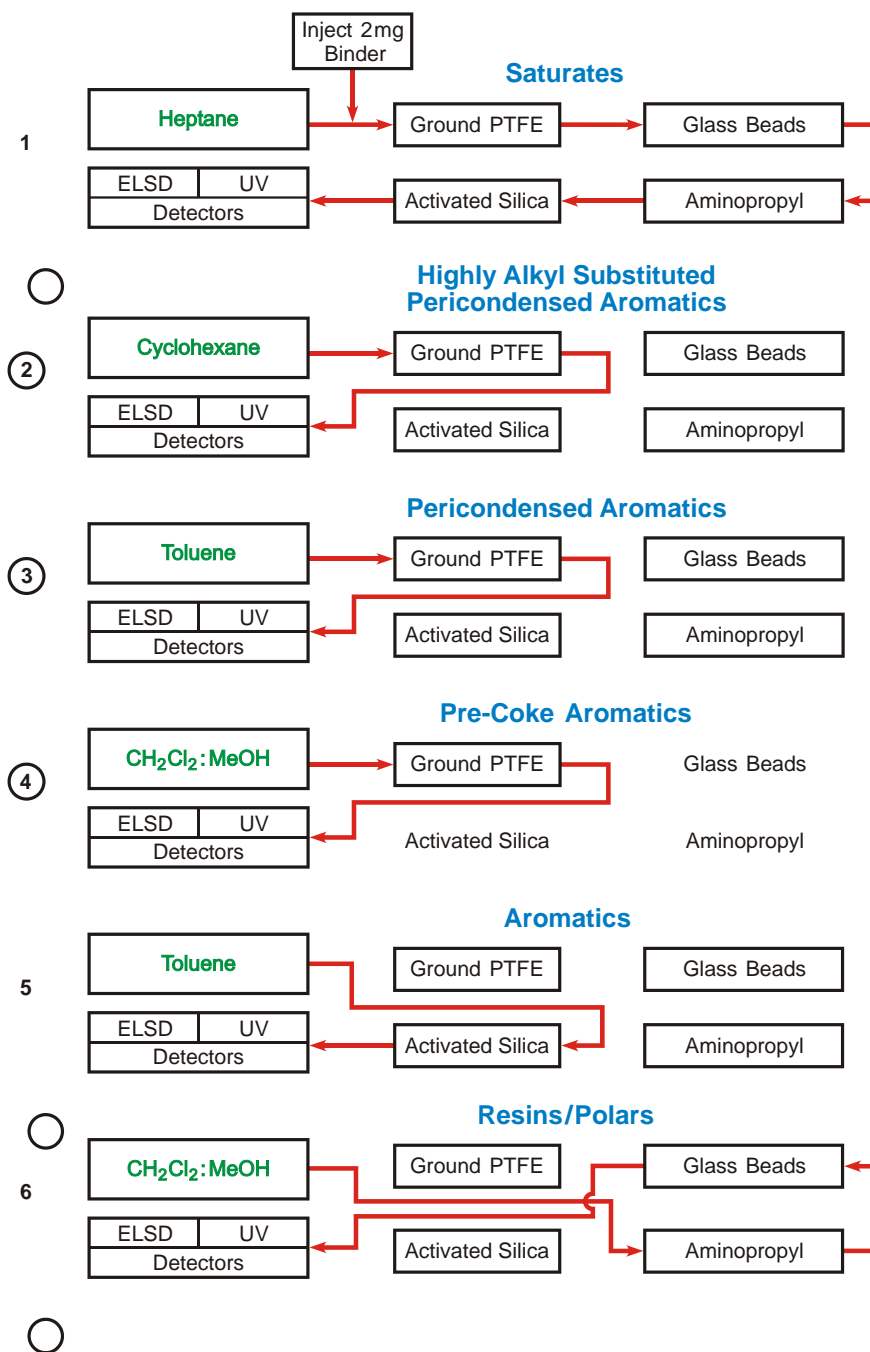


Figure 2. Diagram. Column switching and solvent flow scheme for automated SAR-AD separations.

Optimized separation times consist of the following:

- 25 minutes of heptane flow forward through all four columns,
- 10 minutes each of cyclohexane, toluene, CH₂Cl₂:MeOH (98:2 v:v), and heptanes, respectively, forward through the PTFE column,
- Forward flow through the activated silica column with toluene for 15 minutes followed by heptane for 5 minutes,
- Backflow through the aminopropyl then glass bead columns with CH₂Cl₂:MeOH (98:2 v:v) for 10 minutes and, finally, 10 minutes with toluene.

The column regeneration sequence is a two step process that is performed immediately prior to a separation. Consequently, when the system is idle, the columns are neither regenerated nor ready for a separation. The first regeneration step involves a 40 minutes forward flow of toluene through the PTFE column and backflow through the aminopropyl followed by glass bead columns. The second step is 100 minutes of heptane forward through the PTFE, glass bead, aminopropyl, and activated silica columns, respectively. All flow rates are 2.0 mL/min and pressures are typically <400 psi. Pump pressure fluctuates widely throughout the separation and column regeneration due to column and solvent switching.

Blank separation profiles are electronically subtracted from the sample profiles. The total area count and the individual area counts for the six resulting peaks are integrated to determine the relative peak areas corresponding to each of the six fractions. It is assumed that the relative peak areas from the six peaks in each ELSD chromatogram are directly proportional to the amount of material in each of the fractions. The assumption is that the ELS detector shows uniform response regardless of sample type or quantity within these sample ranges. There are some possible minor deviations from this assumption, but they are not considered in this text. A quality control sample is injected at the beginning of the sequence and again at the end of the sequence to ensure that no significant changes have occurred in column. Figure 3 shows example chromatograms from a separation on this system.

The model aliphatic compounds cholestane and microcrystalline elute with the saturates fraction. The highly olefinic compound squalene, the polycyclic aromatic compound benzo[a]pyrene and the aromatic polymer polystyrene all elute with the aromatics fraction. Materials containing pericondensed aromatic chromophores that absorb light at 500 nm elute with the polar and asphaltene fractions, and not in the aromatics fraction. The saturates fraction shows zero absorption at 260 nm.

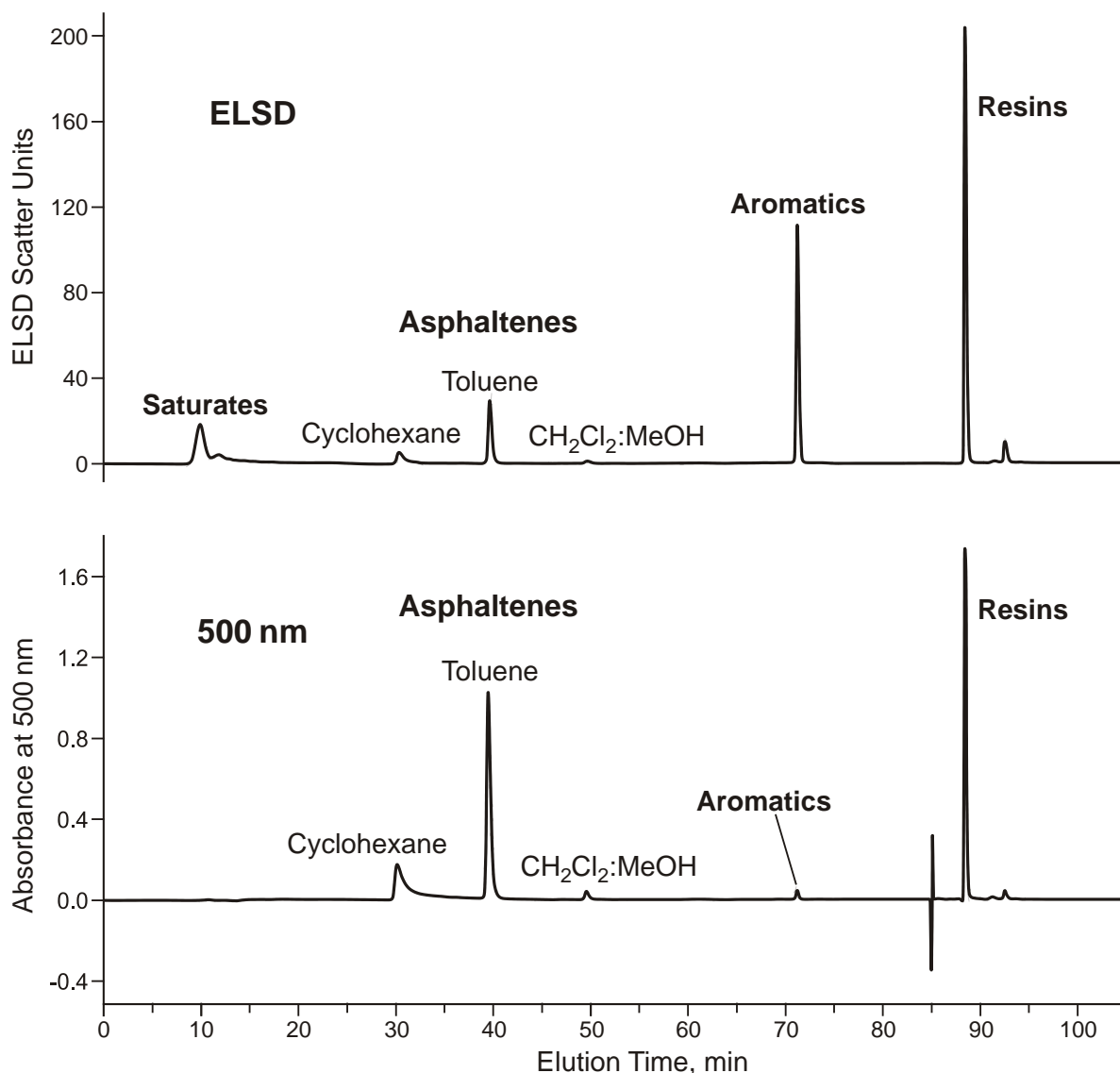


Figure 3. Graph. Automated SAR-AD separation profile for 2 mg asphalt.

RESULTS AND DISCUSSION

Separation profiles from the SAR-AD are being explored for the possibility of developing 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 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 resins 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 (Mullins et al. 2007).

The total pericondensed aromaticity (TPA) is the ratio of the mass of material that absorbs 500 nm 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 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. This approach is not affected by the solvent, temperature, or other experimental conditions that can cause significant variations in quantities of SARA fractions.

The ELSD toluene to aromatics ratio is an empirical ratio that may be useful in predicting physical properties including service life of a binder. More data and research is needed to validate the utility of this ratio and subsequent correlations.

This method was applied to SHRP core binders and binders from the Accelerated Load Facility (ALF) in support of task 3.D under the FPIII contract. The SHRP results, as presented in table 1, show real differences between binders as well as significant changes upon air blowing as AAE-1 is airblown AAA-1. Through the oxidation process, molecules from the resin fraction become asphaltenes, and aromatic species oxidize to become resins. Data at 700 nm are not included because that detector was not operational for these separations. These SARA results show significant differences from the separations performed during the original Strategic Highway Research Program (Jones 1993). In particular, the quantity of saturates are greater in the current method. Differing separation mediums between these two studies is likely responsible for this discrepancy. Time did not permit a more exhaustive study of these SHRP binders and their aging profiles and no clear correlation or binder ranking based on the SAR-AD separation is yet available.

The SAR-AD results from ALF binders at varying degrees of laboratory and field aging and different modifiers/processes are presented in table 2. It is clear that aging increases asphaltene content, in particular toluene asphaltenes, and decreases aromatic content. Total pericondensed aromaticity, toluene/aromatics ratio, and ADAIR all increase with aging severity. The quantity of resins, saturates, cyclohexane and methylenechloride asphaltenes remain relatively unchanged with aging. More data is needed on different binders and aging sequences to validate and correlate changes in SARA fractions with aging. The data on modified/processed binders show that this technique can be performed on binders containing a variety of modifiers. The effect of modification on the SAR-AD fractions is predominantly evident in the toluene asphaltene and resins.

Table 1. Automated SAR-AD results for SHRP core binders.

Sample	Detector	Maltenes			Asphaltenes				Absorbance Aging Index	Toluene to Aromatics Ratio	TPA
		Saturates	Aromatics	Resins	CyC ₆	Toluene	CH ₂ Cl ₂ : MeOH	Total ELSD Asphaltenes			
AAA-1	ELSD 500 nm	19.0	19.9	47.4	5.2	8.3	0.2	13.6	1.2	0.4	20.2
			0.6	31.9	27.6	37.7	2.3				
AAE-1	ELSD 500 nm	16.9	10.4	50.4	4.7	17.4	0.2	22.3	1.7	1.7	31.3
			0.4	28.4	19.2	49.4	2.6				
AAB-1	ELSD 500 nm	18.0	15.5	54.6	3.3	8.5	0.1	11.9	1.1	0.5	18.9
			0.5	36.6	18.1	41.5	3.3				
AAC-1	ELSD 500 nm	29.2	13.1	51.6	2.2	3.8	0.1	6.1	0.6	0.3	12.1
			0.9	48.7	17.0	30.5	2.9				
AAD-1	ELSD 500 nm	11.8	15.5	54.7	5.8	12.2	0.1	18.1	1.7	0.8	24.8
			0.6	26.6	23.8	46.3	2.7				
AAF-1	ELSD 500 nm	17.4	13.2	62.1	2.5	4.7	0.0	7.2	0.7	0.4	13.7
			0.8	46.5	18.8	31.9	2.1				
AAG-1	ELSD 500 nm	18.0	12.4	67.3	0.5	1.8	0.0	2.3	0.3	0.1	7.0
			1.5	65.8	9.4	20.9	2.5				
AAK-1	ELSD 500 nm	11.3	18.6	54.9	4.3	10.9	0.1	15.3	1.4	0.6	22.2
			0.5	30.7	23.5	42.4	3.0				
AAM-1	ELSD 500 nm	18.3	13.7	65.9	0.8	1.2	0.1	2.1	0.1	0.1	9.4
			1.1	76.6	8.8	11.4	2.2				

Table 2. Automated SAR-AD results from ALF binders.

ALF Sample	Detector	Maltenes			Asphaltenes				Absorbance Aging Index	Toluene to Aromatics Ratio	TPA
		Saturates	Aromatics	Resins	CyC ₆	Toluene	CH ₂ Cl ₂ : MeOH	Total ELSD Asphaltenes			
6298 Reference RTFO	ELS	16.5	18.1	54.2	2.2	8.8	0.2	11.2		0.5	17.3
	500 nm		0.3	35.0	19.8	42.8	2.1		1.2		
	700 nm		0.3	25.4	22.7	48.8	2.9		1.9		
6298 Reference RTFO/PAV	ELS	17.5	15.7	52.6	2.7	11.5	0.2	14.3		0.7	20.3
	500 nm		0.2	29.6	19.4	49.2	1.6		1.7		
	700 nm		0.2	20.3	21.9	55.4	2.2		2.7		
L2S3 Ambient Bottom ½"	ELS	16.9	17.8	50.3	2.6	12	0.4	15		0.7	21
	500 nm		0.2	28.4	18.4	49.4	3.5		1.7		
	700 nm		0.2	19.7	20.4	55.1	4.5		2.8		
L2S3 Ambient Third ½"	ELS	16.6	16.4	51.3	2.6	12.7	0.4	15.7		0.8	21.6
	500 nm		0.2	27.2	18	50.9	3.7		1.9		
	700 nm		0.2	18.5	19.8	56.6	4.8		3		
L2S3 Ambient Second ½"	ELS	15.7	9.9	54.6	2.2	16.9	0.8	19.9		1.7	25.3
	500 nm		0.2	21.3	13.7	59.2	5.7		2.8		
	700 nm		0.2	12.9	14.7	65.2	7.1		5		
L2S3 Ambient Top ½"	ELS	13.2	8.2	55.4	2.4	19.9	1	23.3		2.4	28.9
	500 nm		0.1	19.3	13.2	61.5	6		3.2		
	700 nm		0.2	11.4	14.1	66.9	7.5		5.8		
L2S4 Accelerated Top ½"	ELS	13.7	8.0	52.0	2.8	22.3	1.0	26.2		2.8	31.6
	500 nm		0.1	17.1	14.0	63.6	5.2		3.7		
	700 nm		0.1	9.8	15.0	68.9	6.3		7.0		

Table 2 continued.

ALF Sample	Detector	Maltenes			Asphaltenes				Absorbance Aging Index	Toluene to Aromatics Ratio	TPA
		Saturates	Aromatics	Resins	CyC ₆	Toluene	CH ₂ Cl ₂ : MeOH	Total ELSD Asphaltenes			
6298 Reference	ELS	18.0	20.7	51.6	1.9	7.7	0.2	9.7		0.4	15.8
Lane 2	500 nm		0.3	38.1	17.9	41.3	2.3		1.1		
Unmodified	700 nm		0.3	27.5	20.9	48.1	3.2		1.7		
6286	ELS	21.4	19.6	44.0	2.8	11.9	0.4	15.0		0.6	20.8
Lane 5	500 nm		0.3	27.5	17.6	50.6	4.0		1.8		
TBCR	700 nm		0.4	16.2	18.4	56.8	8.2		3.4		
6292	ELS	15.0	20.6	54.7	1.3	7.8	0.7	9.7		0.4	14.8
Lane 7	500 nm		0.3	34.0	16.2	41.9	7.6		1.2		
Polyester	700 nm		0.3	23.8	18.4	47.3	10.2		2.0		
6295	ELS	17.1	20.2	50.6	5.7	6.2	0.2	12.1		0.3	20.4
Lane 4	500 nm		0.4	40.3	25.2	32.9	1.3		0.8		
SBS	700 nm		0.5	27.2	30.8	39.5	2.0		1.4		
6289	ELS	21.1	21.6	48.0	0.8	6.0	2.6	9.4		0.3	14.1
Lane 6	500 nm		0.3	33.3	9.6	38.0	18.9		1.1		
GMA	700 nm		0.3	21.2	10.7	43.4	24.4		2.0		
6281	ELS	21.8	18.4	44.1	3.3	12.3	0.2	15.7		0.7	21.5
Lane 3	500 nm		0.2	26.6	21.8	49.8	1.6		1.9		
Air Blown	700 nm		0.2	18.5	23.9	55.3	2.1		3.0		

CONCLUSIONS

The automated SAR-AD separation is highly repeatable and gives real content differences between asphalt binders that allow for correlations between chemical content and physical properties. The TPA, aging index, and toluene to aromatics ratios can also be used for performance correlations. The columns can be regenerated between separations making the system fully automated allowing for a complete separation and column regeneration in 4 hours.

RECOMMENDATIONS

The development of this method required a large effort including working through numerous complexities that are not practical to describe in this text. It is recommended that researchers contact WRI if they have interest in owning an automated HPLC based SAR-AD instrument. Additionally, the AD is a patented technology and the automated SAR separation has a patent pending and both would need to be licensed from WRI.

ACKNOWLEDGMENTS

The authors gratefully acknowledge the Federal Highway Administration, U.S. Department of Transportation, for financial support of this project under contract no. DTFH61-07D-00005.

DISCLAIMER

This document is disseminated under the sponsorship of the Department of Transportation in the interest of information exchange. The United States Government assumes no liability for its contents or use thereof.

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.

REFERENCES

Aske, Narve, H. Kallevik, and J. Sjoblom, 2001, Determination of Saturate, Aromatic, Resin and Asphaltenic (SARA) Components in Crude Oils by Means of Infrared and Near-Infrared Spectroscopy. *Energy and Fuels*, 15: 1304-1312.

ASTM D3279-97. *Standard Test Method for n-Heptane Insolubles*, 1997.

ASTM D4124-01. *Standard Test Methods for Separation of Asphalt into Four Fractions*, 2001.

- Corbett, L.W., 1969, Composition of Asphalt Based on Generic Fractionation, Using Solvent Deasphalting, Elution-Adsorption Chromatography, and Densimetric Characterization. *Analytical Chemistry*, 41 (4): 576-579.
- Fan, T., and J. S. Buckley, 2002, Rapid and Accurate SARA Analysis of Medium Gravity Crude Oils. *Energy and Fuels*, 16: 1571-1575.
- Grizzle, P. L., and D. M. Sablotny, 1986, Automated Liquid Chromatographic Compound Class Group-Type Separation of Crude Oils and Bitumens Using Chemically Bonded Aminosilane. *Analytical Chemistry*, 58: 2389-2396.
- Jewel, D. M., J. H. Weber, J. W. Bunger, H. Plancher, and D. R. Latham, 1972, Ion-Exchange, Coordination, and Adsorption Chromatographic Separation of Heavy-End Petroleum Distillates. *Analytical Chemistry*, 44 (8): 1391-1395.
- Jiang, C., S. R. Larter, K. J. Noke, and L. R. Snowdon, 2008, TLC-FID (Iatroscan) analysis of heavy oil and tar sand samples. *Organic Geochemistry*, 39 (5): 1210-1214.
- Jones, D. R., 1993, *SHRP-A-645, SHRP Materials Reference Library: Asphalt Cements: A Concise Data Compilation*. Strategic Highway Research Program, National Research Council, Washington, DC.
- Karlsen, D. A., and S. R. Larter, 1991, Analysis of petroleum fractions by TLC-FID: applications to petroleum reservoir description. *Organic Geochemistry*, 17 (5): 603-617.
- Kharrat, A. M., J. Zacharia, V. J. Cherian, and A. Anyatonwu, 2007, Issues with Comparing SARA Methodologies. *Energy and Fuels*, 21: 3618-3621.
- Masson, J-F., T. Price, and P. Collins, 2001, Dynamics of Bitumen Fractions by Thin-Layer Chromatography/Flame Ionization Detection. *Energy and Fuels*, 15: 955-960.
- Mullins, O. C., E. Y. Sheu, A. Hammami, and A. G. Marshall, Eds., 2007, *Asphaltenes, Heavy Oils, and Petroleomics*, Springer, New York; ISBN: 10:0-387-31734-1.
- Schabron, J. F., and J. F. Rovani, 2008, On-Column Precipitation and Re-Dissolution of Asphaltenes in Petroleum Residua. *Fuel*, 87: 165-175.
- Schabron, J. F., J. F. Rovani, and M. M. Sanderson, 2010, Asphaltene Determinator Method for Automated On-Column Precipitation and Redissolution of Pericondensed Aromatic Asphaltene Components. *Energy and Fuels*, 24: 5984-5996.
- U.S. Patent 4,988,446, Haberman, J. L., R. E. Overfield, and W. K. Robbins, 1991. Method for Spectroscopic Analysis of Hydrocarbons.
- Wan, C. C., T. H. Waters, and R. D. Wolever, 1992, Development of a Reproducible Iatroscan Method to Chemically Characterize Asphalt. *ACS Div. Fuel Chem. Prepr.*, 1350-1359.