

**TOPICAL REPORT**

**HEAVY OIL PROCESS MONITOR: AUTOMATED ON-COLUMN  
ASPHALTENE PRECIPITATION AND RE-DISSOLUTION**

**Work Performed Under Cooperative Agreement  
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## EXECUTIVE SUMMARY

An automated separation technique was developed that provides a new approach to measuring the distribution profiles of the most polar, or asphaltenic components of an oil, using a continuous flow system to precipitate and re-dissolve asphaltenes from the oil. Methods of analysis based on this new technique were explored.

One method based on the new technique involves precipitation of a portion of residua sample in heptane on a polytetrafluoroethylene-packed (PTFE) column. The precipitated material is re-dissolved in three steps using solvents of increasing polarity: cyclohexane, toluene, and methylene chloride. The amount of asphaltenes that dissolve in cyclohexane is a useful diagnostic of the thermal history of oil, and its proximity to coke formation. For example, about 40 % (w/w) of the heptane asphaltenes from unpyrolyzed residua dissolves in cyclohexane. As pyrolysis progresses, this number decrease to below 15% as coke and toluene insoluble pre-coke materials appear. Currently, the procedure for the isolation of heptane asphaltenes and the determination of the amount of asphaltenes soluble in cyclohexane spans three days. The automated procedure takes one hour.

Another method uses a single solvent, methylene chloride, to re-dissolve the material that precipitates on heptane on the PTFE-packed column. The area of this second peak can be used to calculate a value which correlates with gravimetric asphaltene content. Currently the gravimetric procedure to determine asphaltenes takes about 24 hours. The automated procedure takes 30 minutes.

Results for four series of original and pyrolyzed residua were compared with data from the gravimetric methods. Methods based on the new on-column precipitation and re-dissolution technique provide significantly more detail about the polar constituent's oils than the gravimetric determination of asphaltenes.

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## OBJECTIVES

A main objective of the current work is to develop rapid refinery process control analysis schemes to optimize distillation while minimizing risks of fouling. Methods based on a new automated on-column asphaltene precipitation and re-dissolution technique that can be related to the WRI Coking Indexes and asphaltene content were explored. This may provide a rapid analysis for refinery process control resulting in significant efficiency improvement, with less down time and heat wasted in refinery operations.

## INTRODUCTION

### **Background**

A new approach to the characterization of the polar materials in petroleum has been developed (Schabron et al. 2005, 2006). This is a new technique of on-column precipitation and re-dissolution. The separations are performed using an inert stationary phase consisting of ground polytetrafluoroethylene (PTFE). Although high-performance liquid chromatography (HPLC) instrumentation and detectors are used, the separation does not involve chromatographic interactions between the material being separated and the stationary phase. It is strictly solubility based. In the current work, two methods based on the new technique were explored. One method breaks the asphaltenic material into three subfractions of increasing polarity, which provides a quantitative indication of the resins/polars/very polars distribution. A second method provides a measurement that correlates with the total weight percent of asphaltenic material. This approach allows the detection of polar materials in minutes, even for samples that do not precipitate asphaltenes in the gravimetric method. Methods based on the new technique are being evaluated with both upstream and downstream oils, such as crude oils, fuel oils, slurry oils, atmospheric residua, and vacuum residua.

### **The Solvation Shell Coking Index**

The  $K_S$  term is a Coking Index value that we have found to be universally applicable to vacuum or atmospheric residua or whole visbroken oils to measure the pyrolysis or thermal history of oil and its proximity to coke formation. To obtain this value the amount of heptane asphaltenes that dissolve in cyclohexane is measured. For unpyrolyzed residua, about 40 % (w/w) of heptane asphaltenes dissolves in cyclohexane. This corresponds to a  $K_S$  value of 1.7 (Pauli and Branthaver 1998). As pyrolysis progresses, the amount of heptane asphaltenes soluble in cyclohexane decreases below 15% as coke and toluene insoluble pre-coke materials appear, which corresponds to  $K_S$  values below 1.2. This is an indicator of the destruction of the intermediate polarity material (Schabron et al. 2001a, 2001b). The  $K_S$  term is derived from an approach that has been invoked to enhance understanding of various properties of petroleum residua, the Pal and Rhodes suspended particle solution model. This model mathematically

describes solvated dispersed polar particles in a hydrocarbon solvent matrix (Pal and Rhodes 1989). The volume fraction of the core of particles can be estimated by determining the volume fraction of heptane asphaltenes  $\Phi_a$ . The polar core volume fraction is increased by a solvation shell term  $K_S$ . Several solvated shells bind a portion of solvent and increase the effective particle volume by a term  $K_F$ . The term  $K_S K_F$  is called the solvation constant  $K$ . The effective particle volume  $\Phi_{EFF}$  can be calculated by the following equation.

$$\Phi_{EFF} = K \Phi_a = K_F K_S \Phi_a$$

Experimentally,  $K_S$  and  $\Phi_a$  are determined gravimetrically, and  $K_F$  is determined by asphaltene flocculation titration (ASTM D 6703).  $K_S$  can be estimated from the mass fraction of heptane asphaltenes that dissolve in cyclohexane ( $Y$ ) using the equation below.

$$K_S = 1/(1-Y)$$

The above equation assumes that the density of the cyclohexane soluble asphaltenes is essentially the same as the density of the insoluble material.

### **Gravimetric Determination of Asphaltenes**

In the gravimetric method, a sample of oil is weighed and mixed with an excess of aliphatic hydrocarbon solvent such as heptane. The mixture is stirred overnight, and the asphaltenes precipitate while the maltenes remain in solution. The mixture is then filtered with repeated rinsing, and the precipitate is then dried and weighed. This procedure usually takes about 24 hours. To determine the cyclohexane soluble portion of asphaltenes, the precipitate is ground manually, and a portion of this is stirred overnight with an excess of cyclohexane. The next day, the mixture is filtered. The manual method to determine both asphaltenes and the cyclohexane soluble portion of asphaltenes can take up to 3 days to complete.

## **EXPERIMENTAL**

### **Residua**

The four residua studied were Boscan, Lloydminster, and Redwater, B.C. from prior nonproprietary work at Western Research Institute (WRI), and MaxCL2 provided by ConocoPhillips.

### **Determination of Asphaltenes**

Heptane asphaltenes were isolated by heating an excess (40:1 v:w) mixture of reagent-grade n-heptane and residuum to 70 °C (158 °F) for about 30 minutes on a heated stir plate while stirring with a magnetic stir bar. This was followed by overnight stirring at room temperature. The following morning, the stirring was stopped for 30 minutes prior to vacuum



filtration using Ace, 140-mL, 10-20 micron, sintered glass filters. Residual solvent was removed from the asphaltenes on the filters using a vacuum oven set at 120 °C (248 °F) for 30 minutes. The asphaltenes were cooled in a desiccator prior to weighing.

A portion of n-heptane asphaltenes was ground to a fine powder using a mortar and pestle. A 0.5-g portion of this was weighed into a 120-mL jar, and 100 mL of reagent grade cyclohexane and a magnetic stir bar were added. The mixture was stirred overnight. The mixture was allowed to settle for 30 minutes prior to vacuum filtration using Ace, 140-mL, 10-20 micron, sintered glass filters. Solvent was removed from the filtrate by rotary evaporation, and traces of cyclohexane were removed in a vacuum oven at 100 °C (212 °F) for 15 minutes. The cyclohexane soluble materials were cooled in a desiccator prior to weighing.

### **On-Column Asphaltene Precipitation**

The on-column asphaltene precipitation and re-dissolution experiments were conducted using a Waters 717 autosampler, a Waters 60F pump with a model 600 controller, a Waters 1487 ultraviolet/visible absorbance detector, and an Alltech ELSD 800 evaporative light scattering detector. A schematic of the instrumental configuration is provided in Figure 1. Solutions of residua and asphaltenes in methylene chloride:toluene (1:1) (v:v) were injected onto an 10mm i.d. x 250 mm stainless steel column packed with 0.25-0.42 mm ground PTFE. The UV detector at 500 nm is used to monitor the separation profile for a, standard oil, which is injected daily to detect the possible onset of adsorption effects in the stationary phase. If this occurs, the PTFE packing material is replaced. Solvents were reagent grade, with step gradients between solvents. Peak area integration was performed using a Chrom Perfect Spirit 5.5 data system. ELSD peak areas were corrected for small blank peaks due to the step gradient solvent changes.

## **RESULTS AND DISCUSSION**

The new on-column technique provides a rapid separation using an automated continuous flow system to both precipitate and re-dissolve fractions in petroleum based on solubility. Bodusynski et al. reported a gravimetric on-column dissolution method for separating coal liquids deposited onto an inert packing, using heptane, toluene, and pyridine (Bodusynski et al. 1982). Solutions of sample were manually place onto column packing material and the solvent was removed by evaporation. He later expanded this approach to petroleum residua analysis by manually depositing samples onto glass beads, then dissolving the material with a series of solvents of increasing polarity (Bodusynski 1987). The new technique involves on-column precipitation into a low polarity solvent mobile phase combined with subsequent re-dissolution using one or more solvents of increasing solvent strength and polarity. Although high performance liquid chromatography (HPLC) equipment is used, the separation does not involve a chromatographic separation based on adsorption.

During the initial development work, several important aspects to the separation were optimized (Schabron et al. 2005, 2006, Schabron and Rovani 2006). For example, the separation temperature can be near ambient and it does not need to be controlled exactly. Glass wool or glass beads should not be used since they result in strong adsorption effects. The sample amount should be maximized to minimize adsorption effects, while the amount of solvent injected should be at a minimum. Peaks must be spaced apart for good resolution, and the solvent flow rate must be compatible with the ELSD (<6 mL / min).

In the current work, 20 wt./vol. % solutions of the various sample materials are made in methylene chloride, and then diluted to 10 wt./volume % using toluene. This is done since petroleum materials and residua dissolve rapidly in methylene chloride, and the addition of toluene minimizes air bubbles during injection due to volatility.

#### **Four Solvent Separation**

To determine the relative distribution of polar components in the heptane insoluble peak, a 20 uL portion (2 mg) of the 10 wt.% sample solution is injected onto the PTFE column using a heptane mobile phase.

The separation conditions that were established for sample analysis using the four solvent systems are listed below:

1. 250 x 10 mm stainless steel column (Alltech 96511)
2. 0.25-0.42 mm PTFE stationary phase (40-60 mesh)
3. Solvent flow rate: 4 mL/min
4. Step gradient times: 0 min. heptane, 15 min. cyclohexane, 30 min. toluene, 40 min. methylene chloride, 50 min. heptane, inject next sample at 60 min.
5. Sample solutions: 10 wt. % in methylene chloride:toluene (1:1)
6. Amount injected: 20 uL (2 mg)
7. Optical absorbance detector at 500 nm for standard QC check with Boscan residuum
8. Evaporative light scattering detector (ELSD) at 75 °C and 2.5 bar

Heptane insoluble material elutes from the column as a single off-scale peak with the ELSD detector, which can not be integrated (Figure 2). The mobile phase is then switched by step gradient sequence to a series of three solvents of increasing polarity: cyclohexane, toluene, and methylene chloride. The resulting three peaks provide information on the relative polarity distribution of the heptane insoluble material. The methylene chloride peak represents the most polar component in the sample.

Four-solvent separation results with the ELSD detector are provided for a series of original and pyrolyzed residua in Table 1. The peak area of the cyclohexane soluble peak can be used to calculate an area% cyclohexane soluble portion of the asphaltenes, which can be used as a rapid

means for determining  $K_S$  Coking Index values to diagnose the pyrolysis history of thermally treated oils (Figure 3).

The ratios of the cyclohexane to methylene chloride peak areas also can be used as a sensitive coking index and also to provide a measure of the thermal history of the material. (Table 1, Figure 4). A ratio less than one is diagnostic of pyrolyzed oils nearing the coke formation threshold in the coke formation induction period (Figure 5).

#### **Four Solvent Separation Results With Heptane Asphaltenes**

Portions of heptane asphaltenes obtained from the gravimetric procedure were injected onto the column using the four-solvent step gradient procedure, using methylene chloride as the fourth solvent. The amounts injected corresponded to the amounts of asphaltenes that would be present in two milligrams of whole residua sample, based on the gravimetric separation. The ELSD response profile for a blank separation is shown in Figure 6. The ELSD separation profile for 0.38 mg heptane asphaltenes from unpyrolyzed Boscan residuum is presented in Figure 7. The ELSD peaks in the blank separation are due to the step gradient solvent changes. As mentioned in the Experimental Section, ELSD peak areas for the blanks were subtracted from the sample areas. The relative blank corrected peak areas are provided in Table 2. The blank peaks are near in size to some of the sample peaks, which makes an exact calculation of sample areas somewhat difficult. The gravimetric asphaltenes (Table 2) are relatively deficient in the content of cyclohexane soluble portions relative to the polar materials from the whole sample separations (Table 1). Therefore, the gravimetric and on-column separations provide different results.

A plot of the relative areas of all four peaks as a function of pyrolysis time at 40-0 C is provided in Figure 8. It is interesting to note that the relative peak areas for the least polar material, represented by the heptane soluble material peak and the most polar material represented by the methylene chloride soluble material peak, both increase with pyrolysis time. The amount of intermediate polarity material represented by the cyclohexane soluble and toluene soluble material peaks, decreases with increasing pyrolysis time. A plot of the ratio of the combined relative areas for the heptane plus methylene chloride peaks to the cyclohexane plus toluene peaks as a function of pyrolysis time is provided in Figure 9. This is a graphic illustration of the decrease in the relative amount of intermediate polarity material with increasing pyrolysis time.

The separation profiles for the gravimetric asphaltenes all showed a peak for heptane soluble maltenes material (Table 2, Figure 7). This reinforces the concept that the gravimetric asphaltenes that precipitate in heptane from oils are complexes of polar and intermediate polarity material, with some entrained solvent phase material.

## **Two Solvent Separation for the Determination of Asphaltenes**

To provide a correlation between the on-column precipitation method and gravimetric determination of asphaltenes, separations of methylene chloride solutions of the original and pyrolyzed residua were conducted using a two-solvent step gradient using heptane and methylene chloride. Portions of 5  $\mu$ L (0.5 mg) of 10 wt.% sample solutions were injected to provide both peaks on scale with the ELSD detector (Figure 9).

The separation conditions that were established for sample analysis using the two solvent systems are listed below.

1. 250 x 10 mm stainless steel column (Alltech 96511)
2. 0.25-0.42 mm PTFE stationary phase (40-60 mesh)
3. Solvent flow rate: 4 mL/min
4. Step gradient times: 0 min. heptane, 15 min. methylene chloride, 25 min. heptane, inject next sample at 30 min.
5. Sample solutions: 10 wt. % in methylene chloride:toluene (1:1)
6. Amount injected: 5  $\mu$ L (0.5 mg)
7. Optical absorbance detector at 500 nm for QC check
8. Evaporative light scattering detector (ELSD) at 75 °C and 2.5 bar

Small portions of 0.5 mg sample are not useful if the four-solvent separation is employed, because the polar peaks are in many cases smaller than the corresponding blank peaks, and quantitation becomes inaccurate. For the two solvent separations, the two peaks are generally sufficiently large that this is not an issue, unless the material has low asphaltene content (i.e., 1%). In such cases, more sample needs to be injected, and alternative approaches for processing the peak area information to provide a measure of asphaltene content need to be developed. The two peaks represent the heptane soluble non-polar material, and all the remaining polar material, which is fully soluble in methylene chloride.

In this separation, heptane insoluble material elutes from the column as a single on-scale peak, which can be integrated (Figure 9). For Rayleigh scattering of light from unassociated particles or molecules which are much smaller in diameter than the wavelength of the incident light, the intensity of scattering is proportional to the number of molecules and the square of the molecular volume (Scott 1982). Since the ELSD response is generally based on the number of non-volatile molecules, a response factor correction can be invoked to convert peak area percent into an estimate of weight percent of different types or classes of materials. This was accomplished by comparing the average response for gravimetric asphaltenes to the average response to gravimetric maltenes (Table 3). The ratio of the two response factors is 1.4, which is approximately the square of the ratio of the density of the polar asphaltenes to the density of the maltenes. Data for the original and pyrolyzed residua are provided in Table 4. In addition, the separation was performed on asphalt samples obtained from the Strategic Highway Research Program (SHRP 1993), and selected heptane soluble maltenes from these materials (Table 5).

The relative peak areas correlate well with gravimetric asphaltene determinations (Figure 10). It is interesting to note that the gravimetric heptane maltenes exhibit some polar peak material in the automated separation. This is possibly due to the presence of associated complexes, which retain polar materials in solution during the gravimetric procedure. Possibly the associated complexes are broken apart in solutions with methylene chloride, which are injected on to the PTFE column and precipitated with the heptane mobile phase. Methylene chloride appears to be able to break up the associated complexes efficiently, and the individual molecules are possibly in true solution. On precipitation, the insoluble molecules appear to coat onto the PTFE mobile phase. For solid materials, there is no entropy of solution. As the molecules coated onto the PTFE surface are exposed to solvents of increasing polarity, they become dissolved from the solid surface based on enthalpic solubility parameter interactions, and they go into solution, in which both enthalpy and entropy favor maintaining the material in solution. Methylene chloride is known to be one of the best solvent for petroleum residua. Full solution is achieved rapidly. This is possibly due to the solvation of individual molecules, rather than larger associated moieties. In the case of precipitation from methylene chloride based solution, the separation is likely based more on an individual molecular level than by associated complexes. This aspect needs to be explored further. If this is the case, the on-column separation provides a more distinct profile of the non-polar and polar material distribution in petroleum materials than does the gravimetric asphaltene procedure.

Weight percents of polar materials calculated from the two solvent separations using the ELSD detector are listed in Tables 4 and 5. Weight percents of asphaltenes from the gravimetric procedure are plotted against weight percents of ELSD asphaltenes from the two column separation in Figure 10. The plot shows that there appears to be minimal amount of polar material required, before gravimetric asphaltenes appear. There are four points near the top of the line that are off of the line to the right. These represent the unpyrolyzed and 10-minute pyrolyzed Boscan residuum, and the unpyrolyzed Lloydminster and MaxCL2 residua. The asphaltenes from these materials possibly are highly associated and have significant low polarity solvation shells, so they exhibit enhanced solubility in the gravimetric separation than would be expected from the ELSD correlation line.

### **Additional Considerations**

The ELSD is a light scattering detector, and as such, is not expected to provide a linear response over a wide concentration range. Also, different classes of chemicals may exhibit somewhat different response factor characteristics. Additional development work needs to be pursued for sample materials such as crude oils or various refinery process streams, which contain relatively volatile hydrocarbon components, which will vaporize in the ELSD solvent evaporation chamber. Novel approaches for characterizing the less volatile polar materials such as asphaltenes in these materials need to be explored in the future.

## CONCLUSIONS

Two methods based on the new rapid, automated on-column precipitation and re-dissolution method for examining the polar components of original and pyrolyzed residua were explored. Polar material that precipitates in heptane can be further separated into three fractions of increasing polarity using a four-solvent method. Total weight percent of polar materials can be estimated by a two-solvent method, in which the precipitated material is dissolved in methylene chloride. Methods based on the new on-column precipitation and re-dissolution separation technique can provide significantly more information about the polar components in petroleum material than the gravimetric determination of asphaltenes. Additional work needs to be conducted with oils from both upstream and downstream operations. In addition, novel approaches for extraction useful in formation from these separation profiles need to be explored. The materials that constitute the various fractions need to be characterized chemically following preparative scale separations. In addition, a scaled up separation based on the new technique could possibly be designed to provide a process for removing the most polar, refractory components from petroleum materials for subsequent processing or use.

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**Table 1. On-Column Separation of 2.0 mg Portions of Whole Residua with Four Solvents: Heptane, Cyclohexane, Toluene, and Methylene Chloride**

	Pyrolysis time at 400 °C,min.	Relative ELSD Asphaltenes Peak Areas			CyC <sub>6</sub> /CH <sub>2</sub> Cl <sub>2</sub> Area Ratio
		Cyclohexane	Toluene	CH <sub>2</sub> Cl <sub>2</sub>	
Boscan	0	0.364	0.603	0.032	11.22
	10	0.283	0.651	0.066	4.30
	15	0.203	0.706	0.092	2.21
	20	0.198	0.708	0.094	2.10
	35	0.123	0.731	0.146	0.84
	50	0.088	0.679	0.233	0.38
MaxCL2	0	0.320	0.595	0.085	3.77
	15	0.185	0.697	0.118	1.57
	20	0.169	0.708	0.123	1.38
	35	0.121	0.698	0.181	0.67
	40	0.094	0.716	0.190	0.50
	50	0.080	0.679	0.241	0.33
Lloydminster	0	0.379	0.563	0.059	6.47
	15	0.209	0.697	0.094	2.23
	20	0.155	0.728	0.117	1.33
	35	0.120	0.716	0.164	0.73
	40	0.103	0.707	0.190	0.54
	60	0.088	0.700	0.212	0.41
Redwater, B.C.	0	0.288	0.598	0.113	2.54
	25	0.186	0.689	0.125	1.49
	35	0.169	0.709	0.122	1.38
	50	0.129	0.708	0.163	0.80
	55	0.097	0.753	0.150	0.65
	75 (coke)	0.069	0.724	0.206	0.34



**Table 2. On-Column Separation of Gravimetric Heptane Asphaltenes with Four Solvents: Heptane, Cyclohexane, Toluene, and Methylene Chloride**

	Pyrolysis time at 400 °C,min.	mg <sup>a</sup>	Relative ELSD Asphaltenes Peak Areas			
			Heptane	Cyclohexane	Toluene	CH <sub>2</sub> Cl <sub>2</sub>
Boscan	0	0.36	0.153	0.189	0.618	0.039
	15	0.38	0.197	0.091	0.619	0.093
	35	0.49	0.230	0.066	0.566	0.138
	50	0.57	0.261	0.047	0.506	0.186
MaxCL2	0	0.34	0.092	0.075	0.742	0.091
	15	0.39	0.124	0.046	0.657	0.173
	35	0.46	0.170	0.031	0.560	0.239
	50	0.52	0.194	0.033	0.527	0.246
Lloydminster	0	0.34	0.055	0.098	0.757	0.089
	15	0.32	0.080	0.032	0.713	0.175
	35	0.40	0.146	0.046	0.617	0.191
	60	0.46	0.197	0.031	0.564	0.208
Redwater, B.C.	0	0.18	0.086	0.044	0.673	0.197
	35	0.28	0.122	0.041	0.641	0.196
	55	0.33	0.163	0.057	0.593	0.187
	75 (coke)	0.38	0.208	0.038	0.545	0.209

a. Corresponds to the amount of gravimetric asphaltenes in 2.0 mg residuum

**Table 3. ELSD Response Factors, Peak Area / mg**

Whole residua

53.9, n = 24, rsd = 6.4%

Heptane maltenes

56.9, n = 3, rsd = 6.3%

Heptane asphaltenes

39.6, n = 16, rsd = 19.6%

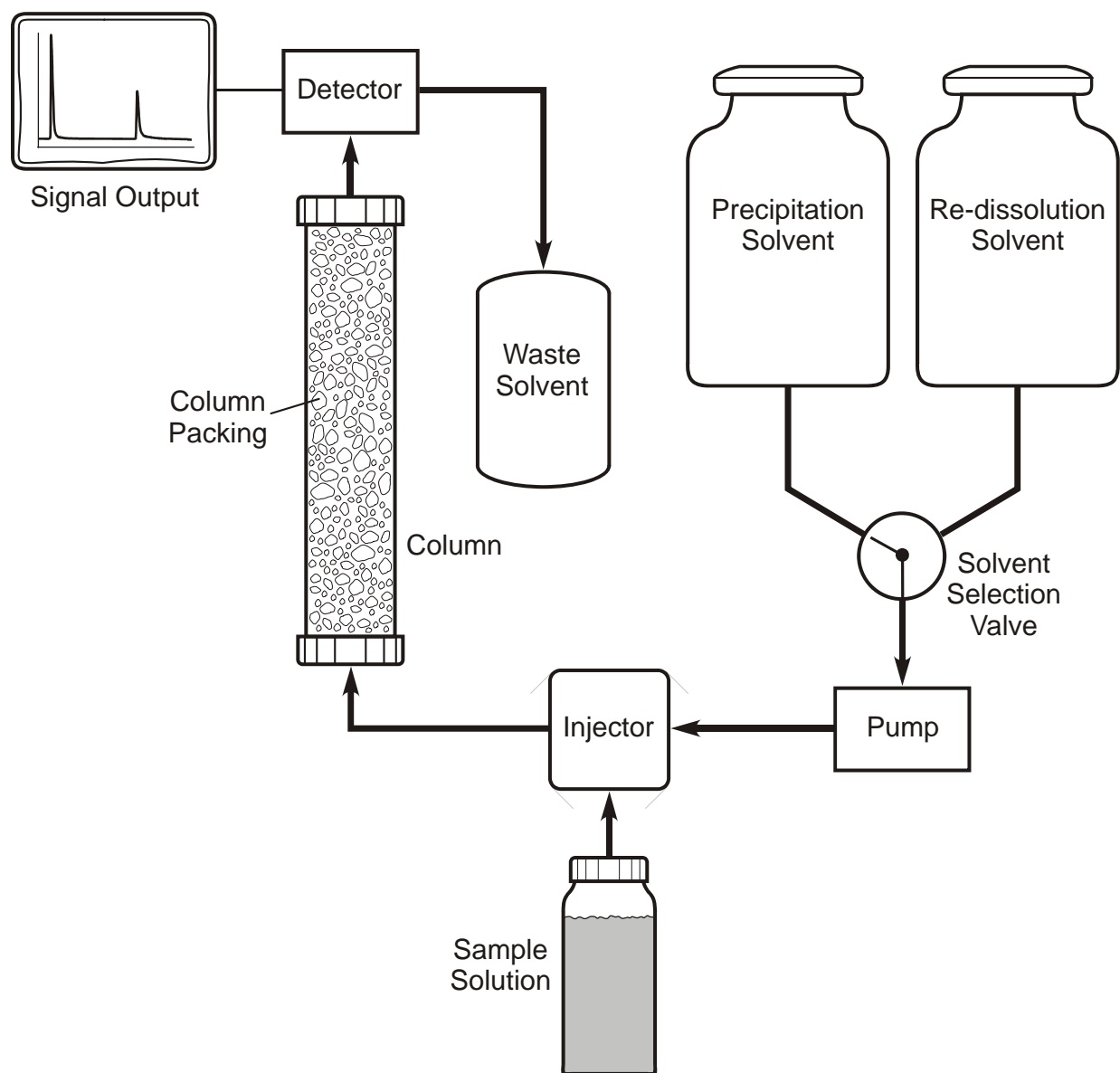
**Maltenes/asphaltenes response factor ratio = 1.4**

**Table 4. On-Column Separation of 0.50 mg of Whole Residua with Two Solvents: Heptane and Methylene Chloride**

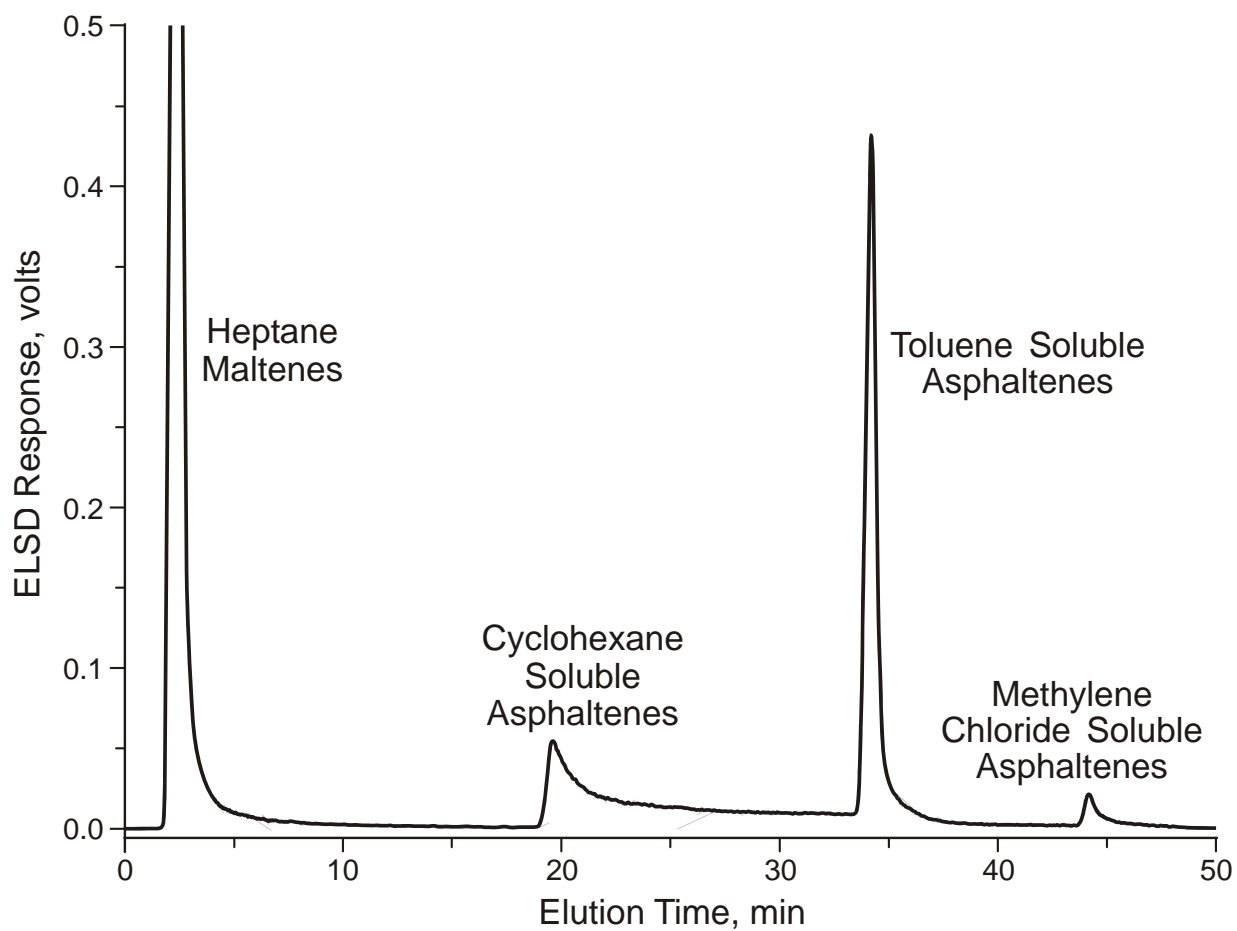
	Pyrolysis time at 400 °C, min.	<u>ELSD Peak Area Counts</u>		<u>Polars, area %</u>	wt. %Heptane <u>Asphaltenes</u>
		<u>Maltenes</u>	<u>Polars x 1.4</u>		
Boscan	0	21.40	7.11	24.9	17.7
	10	18.72	5.73	23.4	17.8
	15	19.74	5.84	22.8	19.0
	20	21.04	7.00	25.0	20.2
	35	20.85	8.11	28.0	24.4
	50	20.67	8.67	29.5	28.6
MaxCL2	0	23.70	7.99	25.2	17.0
	15	22.50	7.32	24.6	19.3
	20	21.30	7.39	25.8	23.3
	35	22.74	8.26	26.6	22.9
	40	21.25	9.14	30.1	26.6
	50	19.78	8.29	29.5	26.3
Lloydminster	0	23.35	7.13	23.4	16.9
	15	22.65	6.01	21.0	15.9
	20	18.42	5.26	22.2	18.1
	35	17.59	5.61	24.2	19.6
	40	17.73	6.41	26.6	21.0
	60	19.38	8.80	26.0	23.0
Redwater, B.C.	0	20.96	3.12	13.0	8.9
	25	19.75	3.67	15.7	13.1
	35	19.44	3.84	16.5	14.0
	50	18.76	4.80	20.4	17.0
	55	19.95	4.65	18.9	16.4
	75 (coke)	19.78	5.61	22.1	19.3

**Table 5. On-Column Separation of 0.50 mg of SHRP Asphalts and Residua Heptane Maltenes with Two Solvents: Heptane and Methylene Chloride using ELSD Detector**

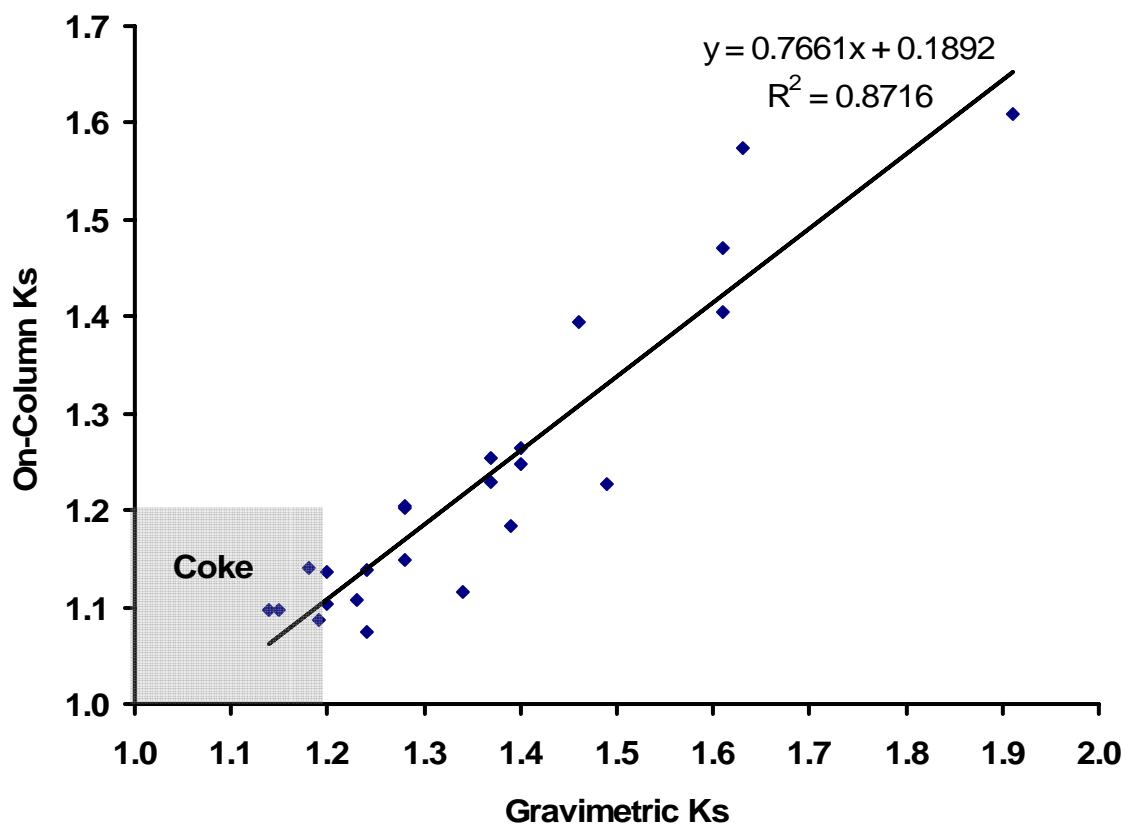
<u>Sample</u>	<u>ELSD Peak Area Counts</u>			<u>wt.% Gravimetric Asphaltenes</u>	
	<u>Maltenes</u>	<u>Polars x 1.4</u>	<u>Polars, area %</u>	<u>Heptane</u>	<u>Isooctane</u>
<u>SHRP Asphalts</u>					
AAA-1	22.04	7.14	24.5	15.8	22.1
AAB-1	23.33	6.76	22.5	17.3	22.4
AAC-1	23.23	3.49	13.1	9.9	15.5
AAD-1	19.23	9.23	32.4	20.2	27.4
AAE-1	18.49	8.78	32.2	22.9	25.9
AAF-1	22.97	5.15	18.3	13.4	18.7
AAG-1	24.32	2.70	10.0	5.0	10.2
AAK-1	19.26	7.78	28.8	20.1	29.7
AAM-1	25.88	3.37	11.5	3.7	11.2
ABA	22.82	5.66	19.9	15.7	-
<u>SHRP Asphalt</u>					
<u>Heptane Maltenes</u>					
AAD-1	23.03	2.00	8.0	0.0	-
AAK-1	25.53	0.57	2.2	0.0	-
AAM-1	24.06	0.52	2.1	0.0	-



**Figure 1. Asphaltene Determinator Technique Flow Schematic.**



**Figure 2. Separation of 2 mg (10 uL) Unpyrolyzed Boscan. Residuum in Methylene Chloride on 250 mm x 10 mm PTFE Column, ELSD Detector. Gradient: 0 min. Heptane, 15 min. Cyclohexane, 30 min, Toluene, 40 min. Methylene Chloride, 50 min. Heptane, 4.0 mL/min.**



**Figure 3.** ELSD Peak and Gravimetric  $K_s$  Values for Four Original and Pyrolyzed Residua in on a 250 mm x 10 mm PTFE Column; Gradient: 0 min. Heptane, 15 min. Cyclohexane, 30 min, Toluene, 40 min. Methylene Chloride, 50 min. Heptane, 4.0 mL/min.

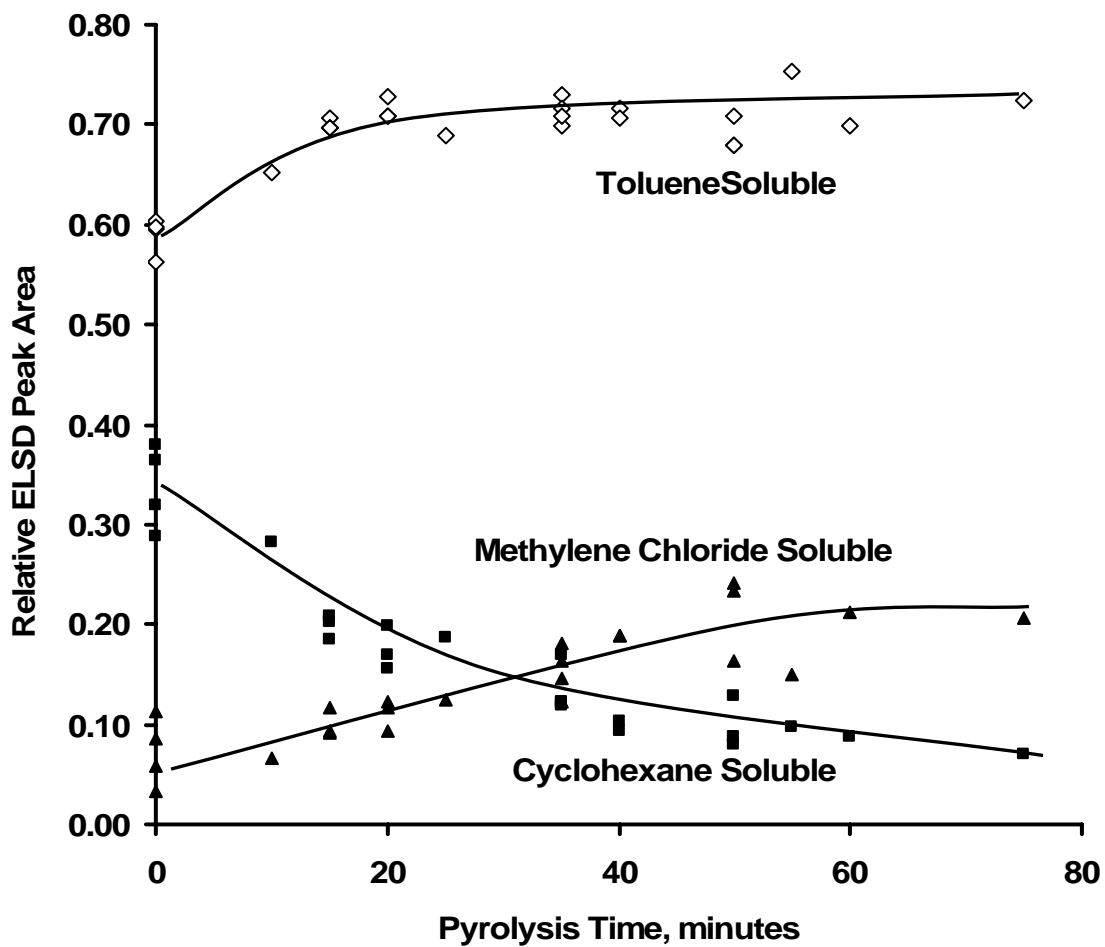
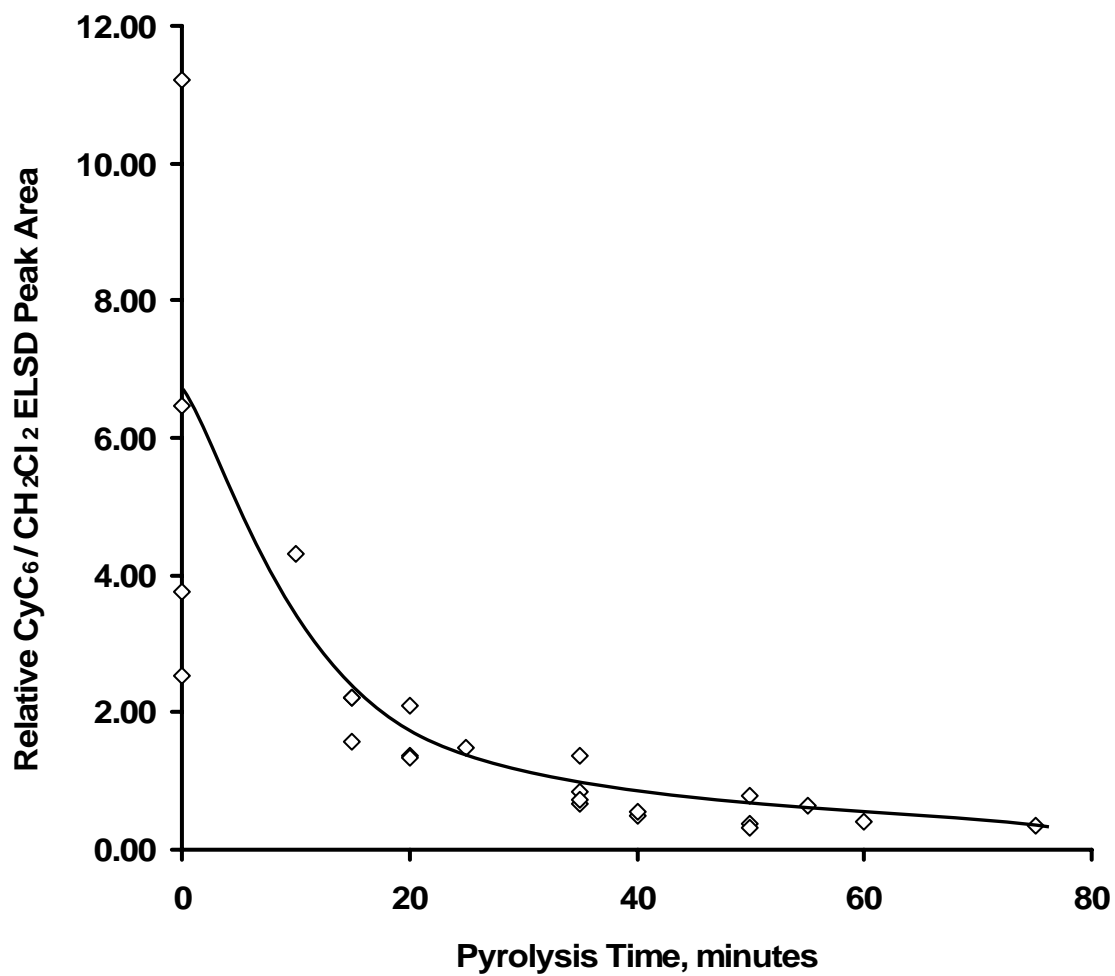
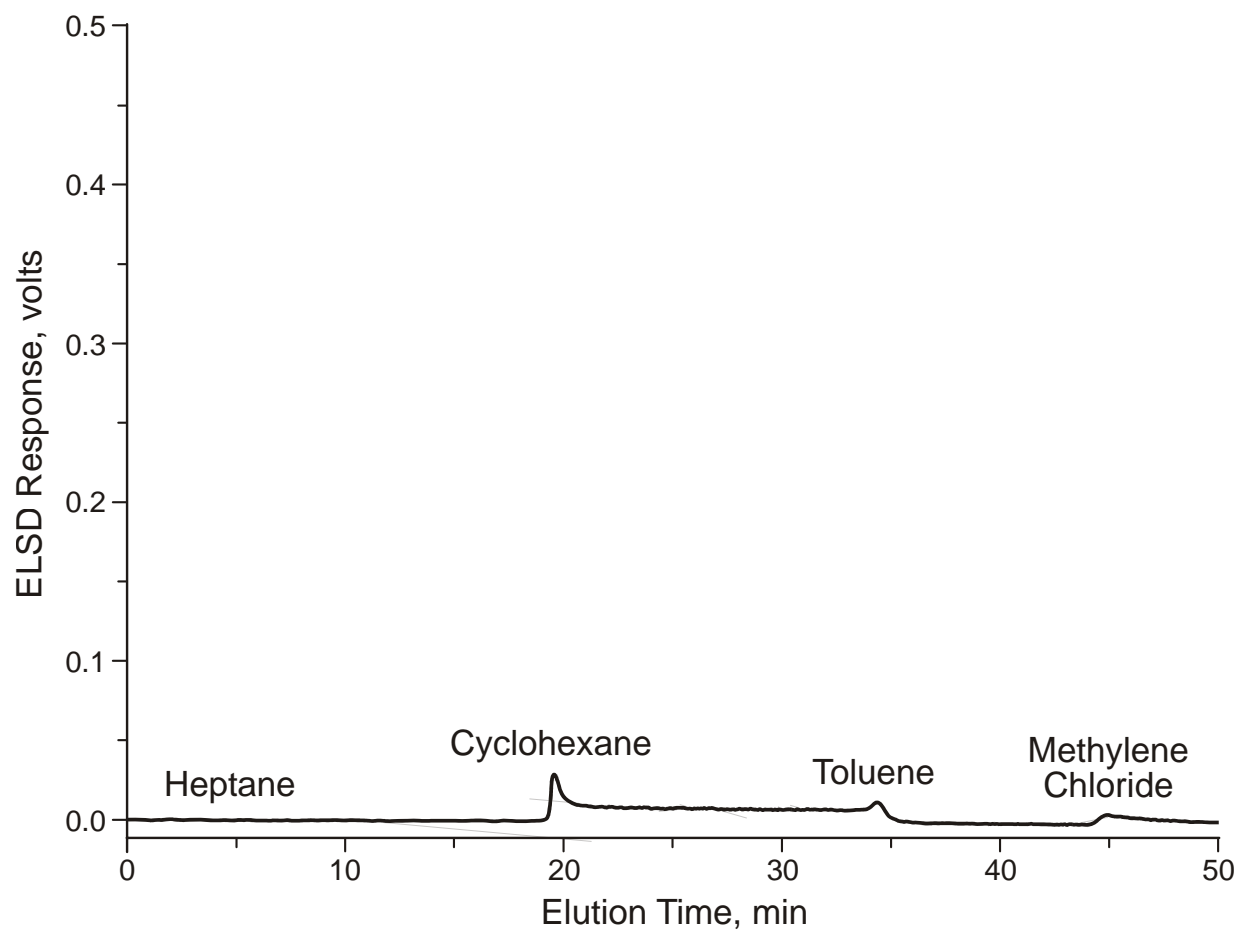


Figure 4. Relative ELSD Peak Areas for Four Original and Pyrolyzed Residua in on a 250 mm x 10 mm PTFE Column; Gradient: 0 min. Heptane, 15 min. Cyclohexane, 30 min, Toluene, 40 min. Methylene Chloride, 50 min. Heptane, 4.0 mL/min.

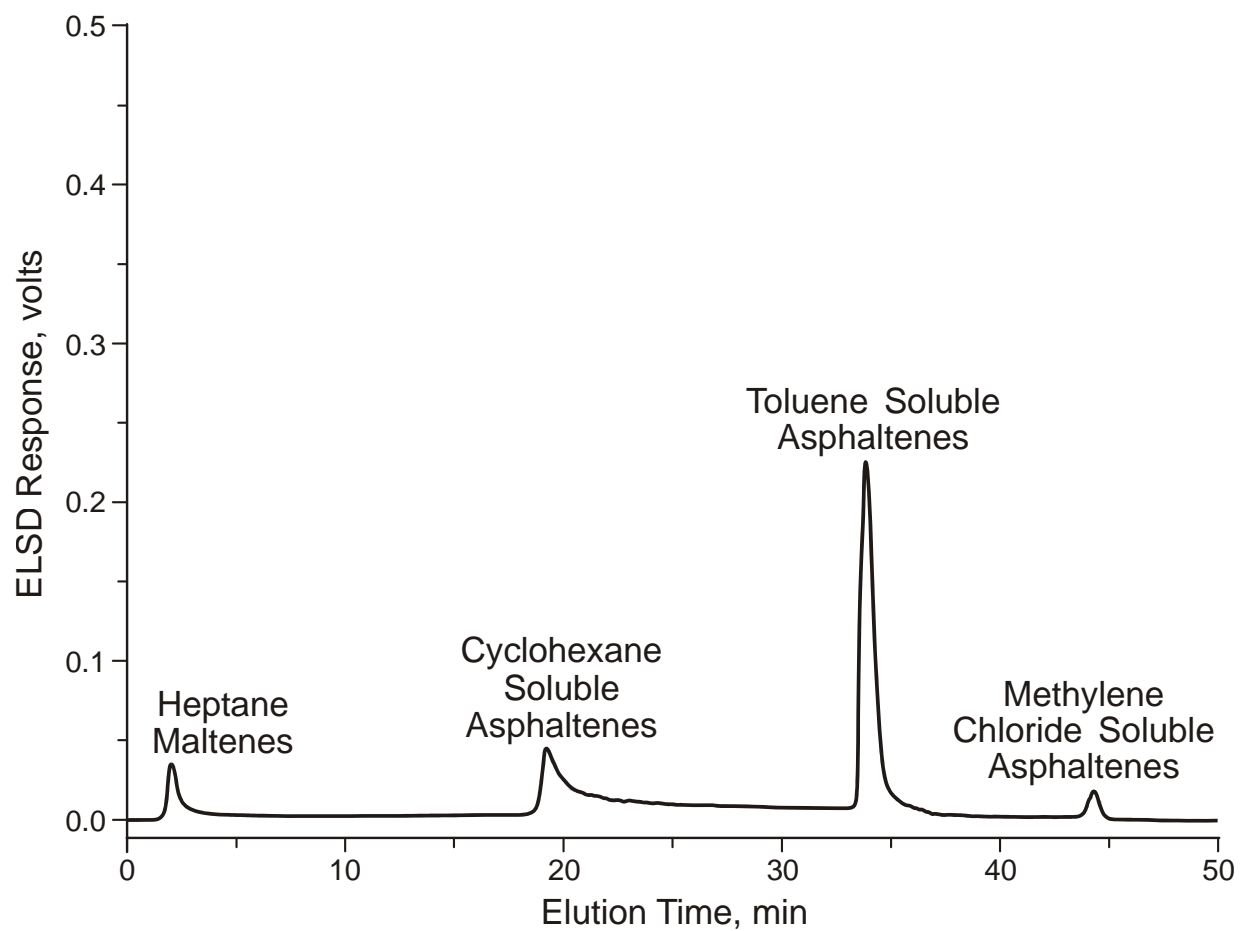


**Figure 5.** Correlation between the ratios of cyclohexane soluble peak areas to methylene chloride soluble peak areas with pyrolysis time at 400 °C.





**Figure 6. ELSD Blank Separation Profile**



**Figure 7. ELSD Separation Profile for 0.38 mg Boscan Heptane Asphaltenes**

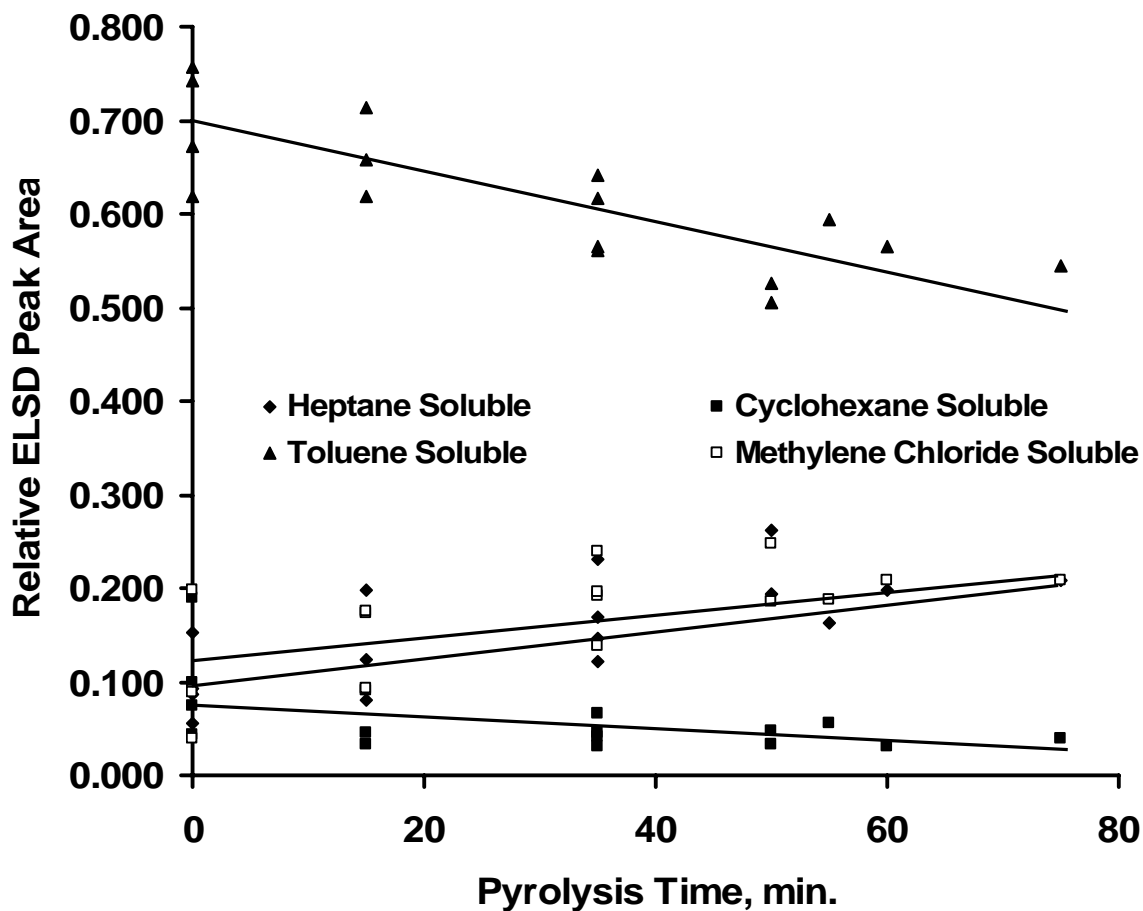
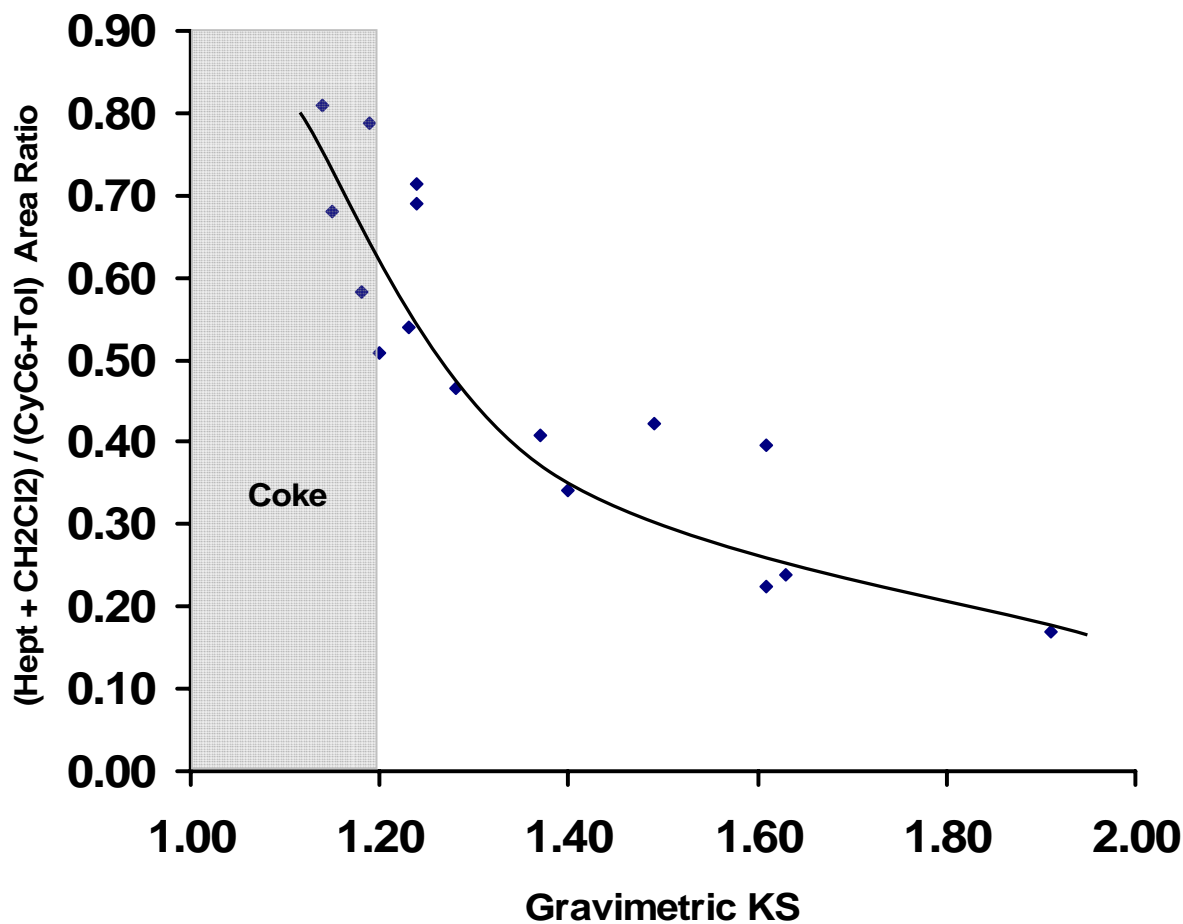
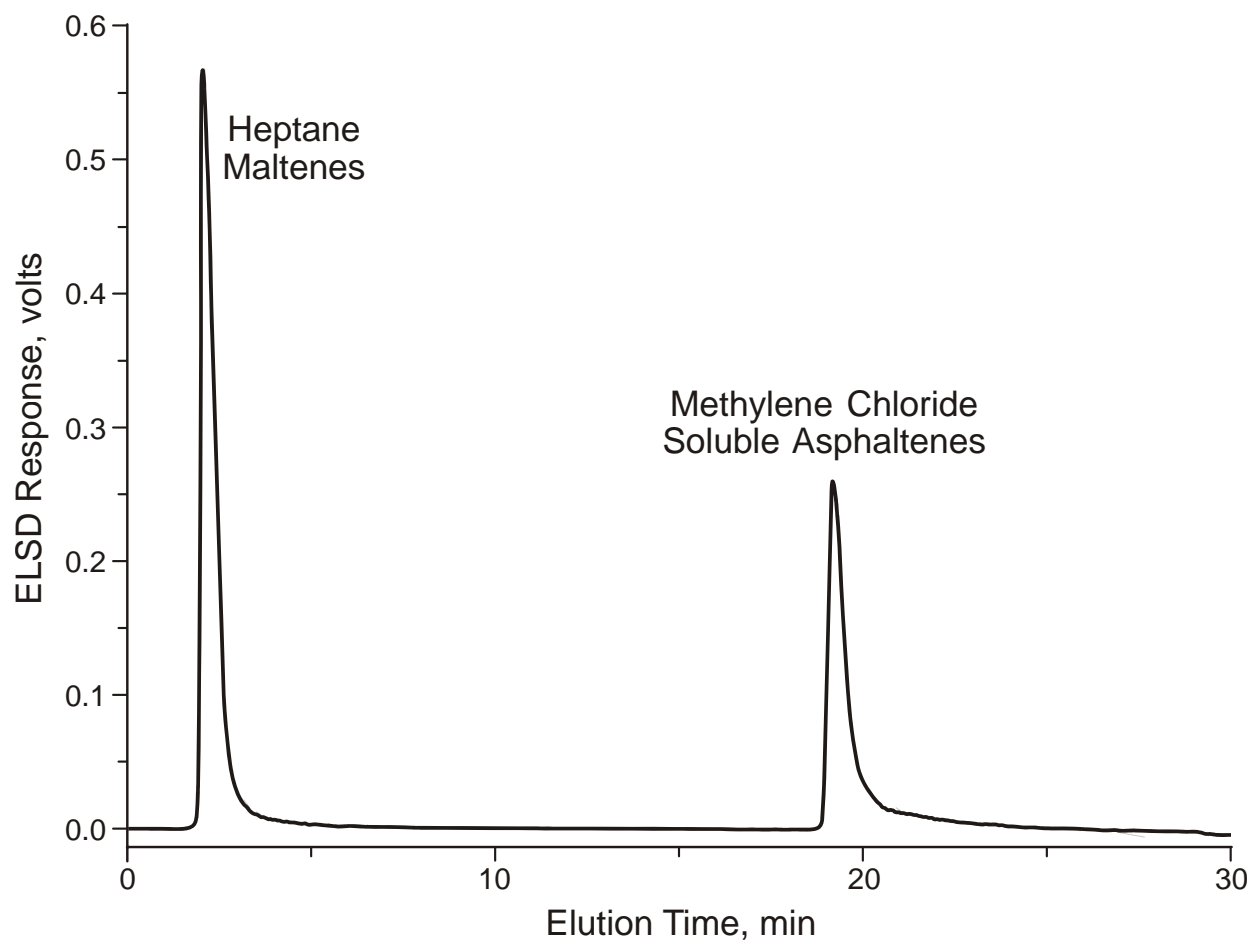


Figure 8. Relative ELSD Peak Areas for Four Original and Pyrolyzed Residua Gravimetric Heptane Asphaltenes in on a 250 mm x 10 mm PTFE Column; Gradient: 0 min. Heptane, 15 min. Cyclohexane, 30 min, Toluene, 40 min. Methylene Chloride, 50 min. Heptane, 4.0 mL/min.



**Figure 9. ELSD Peak Area Ratios of (non-polar+very polar) / (intermediate polarity) for Four Original and Pyrolyzed Residua Gravimetric Heptane Asphaltenes in on a 250 mm x 10 mm PTFE Column; Gradient: 0 min. Heptane, 15 min. Cyclohexane, 30 min, Toluene, 40 min. Methylene Chloride, 50 min. Heptane, 4.0 mL/min.**



**Figure 10. ELSD Separation Profile for 0.50 mg Unpyrolyzed Boscan Residuum**

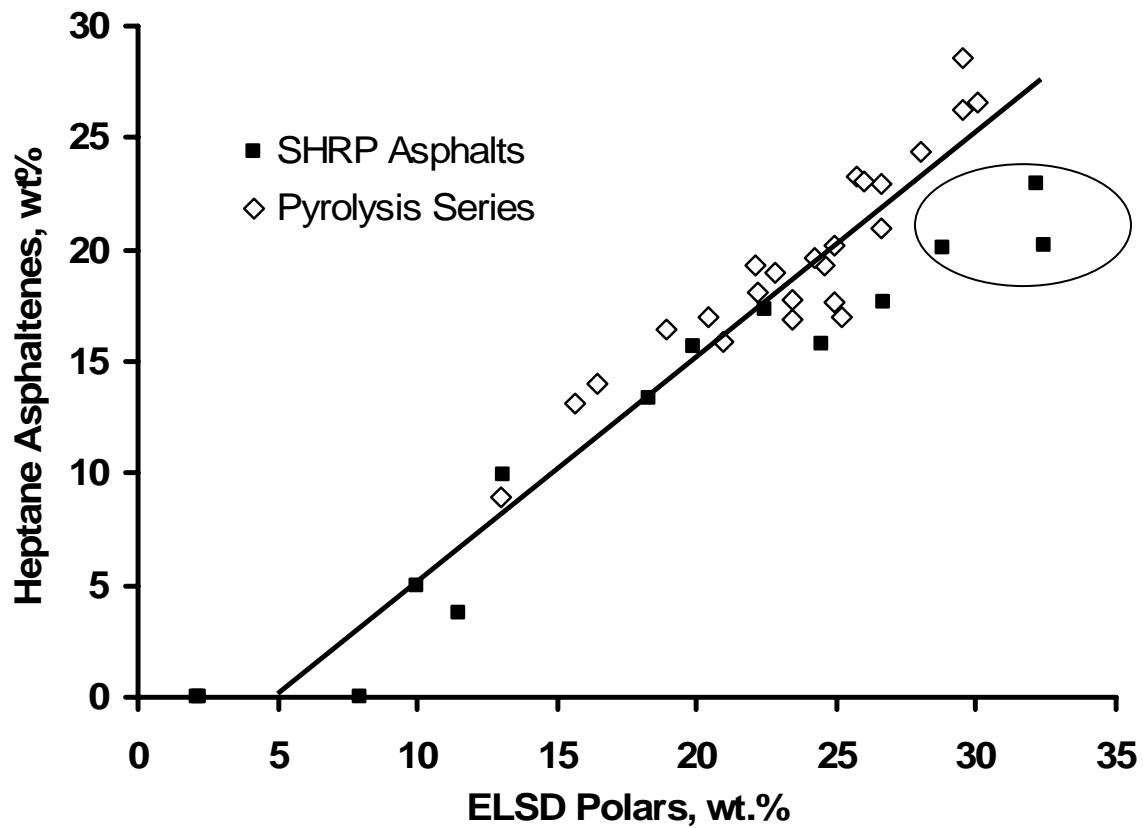


Figure 11. Correlation Between Weight Percent Gravimetric Asphaltenes and Weight Percent ELSD Polars from Two-Solvent Separation.