

## **TOPICAL REPORT**

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

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## ABSTRACT

About 37-50% (w/w) of the heptane asphaltenes from unpyrolyzed residua dissolve in cyclohexane. As pyrolysis progresses, this number decrease to below 15% as coke and toluene insoluble pre-coke materials appear. This solubility measurement can be used after coke begins to form, unlike the flocculation titration, which cannot be applied to multi-phase systems. Currently, the procedure for the isolation of heptane asphaltenes and the determination of the amount of asphaltenes soluble in cyclohexane spans three days. A more rapid method to measure asphaltene solubility was explored using a novel on-column asphaltene precipitation and re-dissolution technique. This was automated using high performance liquid chromatography (HPLC) equipment with a step gradient sequence using the solvents: heptane, cyclohexane, toluene:methanol (98:2). Results for four series of original and pyrolyzed residua were compared with data from the gravimetric method. The measurement time was reduced from three days to forty minutes. The separation was expanded further with the use of four solvents: heptane, cyclohexane, toluene, and cyclohexanone or methylene chloride. This provides a fourth peak which represents the most polar components, in the oil.

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## **EXECUTIVE SUMMARY**

A major focus of the current work is to explore the possibility of developing a rapid Coking Index laboratory analysis method. One measurement that we have found to be universally applicable is the amount of heptane asphaltenes that dissolve in cyclohexane. Currently this measurement requires a three-day timeframe that includes stirring samples overnight. For unpyrolyzed residua, about 37-50% (w/w) of the heptane asphaltenes dissolve in cyclohexane. As pyrolysis progresses, this number decreases to below 15% as coke and toluene insoluble pre-coke materials appear. This measurement can be used after coke begins to form, unlike the flocculation titration which cannot be applied to multi-phase liquid systems. A better, more rapid method to measure asphaltene solubility was explored using a novel on-column asphaltene precipitation and re-dissolution technique. This was automated using high performance liquid chromatography (HPLC) equipment with a step gradient sequence using the solvents: heptane, cyclohexane, toluene:methanol (98:2). Results for a series of four original and pyrolyzed residua were compared with data from the gravimetric method. The measurement time was reduced from three days to forty minutes. The separation was expanded further with the use of four solvents: heptane, cyclohexane, toluene, and cyclohexanone or methylene chloride. This provides a fourth peak which represents the most polar components, or pre-coke materials, in the oil.

## **OBJECTIVES**

The objective is to develop rapid refinery process control analysis techniques to optimize distillation while minimizing risks of fouling. A new automated on-column asphaltene precipitation and re-dissolution method that can be related to the WRI Coking Indexes was optimized. 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**

Petroleum residua consist of a continuum of associated polar asphaltene complexes dispersed in a lower polarity solvent phase by intermediate polarity resins. When the residuum is heated to temperatures above 340 °C (650 °F), the ordered structure is systematically and irreversibly destroyed. An important consideration in the refining industry is to be able to measure how close a pyrolyzed material is to forming coke on the coke induction period timeline. Undesired coking during distillation results in significant down time and economic loss. To avoid this problem, conservative heating profiles are often used, which results in less than optimal distillate yield, and less profitability. The proximity to coke formation can be measured using the WRI Coking Indexes, which are calculations based on flocculation titration data or the solubility of heptane asphaltenes in cyclohexane (Schabron et al. 2001a, 2001b). The Coking Index values decrease during pyrolysis to a threshold value below which coke formation begins. Currently, the Coking Indexes require lengthy laboratory analysis of a residuum sample. A new, rapid on-column precipitation and re-dissolution method for rapidly measuring the cyclohexane soluble portion of asphaltenes was developed in the current study.



## The Solvation Shell Coking Index

Some aspects of the ordered structure of petroleum residua can be modeled by the Pal and Rhodes suspended particle solution model of dispersed solvated particles in a solvent matrix (Pal and Rhodes 1989, Schabron et al. 2001c). The volume fraction of the core of particles can be considered as the volume fraction of heptane asphaltenes  $\Phi_a$ . The volume of the core 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  $K_S \cdot K_F$  is called the solvation constant  $K$ . The effective particle volume  $\Phi_{EFF}$  is equal to the core asphaltene fraction volume increased by the solvation terms as shown by the following equation.

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

The volume fraction of polar asphaltene cores,  $\Phi_a$  can be estimated from the mass fraction of heptane asphaltenes  $\chi_a$  divided by an assumed density of  $1.2 \text{ g/cm}^3$  (Rogel and Carbognani 2003).  $K_S$  values for unpyrolyzed residua and asphalt systems are typically near or above 1.6 (Pauli and Branthaver 1998). For pyrolyzed oils the  $K_S$  values decrease as pyrolysis progresses and the protective shell surrounding the polar asphaltene core is destroyed (Schabron et al. 2001a). A method for estimating  $K_S$  is to measure 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 asphaltenes that dissolve in cyclohexane is essentially the same as the density of the insoluble portion.

## Pyrolysis and Coking

When a residuum is heated above the temperature at which pyrolysis occurs ( $340^\circ\text{C}$ ,  $650^\circ\text{F}$ ), there typically is an induction period ranging from a few seconds to over an hour after which coke formation begins (Magaril and Aksenova 1968, Phillips et al. 1985, Wiehe 1993). As pyrolysis progresses, the intermediate polarity material decreases during the induction period. Initial pyrolysis reactions involve the cleavage of benzylic carbon-carbon bonds and aliphatic carbon-heteroatom bonds and hydrogen-heteroatom bonds, resulting in the formation of free radicals that continue scission reactions or condense into carbon-rich material (Singh et al. 1990, Schabron et al. 2001a, Del Bianco et al. 1993).

## Rapid Measurement of Cyclohexane Soluble Asphaltenes

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 obtain this value the amount of heptane asphaltenes that dissolve in cyclohexane is measured. For unpyrolyzed residua, about 37-50 % (w/w) of heptane asphaltenes dissolve in cyclohexane. This corresponds to  $K_S$  values of 1.6 – 2.0. 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, or resins material. An unstable system results when the depletion of the resins disables

the ability of the asphaltene/resin complexes to self-adjust their apparent molecular weights to closely match the solubility parameter of the matrix. At that point on the coke formation induction time line, the ordered system breaks down and the polar asphaltene material is no longer stabilized, and coke begins to form (Schabron et al. 2001a, 2001b). The solubility measurement can be applied to a sample even after coke begins to form, unlike the flocculation titration which can not be used with multi-phase liquid systems.

## **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. Some of the pyrolyzed atmospheric residua samples were the same materials generated and characterized in an earlier phase of this study (Schabron et al. 2004, Schabron and Rovani 2005). Additional pyrolyzed materials were generated in the current work.

### **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 ½ hour 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.

### **Pyrolysis**

Pyrolysis experiments were performed at various residence times with 500-g residua samples in a 4-inch diameter reactor with continuous stirring and distillate removal using a condenser at atmospheric pressure. Residua were evaluated as atmospheric bottoms material without distillate. Coke and pre-coke materials were determined as toluene insolubles (TI) retained on a 10-micron filter.

### **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 600 controller, a Waters 1487 ultraviolet/visible absorbance detector, and an Alltech ELSD 800 detector. Step gradients were

used between solvents. Solutions of residua and asphaltenes were injected. Peak area integration was performed using a Chrom Perfect Spirit 5.5 data system. Various columns and conditions were tested. Pyrolyzed sample solutions were filtered through a 0.45 micron PTFE filter prior to injection. All solvents used were reagent grade.

## RESULTS AND DISCUSSION

A new 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.

### The Manual Method

To measure the amount of asphaltenes using the manual 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 and the precipitate is rinsed repeatedly with the hydrocarbon solvent until the filtrate is clear. The precipitate is then dried thoroughly, usually in a vacuum oven, and weighed. This procedure usually takes about 24 hours. To determine the cyclohexane soluble portion of the asphaltenes, the precipitate is ground manually, and a portion of the ground precipitate is stirred overnight with an excess of cyclohexane. The next day, the mixture is filtered to separate the cyclohexane soluble and insoluble portions. The full manual method to determine asphaltenes and the cyclohexane soluble portion of asphaltenes can take up to 3 days to complete.

### The Automated Separation Method

The new on-column separation provides a rapid method using an automated continuous flow system. Bodusynski et al (1982) reported a gravimetric on-column dissolution method for separating coal liquids deposited onto an inert packing with heptane, toluene, and pyridine. The current method involves on-column precipitation combined with re-dissolution. Although high performance liquid chromatography (HPLC) equipment is used, the separation does not involve a chromatographic separation based on adsorption. A weighed portion of oil is dissolved in decahydronaphthalene (decalin), or toluene which both have the same solubility parameter  $(8.9 \text{ (cal/cc)}^{1/2})$ . An aliquot of the solution is injected onto a column packed with ground polytetrafluoroethylene (PTFE). The initial solvent in the column and the solvent into which the sample solution is injected is heptane. Once the sample solution enters the column with the heptane mobile phase, the heptane displaces and dilutes the injected solvent, and heptane asphaltenes precipitate. The soluble maltenes continue to move with the heptane and they elute from the column. The solvent is then switched to cyclohexane. The portions of precipitated asphaltenes that are soluble in cyclohexane dissolve, and elute from the column. The solvent is then switched to one or two more polar solvents, which dissolve and elute the remaining material, the cyclohexane insoluble, portion of the asphaltenes. The solvent is then switched back to heptane in preparation for the next sample injection. Another injection is then made by the autosampler, and the cycle is repeated. Since the elution solvents are being changed, a refractive index detector can not be used. An optical absorbance detector can be used; however, there is some variation in the absorptivities between asphaltenes from different residua,

pyrolyzed and unpyrolyzed asphaltenes, and the cyclohexane soluble and insoluble portions of asphaltenes. In the current study, the use of an evaporative light scattering detector (ELSD), which responds more uniformly to a given mass of each of the above materials, was established. The result should provide be a powerful new automated tool for process control and heavy oil evaluation.

## Pyrolysis

Pyrolysis experiments were performed with the four residua to provide additional pyrolyzed atmospheric bottoms samples for different pyrolysis times at 400 °C. The amounts of heptane asphaltenes and toluene-insoluble materials in the original and pyrolyzed residua materials are provided in Table 1. Also provided are the calculated  $K_S$  values. The  $K_S$  values for the four unpyrolyzed residua are all 1.6 or larger, indicating that the residua are far from producing coke on the coke formation induction time line (Schabron and Rovani 2005). The data in Table 1 show the characteristic decrease in the  $K_S$  Coking Index values as pyrolysis progresses. There are no toluene insoluble materials greater than 10 microns in size in any of the product oils except for the 90-minute Boscan oil and the 75-minute Redwater, B.C. which were pyrolyzed beyond the coke formation threshold.

## On-Column Asphaltene Precipitation Optimization Experiments

Experimental conditions were explored to optimize a single set of separation conditions for comparing various original and pyrolyzed residua. The optical absorptivities of heptane asphaltenes, and the cyclohexane soluble and insoluble components of heptane asphaltenes in toluene solution for original and pyrolyzed residua for wavelengths ranging from 400 nm to 700 nm have been evaluated (Schabron and Rovani 2005). The purpose of these experiments was to determine the wavelength at which the absorptivities showed the least variation between the different materials. Results showed that the shorter wavelength (400 nm) provides more uniform absorptivities than the higher wavelength (700 nm). Wavelengths below 400 nm were not considered due to the strong absorbance of toluene. Although the results indicate that the shorter wavelength of 400 nm should be used, the absorbance for some of the samples was too high at this wavelength for the sample amounts injected in the initial development work. Therefore, 700 nm was selected for the initial development work. It is important to note in the discussions that follow that only materials that absorb light at 700 nm are being detected. Saturated aliphatic, naphthenic, and aromatic structures that do not exhibit brown color in the visible region are not detected.

## Sample Amount Injected

The amount of sample injected and the column size to be used are important variables. Figure 1 shows an initial separation profile at 700 nm for unpyrolyzed Redwater, B.C. residuum obtained early in this study. Although the separation looks good, the resolution between peaks is not optimal. Also, this particular column size is no longer available. A series of systematic experiments was subsequently performed to better understand the effect of column size, volume injected, and sample amount injected. The study also explored any differences that might occur if either toluene or decalin were used as the sample solvent. Figures 2-4 show the peak areas for the total asphaltenes (cyclohexane soluble plus cyclohexane insoluble) as a function of amount

injected for three different stainless steel column sizes, each packed with 0.25-0.42 mm PTFE stationary phase. The results indicate that the separation conditions are easier to control with the larger column, and that at a low injection volume (<50 uL), toluene can be used as the sample solvent. This is an important finding since residua samples dissolve in toluene much faster than in decalin.

### Separation Considerations

Over the course of the initial development work, several important aspects to the separation were better understood (Schabron and Rovani 2005). 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 amount of sample injected should be maximized to minimize adsorption effects, while the amount of solvent injected should be kept at a minimum. Peaks must be resolved well, despite some tailing which is due to continuous re-dissolution of small amounts of material precipitated on the packing. The solvent flow rate must be compatible with the ELSD (<6 mL / min). Since some pyrolyzed samples result in off-scale asphaltene peaks at 400 nm when 2 mg sample portions are injected, a wavelength of 500 nm was selected for the absorbance detector. Blank correction is required for the ELSD peak areas since small, repeatable peaks are observed when the solvents are changed.

### Three Solvent Separation Conditions

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

1. 250 x 10 mm stainless steel column (Alltech 96511)
2. 0.25-0.42 mm PTFE stationary phase
3. Solvent flow rate: 4 mL/min
4. Step gradient times: 0 min. heptane, 15 min. cyclohexane, 30 min, toluene:methanol (98:2) (v:v), 40 min. heptane.
5. Sample solutions: 20 wt.% in toluene
6. Amount injected: 10 uL (2 mg)
7. Optical absorbance detector at 500 nm
8. Evaporative light scattering detector (ELSD) at 60 °C and 1.5 bar nitrogen

### Three Solvent Separation Results

Separation profiles for 10 uL of 20 wt. % unpyrolyzed Boscan residuum in toluene using an absorbance detector at 500 nm and an ELSD are provided in Figures 5 and 6, respectively. A comparison of  $K_S$  values determined gravimetrically with  $K_S$  values determined by the new on-column precipitation and re-dissolution method is provided in Table 2 for a series of original and pyrolyzed residua. Results show that the ELSD data closely track the gravimetric data.  $K_S$  values decrease with pyrolysis severity for all four residua. The results for the 500 nm absorbance detector show a similar trend of decreasing  $K_S$  values with increasing pyrolysis times, however, the absolute values tend to be somewhat smaller than the corresponding

gravimetric or ELSD values. This is due to the relatively lower optical absorptivity at 500 nm for the cyclohexane soluble portion of asphaltenes as compared with the cyclohexane insoluble materials (Schabron and Rovani 2005). Both the Boscan 50-minute and the Redwater, B.C. 75-minute pyrolysis product oils contained some insoluble material when the 20 wt.% in toluene solutions were pre-filtered through a 0.45 micron PTFE syringe filter prior to injection. Therefore, it is assumed that not all of the most polar material is being accounted for in the separation profiles for these materials

Gravimetric wt. % heptane asphaltenes and the total asphaltenes peak areas (cyclohexane plus toluene:methanol (98:2)) are listed in Table 3. The total areas of both the cyclohexane soluble and cyclohexane insoluble asphaltene peaks are plotted against the gravimetric heptane asphaltene content in Figure 7. ELSD data show a plateau for the severely pyrolyzed oils. This is probably due to the deposition of pre-coke material onto the PTFE stationary phase. This material is not recovered by elution with toluene:methanol (98:2) (v:v). The purpose of the small amount of methanol in this solvent mixture is to minimize the risk of polar normal-phase adsorption effects. Despite this precaution, the PTFE stationary phase in the first inch of the column is stained with a brown colored material after many sample injections, especially if the samples consist of severely pyrolyzed oils. Since the stationary phase is inert PTFE, the material is probably not adsorbed, but rather deposited on the packing. Experiments showed that this brown colored material readily dissolves in methylene chloride. Toluene insoluble pre-coke material is expected to be soluble in solvents with three-dimensional Hansen solubility parameter component values similar to those of methylene chloride, tetrahydrofuran, and quinoline (Table 4) (Hansen 2000). The separation was modified further to add a stronger solvent to dissolve this toluene-insoluble material, to provide a fourth “pre-coke” peak using a solvent with three-dimensional Hansen solubility parameter values near that of methylene chloride. This is described in the next section.

The 500 nm peak area data appear to correlate fairly well with the heptane asphaltene gravimetric data (Figure 7). The plateau observed with the ELSD for the same separation is not as evident. This is probably due to the increase in absorptivity for the pyrolyzed asphaltenes material at 500 nm compared with the unpyrolyzed material. Thus, the deposition of a portion of this material onto the stationary phase or loss in the sample filtration step would not be as evident with the optical absorbance detector.

#### Four Solvent Separation Conditions

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
3. Solvent flow rate: 4 mL/min
4. Step gradient times: 0 min. heptane, 15 min. cyclohexane, 30 min. toluene, 40 min. solvent four (cyclohexanone or methylene chloride), 50 min. heptane.
5. Sample solutions: 20 wt. % in cyclohexanone or methylene chloride.
6. Amount injected: 10 uL (2 mg)
7. Optical absorbance detector at 500 nm

8. Evaporative light scattering detector (ELSD) at 110 °C and 5 bar nitrogen for cyclohexanone series or 75 °C and 2.5 bar for methylene chloride series

#### Four Solvent Separation Results

From the list of polar solvents with similar Hansen solubility parameters listed in Table 4, two candidate solvents were selected for the four-solvent separation experiments. These were cyclohexanone and methylene chloride. Cyclohexanone does not contain a halogen, and has a boiling point of 155 °C, which is much lower than that of Quinoline (237 °C), so it can be used with the ELSD detector. Our observations in the past have been that there are insoluble components present when solutions of asphaltenes are made up in pyridine, so this solvent was not considered. Tetrahydrofuran is known to be unstable and very reactive, so this also was not considered. Methylene chloride has a low boiling point of 40 °C, and is a very good solvent for asphaltenes. A disadvantage is that it contains a halogen, and waste solvent from the separation must be disposed of in a halogenated waste stream. Solutions of 20 wt. % of the original and pyrolyzed residua were prepared in both cyclohexanone and methylene chloride. It takes a minimum of 2 hours for some pyrolyzed samples to fully dissolve in cyclohexanone, even with agitation in an ultrasonic bath. The samples dissolved within 15 minutes in methylene chloride.

Separation profiles for 10 uL of 20 wt. % unpyrolyzed Boscan residuum in cyclohexanone with cyclohexanone as the fourth solvent using an absorbance detector at 500 nm and an ELSD are provided in Figures 8 and 9, respectively. The upward shift of the baseline for the last peak in Figure 9 is due to the low volatility of cyclohexanone in the ELSD detector. A comparison of the relative peak areas for the three asphaltene peaks (cyclohexane, toluene, and cyclohexanone) are provided in Table 5.

Separation profiles for 10 uL of 20 wt. % unpyrolyzed Boscan residuum in methylene chloride with methylene chloride as the fourth solvent using an absorbance detector at 500 nm and an ELSD are provided in Figures 10 and 11, respectively. A comparison of the relative peak areas for the three asphaltene peaks (cyclohexane, toluene, and cyclohexanone) are provided in Table 6.

It is interesting to note that even the unpyrolyzed residua each contain a small portion of the most polar component of asphaltenes. As pyrolysis progresses, the least polar portion of asphaltenes (cyclohexane soluble) decreases, while the most polar portion (cyclohexanone or methylene chloride soluble) portion increases (Figures 12 and 13). The relative amount of the intermediate polarity material (toluene soluble) drops slowly. Presumably the least polar material passes through a stage of intermediate polarity, which then generates the more polar “pre-coke” material. There is a dramatic increase in the relative amount of the most polar component for the 75-minute pyrolyzed Redwater, B.C. material, as coke begins to form. Different residua are expected to exhibit different rates of internal changes with pyrolysis residence time or severity (Schabron et al. 2001a).

The total asphaltenes peak areas are listed in Table 5 for the cyclohexanone separations and in Table 6 for the methylene chloride separations. The total areas of the three asphaltene peaks (cyclohexane soluble, toluene soluble, and cyclohexanone or methylene chloride soluble) are plotted against the gravimetric heptane asphaltene content in Figures 14 and 15. As with the

three-solvent profile in Figure 7, the ELSD data show a more severe plateau than the 500 nm data for the severely pyrolyzed oils. This is not due to the deposition of pre-coke material onto the PTFE stationary phase, since the last solvent completely dissolves this material. The plateau profiles in Figures 14 and 15 with the ELSD detector indicate that the gravimetric separation of heptane insolubles provides a different result from the on-column precipitation and re-dissolution experiment. The on-column separation provides more detail on the interior structure of the most polar components of residua than a simple gravimetric procedure. The gravimetric separation appears to provide some additional mass which is not accounted for in the on-column separation. The plateau observed with the ELSD for the same separation is not as evident with the 500 nm absorbance detector. This is probably a coincidence which is due to the increase in absorptivity for the pyrolyzed asphaltenes material at 500 nm compared with the unpyrolyzed material. Preliminary results with the separation of asphaltenes isolated gravimetrically, and separated with the new on-column precipitation and re-dissolution technique show that the materials obtained gravimetrically, that the separation profiles contain significant amounts of heptane soluble materials (bound maltenes). Therefore, the gravimetric determination of asphaltenes does not provide a true indication of the more polar components of residua. This aspect will be explored in more detail in the next phase of this work.

### A New Stability Gauge

A new parameter that can provide insight into the degree of stability of a petroleum material can be defined from the results of this work. This is the ratio of the peak area for the cyclohexane soluble asphaltenes peak to the cyclohexanone or methylene chloride soluble asphaltenes peak area from the on-column precipitation and re-dissolution profile. The ratios for both solvents using both 500 nm absorbance and ELSD detectors are provided in Table 7. The ratios decrease dramatically with increasing pyrolysis times. Based on these values, threshold values could be established for a particular detector and solvent series used for the separation. The separation could be used as a sensitive tool to diagnose the severity of pyrolysis to which a particular heavy oil material has been subjected. It also can be used as a rapid means of refinery distillation process control, to determine the actual “reserve pyrolysis capacity” of a residuum.

## CONCLUSIONS

Experimental conditions for a new rapid, automated on-column precipitation and re-dissolution method for examining the polar components of original and pyrolyzed residua have been developed. The ratio of ELSD areas of the least polar asphaltene components (cyclohexane soluble) to the most polar components (cyclohexanone or methylene chloride soluble) provides a sensitive indicator of the degree of thermal treatment that the sample has undergone.

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**Table 1. Data for Original Vacuum Residua and Atmospheric Pyrolysis Bottoms**

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<u>Residuum</u>	<u>Pyrolysis time @ 400 °C, min</u>	<u>Wt.% C7 Asphaltenes</u>	<u>Wt.% CyC6 Sol.</u>	<u>K<sub>S</sub></u>	<u>Wt.% Distillate</u>	<u>Wt% Toluene Insolubles (TI)</u>
Boscan	0	17.7	38.5	1.6	na	<0.1
	10	17.8	31.6	1.5	3.9	<0.1
	15	19.0	26.8	1.4	13.4	<0.1
	20	20.2	28.7	1.4	10.5	<0.1
	35	24.4	15.4	1.2	19.5	<0.1
	50	28.6	12.3	1.1	26.1	0.1
	90	16.5	6.0	1.0	39.3	23.8
MaxCL2	0	17.0	37.8	1.6	na	<0.1
	15	19.3	32.8	1.5	4.8	<0.1
	20	23.3	21.9	1.3	5.9	<0.1
	35	22.9	19.5	1.2	11.7	<0.1
	40	26.6	16.6	1.2	12.1	<0.1
	50	26.3	15.8	1.2	16.8	<0.1
Lloydminster	0	16.9	47.7	1.9	na	<0.1
	15	15.9	28.6	1.4	7.6	<0.1
	20	18.1	28.2	1.4	12.2	<0.1
	35	19.6	16.9	1.2	16.5	<0.1
	40	21.0	25.4	1.3	19.5	<0.1
	60	23.0	13.0	1.1	24.5	<0.1
Redwater, B.C.	0	8.9	37.9	1.6	na	<0.1
	25	13.1	27.1	1.4	6.3	<0.1
	35	14.0	21.6	1.3	8.2	<0.1
	50	17.0	22.2	1.3	12.9	<0.1
	55	16.4	19.0	1.2	13.2	<0.1
	75	19.3	16.0	1.2	18.7	1.1

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**Table 2. K<sub>S</sub> Data for Original Vacuum Residua and Atmospheric Pyrolysis Bottoms**

<u>Residuum</u>	Pyrolysis time <u>@ 400 °C, min</u>	Weight Percent		On-Column Three-Solvent Area Percent			
		<u>CyC6 Sol.</u>	<u>K<sub>S</sub></u>	500 nm		ELSD	
				<u>CyC6 Sol.</u>	<u>K<sub>S</sub></u>	<u>CyC6 Sol.</u>	<u>K<sub>S</sub></u>
Boscan	0	37.4	1.63	28.3, 29.1	1.60	33.3, 33.1	1.50
	10	31.6	1.46	24.6	1.32	31.4	1.46
	15	26.8	1.37	20.7	1.26	26.8	1.37
	20	28.7	1.40	16.8, 18.7	1.22	21.8, 22.0	1.28
	35	15.4	1.18	9.14	1.10	17.7	1.21
	50	12.3	1.14	1.57	1.02	2.0	1.02
	90 (23.8 %TI)	6.0	1.0	-	-	-	-
MaxCL2	0	35.2	1.61	31.9	1.54	39.0	1.64
	15	32.8	1.49	20.1	1.25	25.4	1.34
	20	21.9	1.28	16.1, 17.6	1.20	20.1, 21.0	1.26
	35	19.5	1.24	12.1	1.14	20.1	1.25
	40	16.6	1.20	10.5	1.12	18.2	1.22
	50	15.8	1.19	7.74	1.08	16.4	1.20
Lloydminster	0	43.3	1.91	35.9	1.76	43.1	1.76
	15	28.6	1.40	23.1	1.30	31.5	1.46
	20	28.2	1.39	18.0	1.22	24.6	1.33
	35	16.9	1.20	11.9	1.14	21.2	1.27
	40	25.4	1.34	11.6	1.13	21.4	1.27
	60	13.0	1.15	6.30	1.07	16.4	1.20
Redwater, B.C.	0	34.4	1.61	33.7	1.52	45.5	1.83
	25	27.1	1.37	21.6	1.28	33.8	1.51
	35	21.6	1.28	18.4	1.22	30.0	1.43
	50	22.2	1.28	13.0	1.15	23.2	1.30
	55	19.0	1.23	12.0	1.13	22.6	1.29
	75 (1.1 % TI)	16.0	1.24	8.23	1.08	21.6	1.28

**Table 3. Heptane Asphaltenes Data for Original Vacuum Residua and Atmospheric Pyrolysis Bottoms**

<u>Residuum</u>	<u>Pyrolysis time @ 400 °C, min</u>	<u>Weight Percent Asphaltenes</u>	<u>Three-solvent on-column separation</u> <u>Total Asphaltenes Peak Area, counts x10<sup>6</sup></u>	
			<u>500 nm</u>	<u>ELSD</u>
Boscan	0	17.7	16.4, 16.9	20.3, 20.3
	10	17.8	21.5	19.3
	15	19.0	24.2	19.5
	20	20.2	24.5, 22.9	19.3 18.0
	35	24.4	30.9	22.9
	50	28.6	32.1	20.9
	90 (23.8 % TI)	16.5	-	-
MaxCL2	0	17.0	18.5	20.4
	15	19.3	23.2	19.8
	20	23.3	23.0, 24.1	19.3, 20.0
	35	22.9	27.1	22.1
	40	26.6	28.4	23.5
	50	26.3	27.6	22.1
Lloydminster	0	16.9	13.7	21.7
	15	15.9	17.8	18.1
	20	18.1	20.7	18.7
	35	19.6	23.3	20.6
	40	21.0	23.5	19.9
	60	23.0	25.6	20.6
Redwater, B.C.	0	8.9	11.6	12.4
	25	13.1	17.0	13.5
	35	14.0	18.8	14.3
	50	17.0	21.3	15.8
	55	16.4	22.0	16.7
	75 (1.1 % TI)	19.3	24.7	25.6

**Table 4. Hansen Solubility Parameter Components, MPa<sup>1/2</sup> (Hansen 2000)**

<u>Solvent</u>	<u>Dispersion</u>	<u>Polar</u>	<u>Hydrogen Bonding</u>
n-Heptane	15.3	0.0	0.0
Cyclohexane	16.8	0.0	0.2
Toluene	18.0	1.4	2.0
Toluene:methanol (98:2)(v:v)	17.9	1.6	2.4
<u>Solvents with solubility parameter components similar to methylene chloride</u>			
Methylene Chloride	18.2	6.3	6.1
Cyclohexanone	17.8	6.3	5.1
Pyridine	19.0	8.8	5.9
Quinoline	19.4	7.0	7.6
Tetrahydrofuran	16.8	5.7	8.0

**Table 5. On-Column Separation with Four Solvents: Heptane, Cyclohexane, Toluene, and Cyclohexanone**

	Pyrolysis time at 400 °C,min.	Total Asphaltenes		Relative Asphaltenes Peak Areas					
		Peak Area, counts		Cyclohexane		Toluene		Cyclohexanone	
		500nm	ELSD	500nm	ELSD	500nm	ELSD	500nm	ELSD
Boscan	0	18.64	22.12	0.199	0.257	0.668	0.701	0.133	0.042
	10	22.76	20.09	0.143	0.179	0.685	0.762	0.171	0.059
	15	25.25	19.34	0.106	0.143	0.680	0.761	0.214	0.096
	20	26.08	20.13	0.099	0.135	0.763	0.754	0.102	0.089
	35	29.71	19.81	0.053	0.091	0.650	0.754	0.298	0.155
	50	32.47	19.35	0.030	0.065	0.611	0.748	0.359	0.187
MaxCL2	0	20.81	19.75	0.193	0.204	0.659	0.749	0.148	0.047
	15	23.74	18.21	0.104	0.107	0.699	0.802	0.198	0.091
	20	25.17	19.44	0.091	0.091	0.700	0.819	0.209	0.091
	35	27.21	19.85	0.060	0.066	0.695	0.809	0.245	0.124
	40	28.70	21.47	0.055	0.068	0.682	0.792	0.263	0.139
	50	29.64	20.70	0.040	0.053	0.666	0.792	0.295	0.155
Lloydminster	0	16.13	21.85	0.214	0.239	0.650	0.728	0.136	0.033
	15	19.08	16.02	0.114	0.123	0.696	0.806	0.190	0.071
	20	21.70	17.19	0.088	0.097	0.705	0.811	0.207	0.092
	35	23.00	16.98	0.064	0.067	0.693	0.813	0.243	0.120
	40	24.92	18.89	0.057	0.076	0.683	0.780	0.260	0.144
	60	25.69	17.44	0.035	0.040	0.670	0.807	0.295	0.154
Redwater, B.C.	0	14.99	9.77	0.174	0.187	0.657	0.764	0.169	0.049
	25	19.01	10.29	0.091	0.095	0.688	0.810	0.221	0.094
	35	20.59	11.32	0.074	0.096	0.685	0.794	0.241	0.110
	50	23.36	11.65	0.060	0.083	0.670	0.796	0.271	0.121
	55	23.12	14.55	0.051	0.057	0.660	0.795	0.290	0.148
	75 (coke)	26.13	12.93	0.038	0.038	0.643	0.774	0.320	0.188

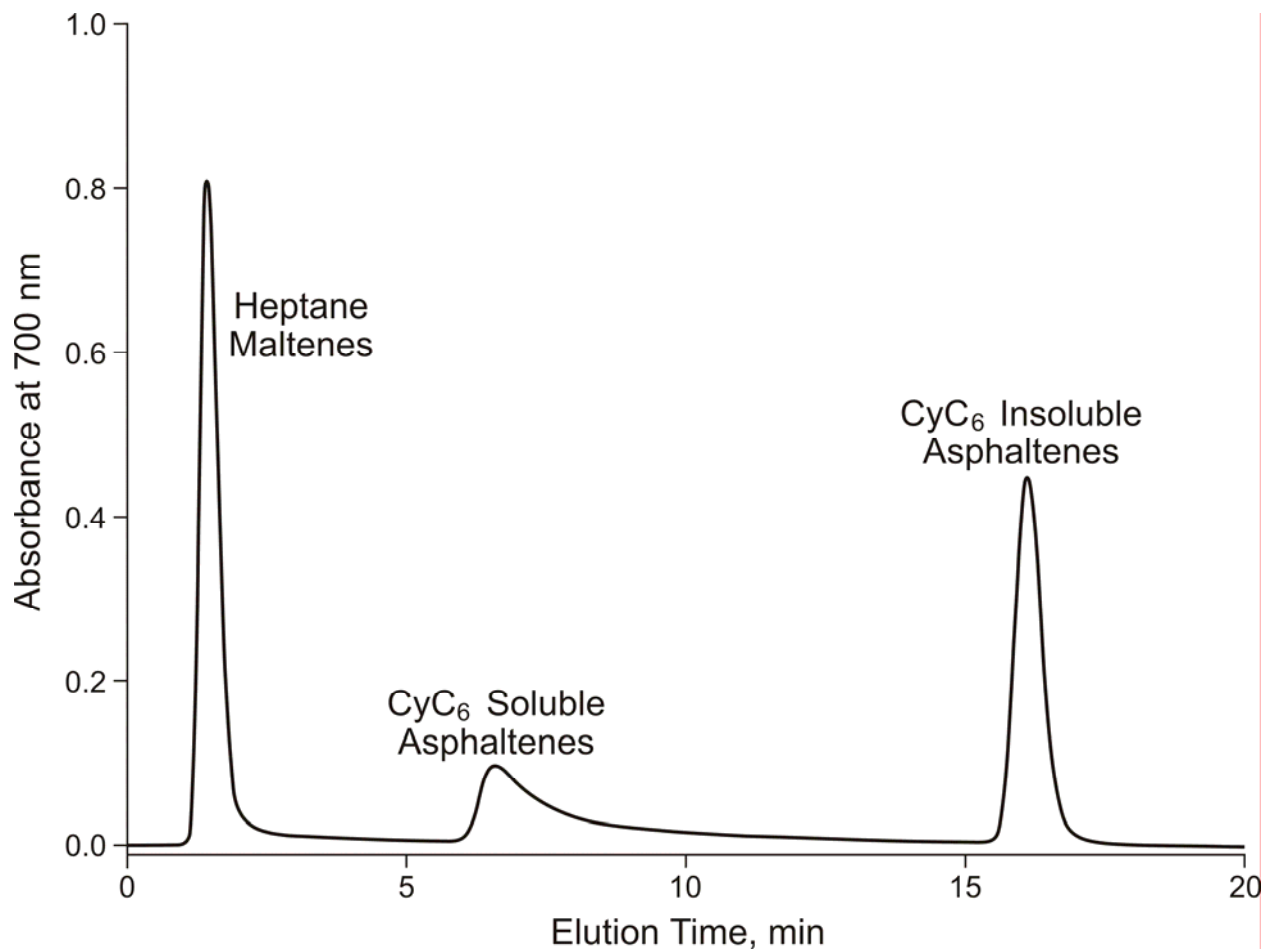
**Table 6. On-Column Separation with Four Solvents: Heptane, Cyclohexane, Toluene, and Methylene Chloride**

	Pyrolysis time at 400 °C,min.	Total Asphaltenes		Relative Asphaltenes Peak Areas					
		Peak Area, counts		Cyclohexane		Toluene		CH <sub>2</sub> Cl <sub>2</sub>	
		<u>500nm</u>	<u>ELSD</u>	<u>500nm</u>	<u>ELSD</u>	<u>500nm</u>	<u>ELSD</u>	<u>500nm</u>	<u>ELSD</u>
Boscan	0	21.41	23.97	0.096	0.151	0.810	0.788	0.094	0.060
	10	23.71	19.68	0.068	0.122	0.797	0.783	0.135	0.095
	15	28.45	21.29	0.050	0.099	0.775	0.767	0.175	0.099
	20	27.53	20.95	0.045	0.098	0.776	0.768	0.179	0.134
	35	29.35	19.73	0.021	0.067	0.720	0.726	0.259	0.206
	50	31.87	20.25	0.017	0.046	0.680	0.699	0.302	0.254
MaxCL2	0	19.50	18.90	0.085	0.130	0.786	0.790	0.130	0.080
	15	24.19	18.94	0.049	0.083	0.769	0.778	0.182	0.139
	20	27.16	21.66	0.043	0.088	0.764	0.761	0.192	0.151
	35	26.67	19.64	0.027	0.062	0.732	0.739	0.241	0.199
	40	29.82	22.38	0.024	0.054	0.700	0.718	0.276	0.228
	50	27.66	19.32	0.017	0.038	0.693	0.714	0.290	0.248
Lloydminster	0	15.31	20.82	0.090	0.146	0.808	0.793	0.102	0.061
	15	17.21	14.99	0.044	0.071	0.790	0.809	0.166	0.119
	20	18.24	15.17	0.033	0.068	0.770	0.785	0.197	0.147
	35	18.91	14.84	0.023	0.057	0.738	0.754	0.239	0.189
	40	21.42	16.76	0.023	0.052	0.714	0.732	0.263	0.216
	60	21.46	15.46	0.017	0.039	0.698	0.721	0.285	0.240
Redwater, B.C.	0	15.64	12.66	0.084	0.107	0.757	0.798	0.141	0.096
	25	17.03	13.17	0.036	0.145	0.757	0.710	0.206	0.145
	35	17.49	11.68	0.029	0.062	0.740	0.757	0.231	0.182
	50	20.03	13.45	0.024	0.052	0.709	0.729	0.266	0.219
	55	18.48	11.63	0.022	0.041	0.695	0.720	0.283	0.239
	75 (coke)	16.04	10.30	0.018	0.020	0.650	0.630	0.332	0.450

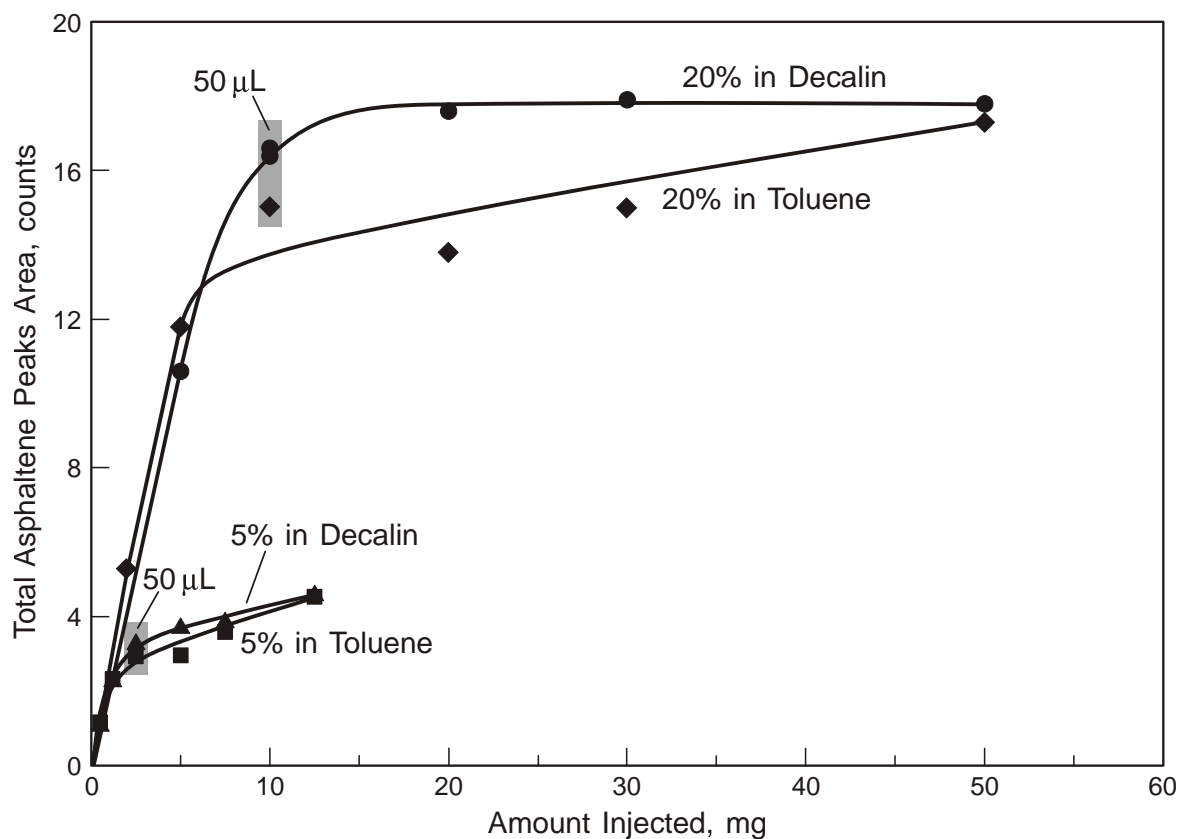
**Table 7. Ratio of Areas of the Cyclohexane Soluble Asphaltene Peaks to the Cyclohexanone-Soluble or Methylene Chloride-Soluble Asphaltene Peaks**

	Pyrolysis time at 400 °C,min.	On-Column Precipitation and Re-dissolution Peak Area Ratios			
		Cyclohexane/Cyclohexanone		Cyclohexane/Methylene Chloride	
		<u>500nm</u>	<u>ELSD</u>	<u>500nm</u>	<u>ELSD</u>
Boscan	0	1.50	6.11	1.02	2.52
	10	0.84	3.02	0.51	1.29
	15	0.49	1.49	0.28	0.74
	20	0.46	1.32	0.25	0.73
	35	0.18	0.58	0.08	0.33
	50	0.08	0.35	0.06	0.18
MaxCL2	0	1.30	4.38	0.65	1.62
	15	0.52	1.17	0.27	0.60
	20	0.44	1.00	0.23	0.59
	35	0.24	0.53	0.11	0.31
	40	0.21	0.49	0.09	0.24
	50	0.14	0.34	0.06	0.15
Lloydminster	0	1.58	7.25	0.88	2.40
	15	0.60	1.74	0.27	0.60
	20	0.42	1.06	0.17	0.46
	35	0.26	0.56	0.10	0.30
	40	0.22	0.53	0.09	0.24
	60	0.12	0.26	0.06	0.16
Redwater, B.C.	0	1.03	3.81	0.60	1.12
	25	0.41	1.01	0.18	1.00
	35	0.31	0.88	0.12	0.34
	50	0.22	0.68	0.09	0.24
	55	0.17	0.38	0.08	0.17
	75 (coke)	0.12	0.27	0.05	0.06

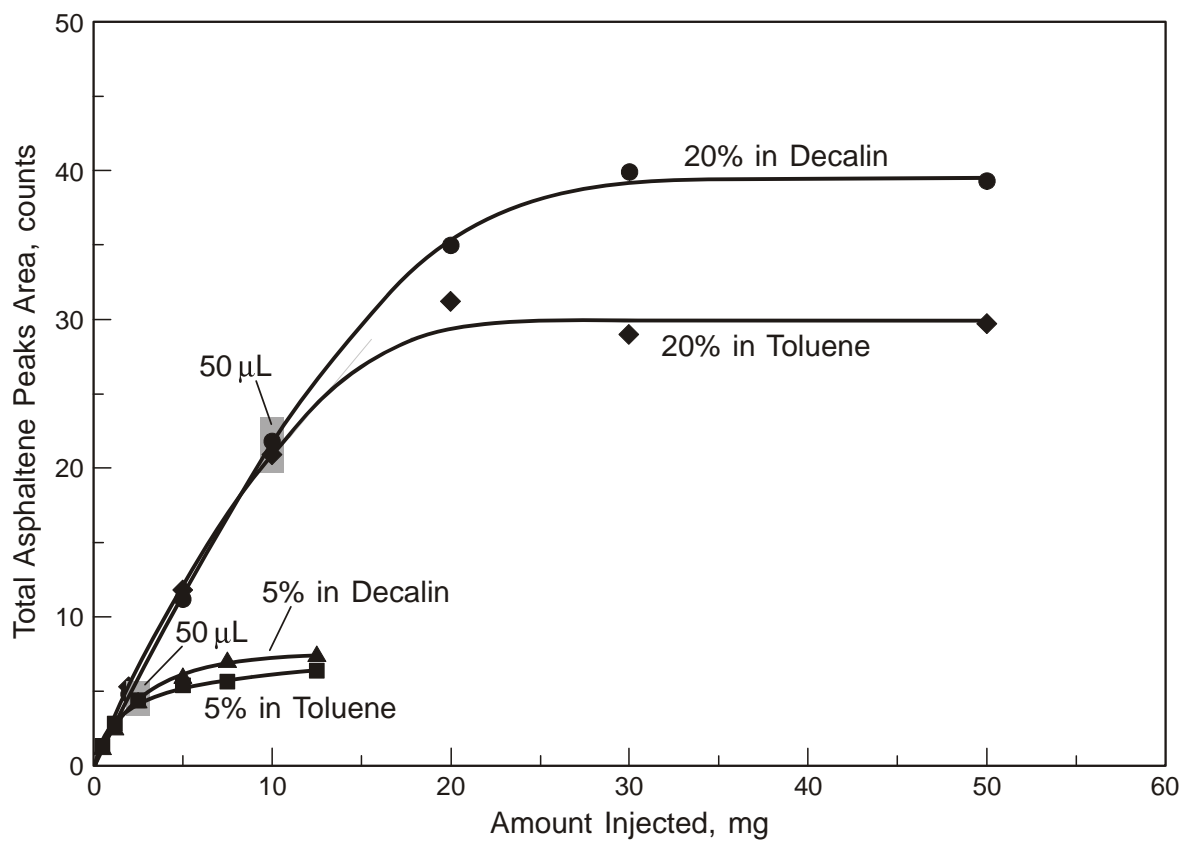




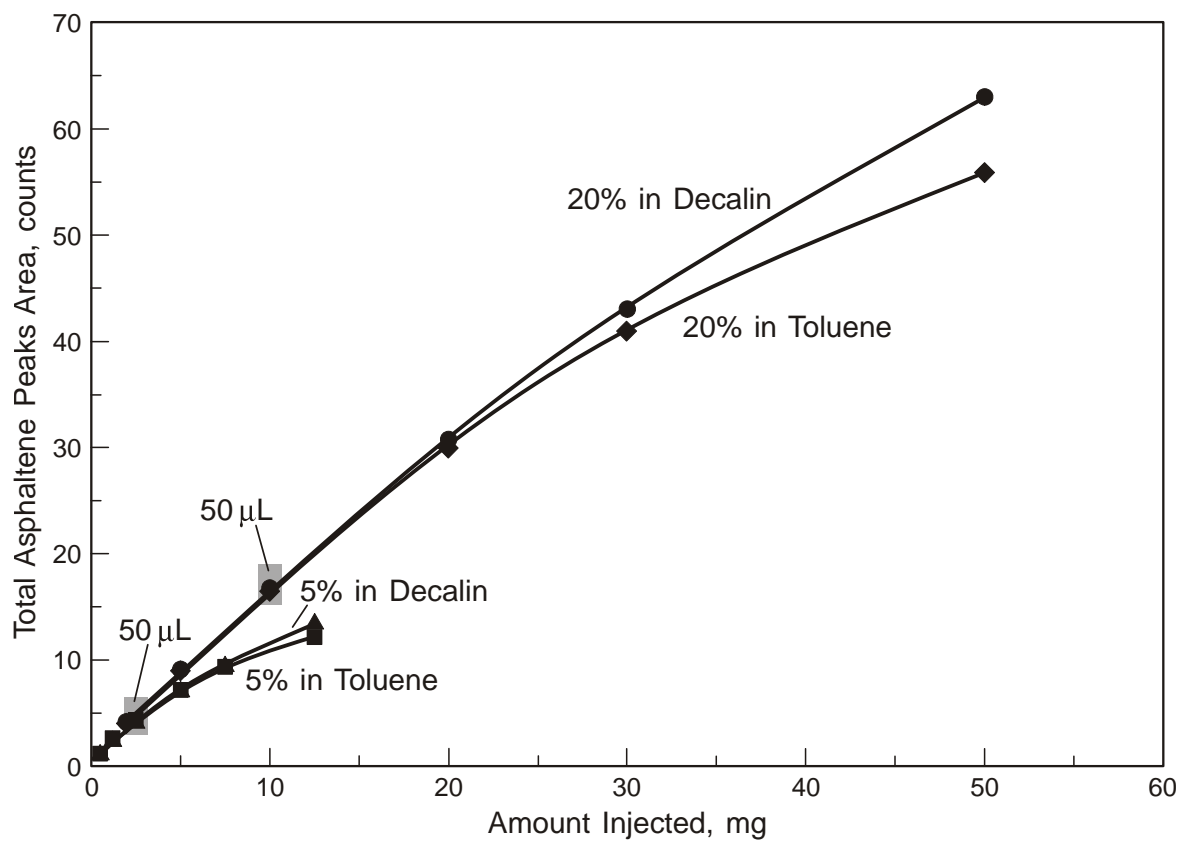
**Figure 1. Separation Profile for 10 mg Redwater, B.C. Residuum on 160 x 8.0 mm PTFE Column ,700 nm Absorbance Detector. Gradient: 0 min. Heptane, 2 min. Cyclohexane, 15 min. Toluene:methanol (98:2), 40 min. Heptane; 3.0 mL/min.**



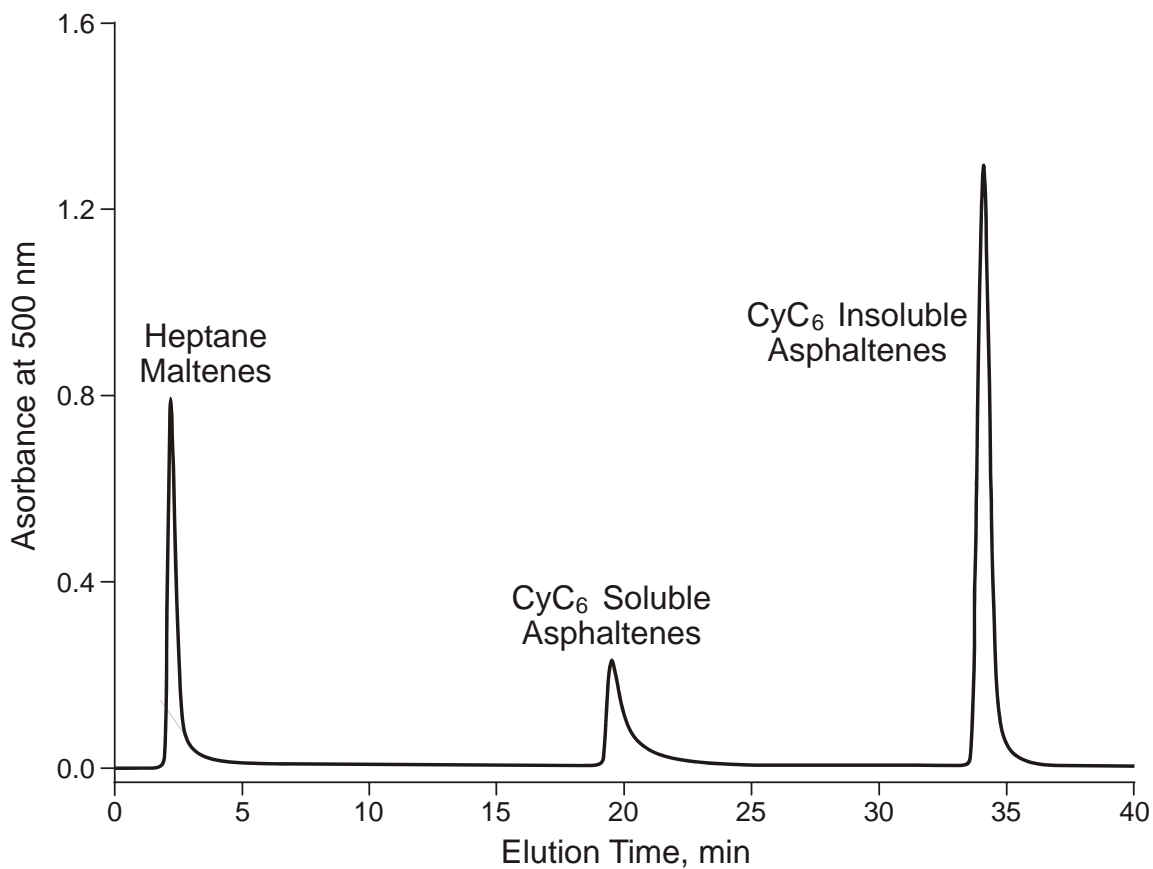
**Figure 2. Sample Size Study with 150 mm x 4.6 mm PTFE Column (2.5 cc Volume), 700 nm Absorbance Detector. Gradient: 0 min. Heptane, 1 min. Cyclohexane, 8 min. Toluene:methanol (98:2) (v:v), 14 min. Heptane; 2.0 mL/min.**



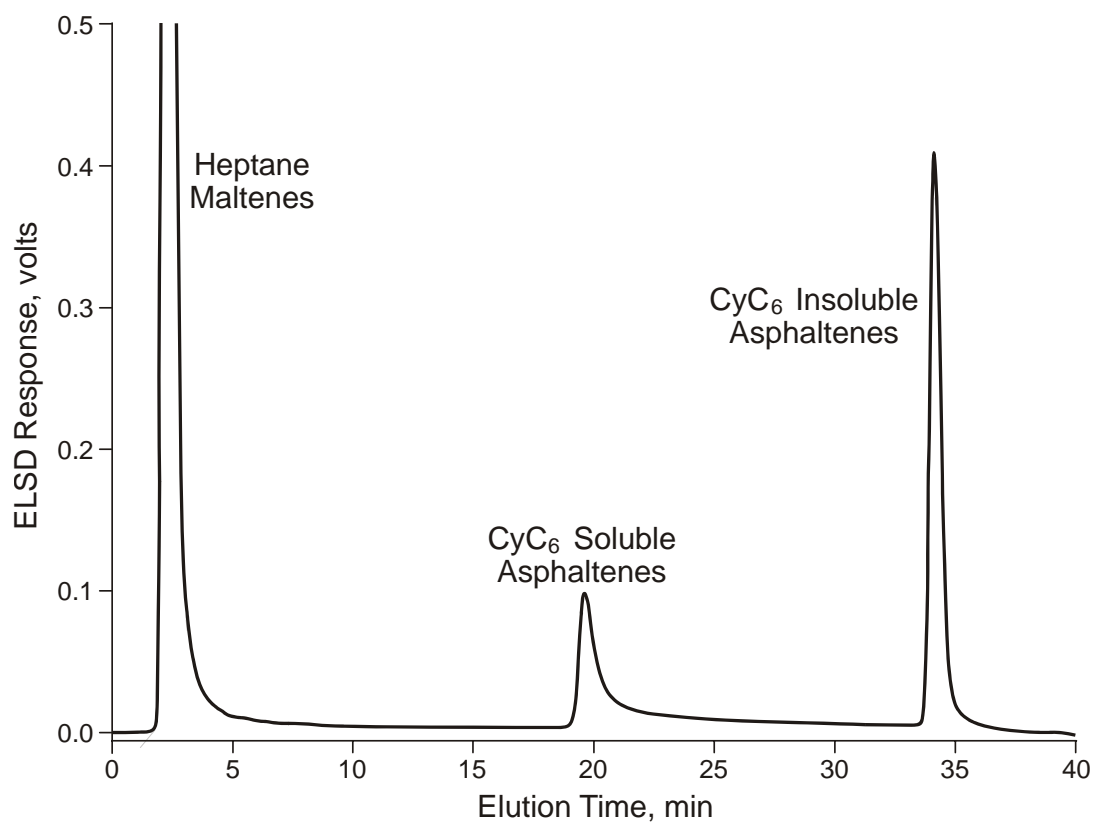
**Figure 3. Sample Size Study with 100 mm x 7.0 mm PTFE Column (3.8 cc Volume), 700 nm Absorbance Detector. Gradient: 0 min. Heptane, 1 min. Cyclohexane, 10 min. Toluene:methanol (98:2) (v:v), 15 min. Heptane; 2.5 mL/min.**



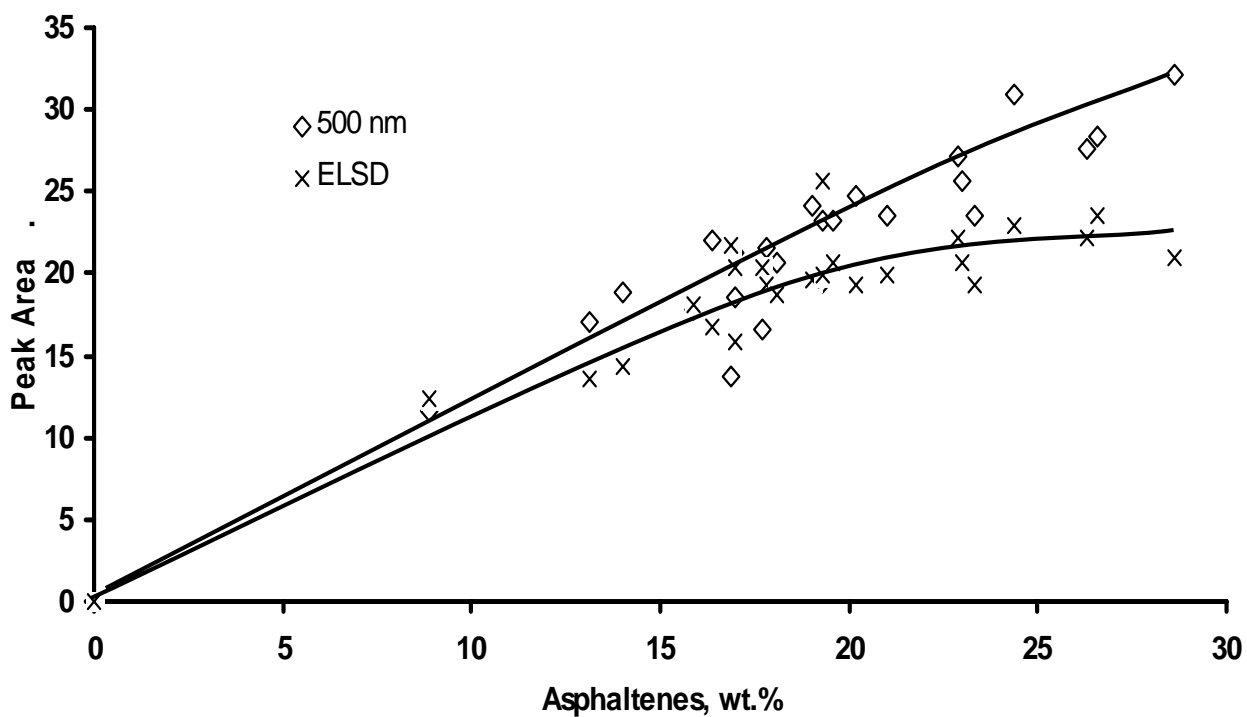
**Figure 4. Sample Size Study with 250 mm x 10 mm PTFE Column (20 cc Volume), 700 nm Absorbance Detector. Gradient: 0 min. heptane, 3 min. Cyclohexane, 13 min. Toluene:methanol (98:2) (v:v), 21 min. heptane; 2.5 mL/min.**



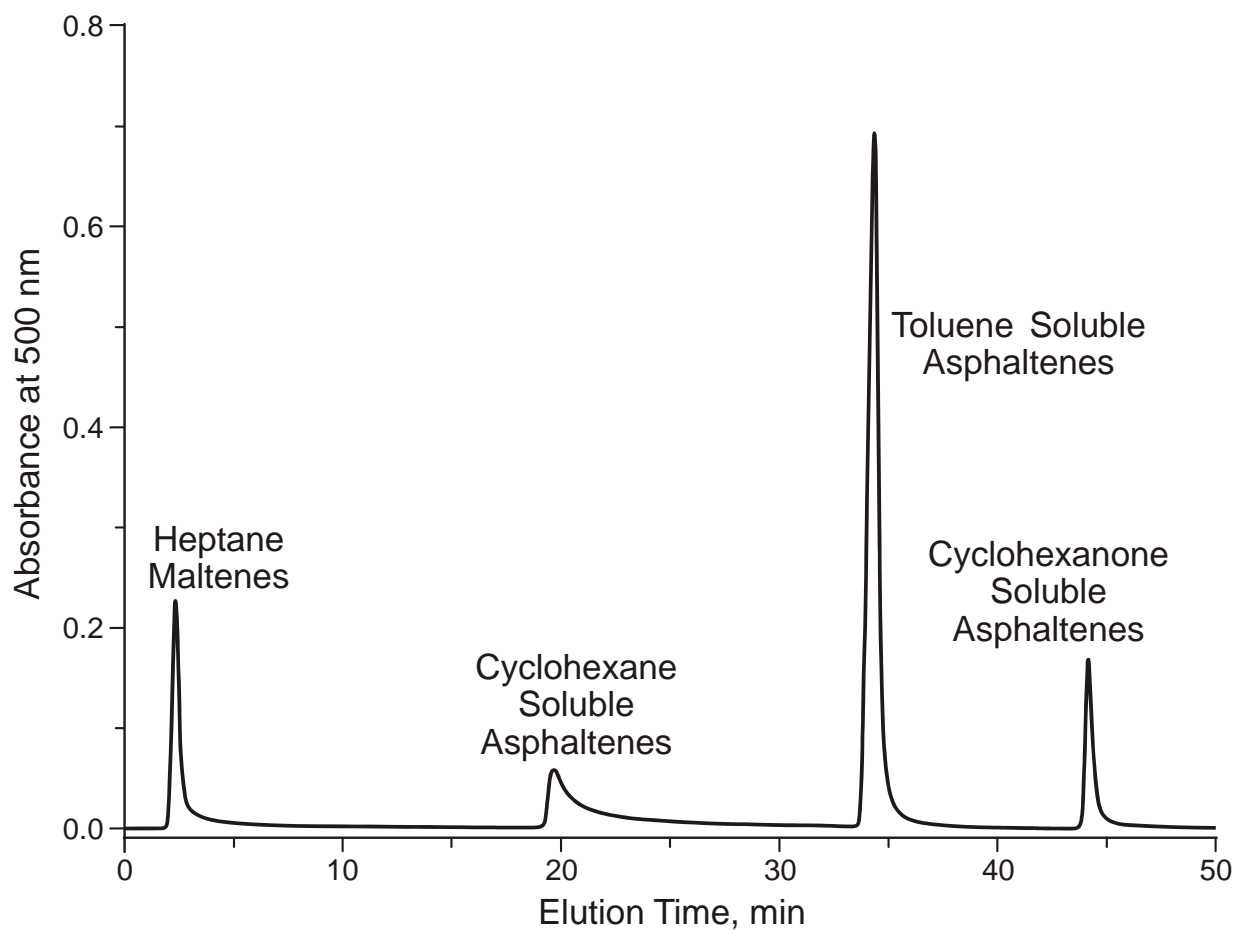
**Figure 5. Separation of 2 mg (10 uL) Unpyrolyzed Boscan. Residuum in Toluene on 250 mm x 10 mm PTFE Column, 500 nm Absorbance Detector. Gradient: 0 min. Heptane, 15 min. Cyclohexane, 30 min, Toluene:methanol (98:2), 40 min. heptane, 4.0 mL/min.**



**Figure 6. Separation of 2 mg (10 uL) Unpyrolyzed Boscan. Residuum in Toluene on 250 mm x 10 mm PTFE Column with ELSD Detector. Gradient: 0 min. Heptane, 15 min. Cyclohexane, 30 min, Toluene:methanol (98:2), 40 min. Heptane, 4.0 mL/min.**

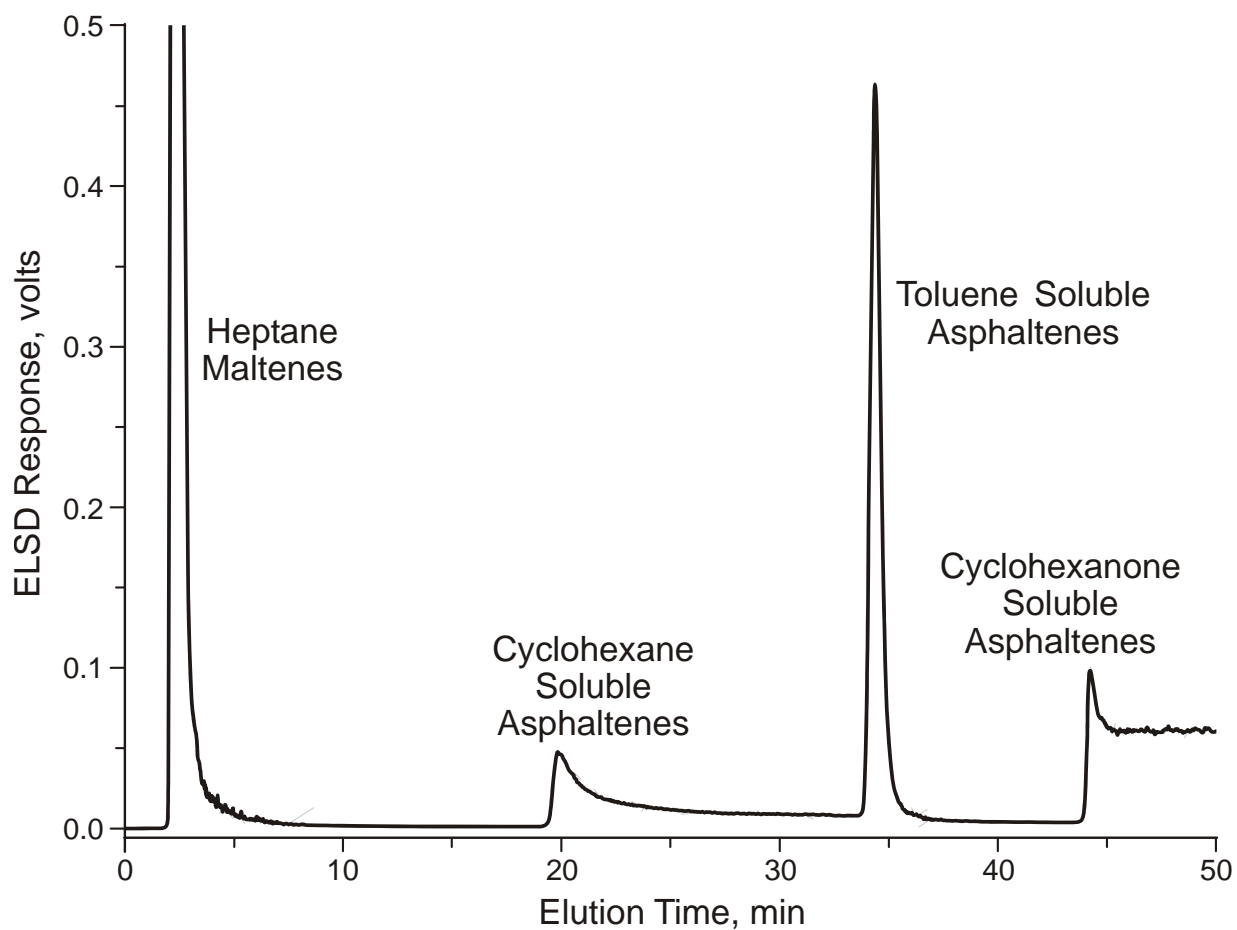


**Figure 7. Correlation of 500 nm Absorbance Detector and ELSD Peak Areas for Three-Solvent Separation with Values from Gravimetric Determination of Heptane Asphaltenes.**

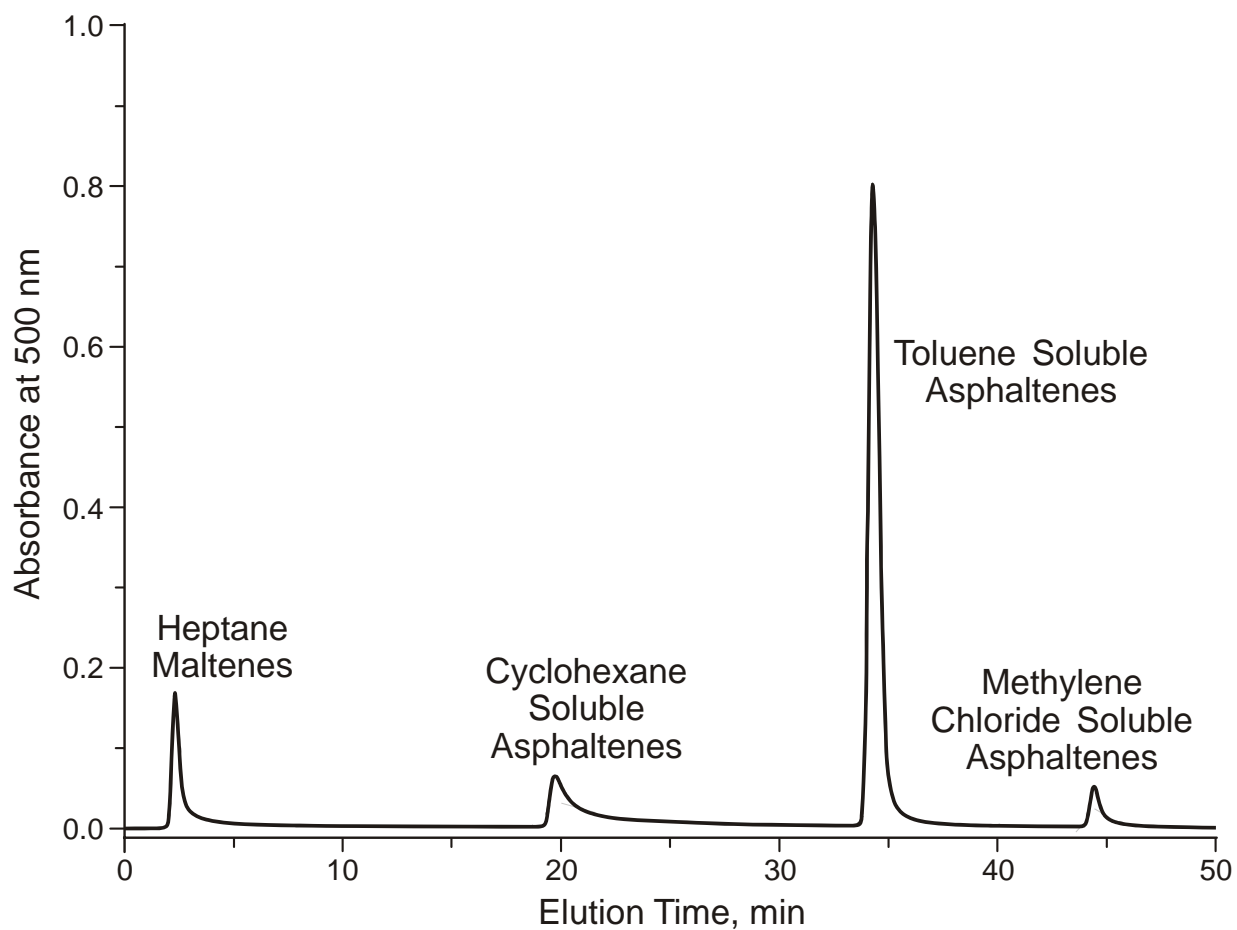


**Figure 8. Separation of 2 mg (10 uL) Unpyrolyzed Boscan. Residuum in Cyclohexanone on 250 mm x 10 mm PTFE Column, 500 nm Absorbance Detector. Gradient: 0 min. Heptane, 15 min. Cyclohexane, 30 min, Toluene, 40 min. Cyclohexanone, 50 min. Heptane, 4.0 mL/min.**

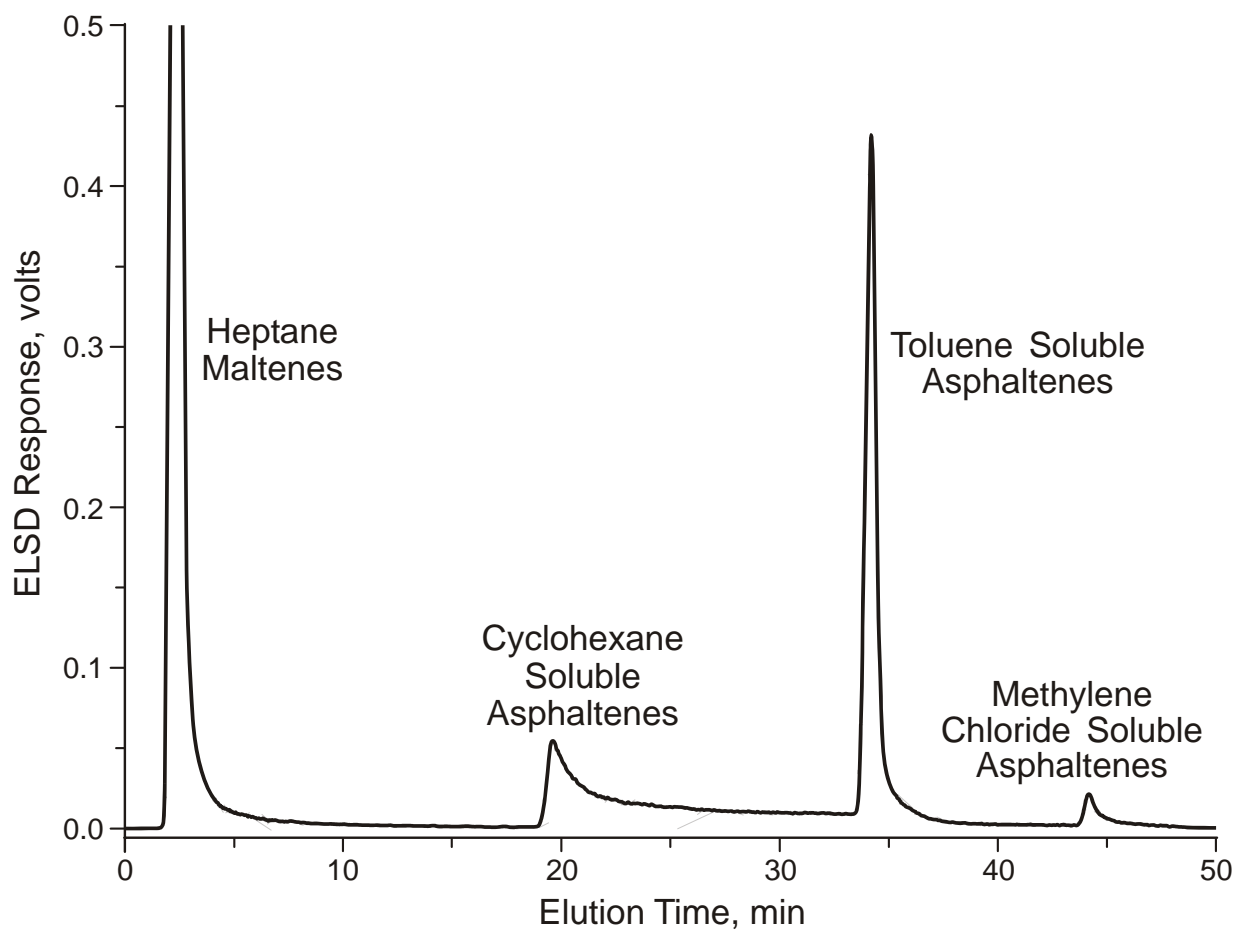




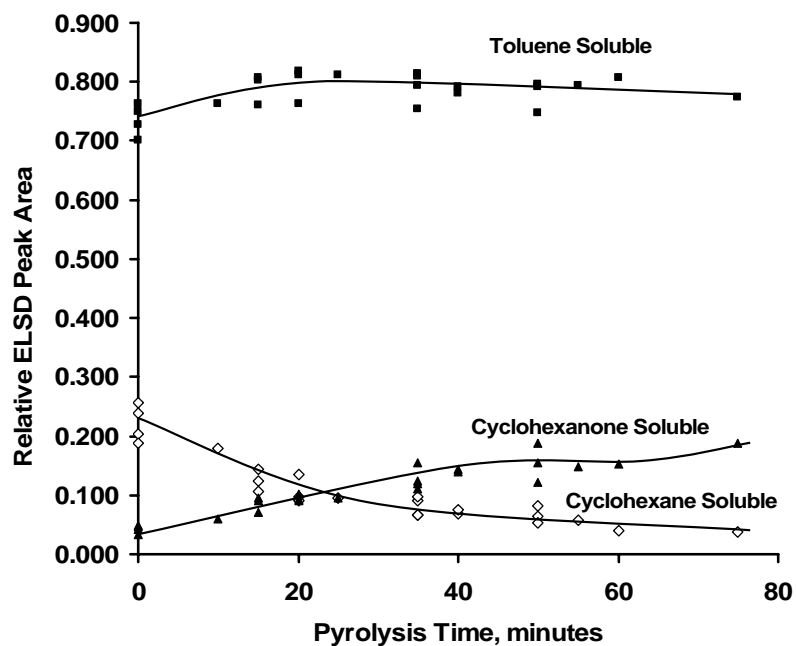
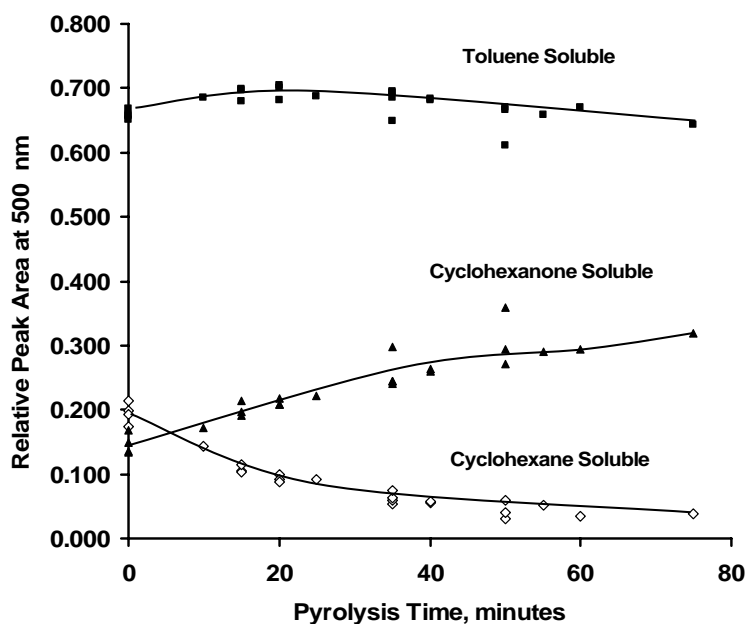
**Figure 9. Separation of 2 mg (10 uL) Unpyrolyzed Boscan Residuum in Cyclohexanone on 250 mm x 10 mm PTFE Column, ELSD Detector. Gradient: 0 min. Heptane, 15 min. Cyclohexane, 30 min, Toluene, 40 min. Cyclohexanone, 50 min. Heptane, 4.0 mL/min.**



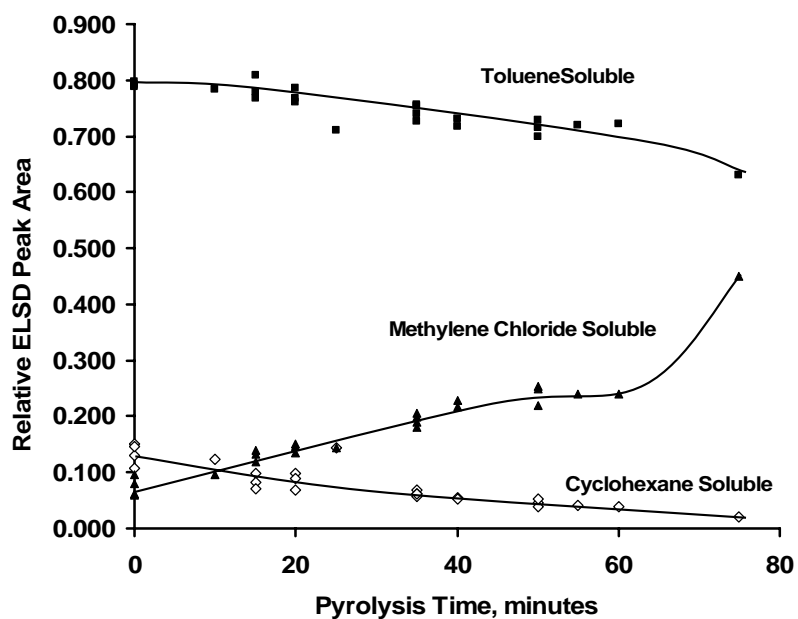
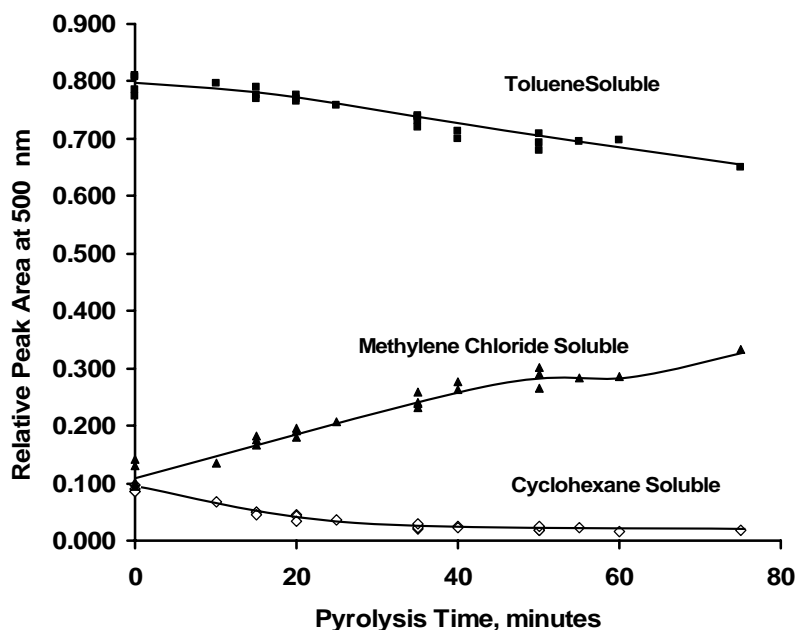
**Figure 10.** Separation of 2 mg (10 uL) Unpyrolyzed Boscan. Residuum in Methylene Chloride on 250 mm x 10 mm PTFE Column, 500 nm Absorbance Detector. Gradient: 0 min. Heptane, 15 min. Cyclohexane, 30 min, Toluene, 40 min. Methylene chloride, 50 min. Heptane, 4.0 mL/min.



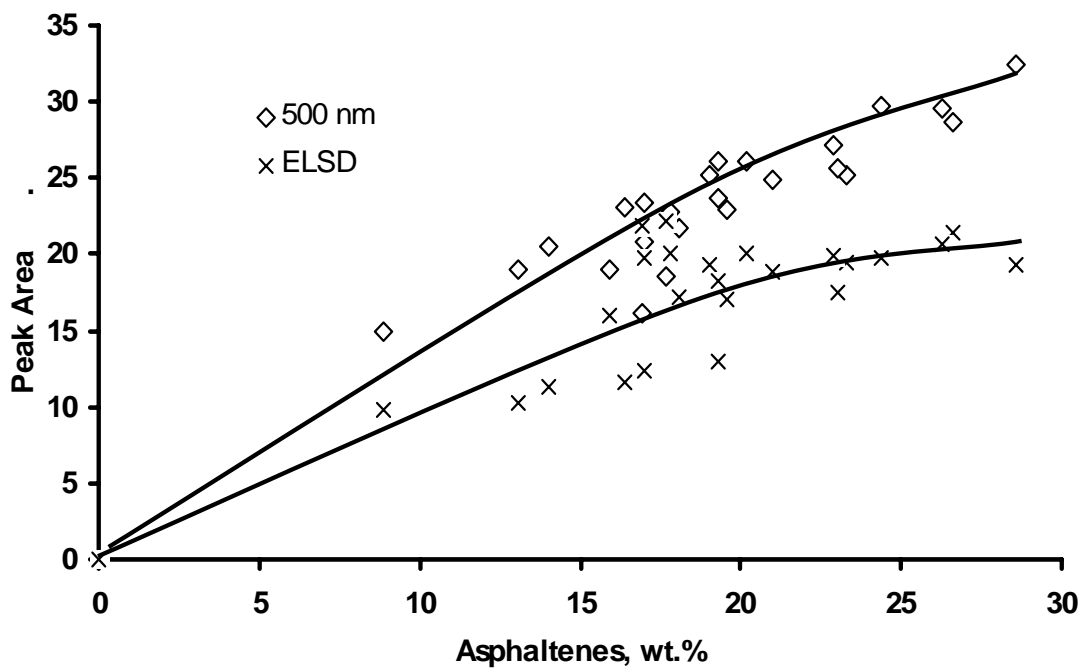
**Figure 11.** Separation of 2 mg (10 uL) Unpyrolyzed Boscan. Residuum in Methylene Chloride on 250 mm x 10 mm PTFE Column, ELSD Detector. Gradient: 0 min. Heptane, 15 min. Cyclohexane, 30 min, Toluene, 40 min. Methylene Chloride, 50 min. Heptane, 4.0 mL/min.



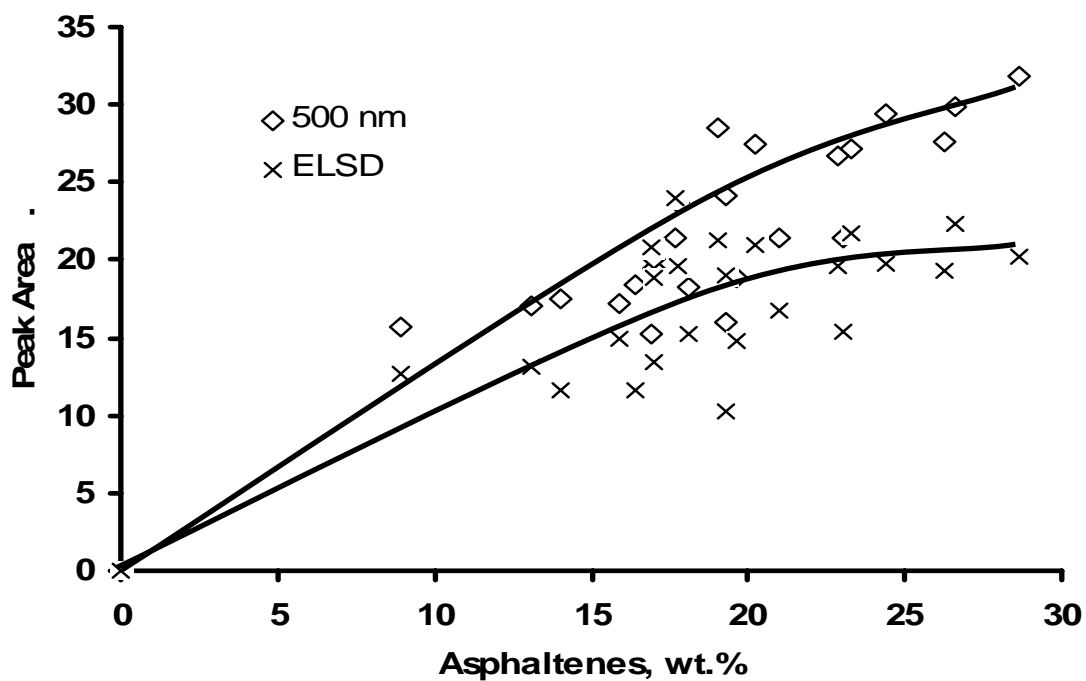
**Figure 12. Relative Peak Areas for Four Original and Pyrolyzed Residua in Cyclohexanone on 250 mm x 10 mm PTFE Column, UV 500 nm Detector (top) and ELSD Detector (bottom). Gradient: 0 min. Heptane, 15 min. Cyclohexane, 30 min, Toluene, 40 min. Cyclohexanone, 50 min. Heptane, 4.0 mL/min.**



**Figure 13. Relative Peak Areas for Four Original and Pyrolyzed Residua in Methylene Chloride on 250 mm x 10 mm PTFE Column, UV 500 nm Detector (top) and ELSD Detector (bottom). Gradient: 0 min. Heptane, 15 min. Cyclohexane, 30 min, Toluene, 40 min. Methylene Chloride, 50 min. Heptane, 4.0 mL/min.**



**Figure 14. Correlation of 500 nm Absorbance Detector and ELSD Peak Areas for Four Solvent Separation with Cyclohexanone with Values from Gravimetric Determination of Heptane Asphaltenes.**



**Figure 15. Correlation of 500 nm Absorbance Detector and ELSD Peak Areas for Four Solvent Separation with Methylene Chloride with Values from Gravimetric Determination of Heptane Asphaltenes.**