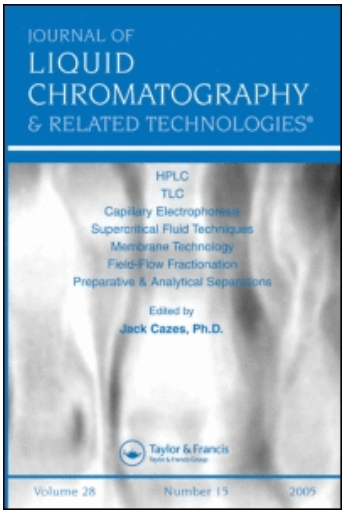

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Shale Oil Separation by High Performance Liquid Chromatography

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SHALE OIL SEPARATION BY HIGH PERFORMANCE LIQUID CHROMATOGRAPHY

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ABSTRACT

In the characterization of syncrudes from alternate fossil fuel sources, there is a need for the rapid separation into hydrocarbon groups. Analytical separations where microgram quantities of sample can be used and preparative separations on multigram scale so that additional characterization and testing can be carried out.

Using samples of shale oil from Utah and Thailand, HPLC techniques are shown that accomplish these aims. The use of a mixed set of normal phase analytical columns for the automated separation into saturates, neutral aromatics by the number of rings and polar aromatics. Separation of multigram quantities of shale oil into major hydrocarbon groups, saturates, neutral aromatics, and polar aromatics is done in under 10 minutes.

INTRODUCTION

The development of transportation fuels and lubricants from highly heterogeneous fossil fuels represents many engineering challenges and requires rapid characterization techniques. There is a need for two types of characterization capabilities; one utilized by laboratory personnel for a complete evaluation of syncrude products, the second a rapid technique used by engineering personnel in the Pilot Plant. High Performance Liquid Chromatography (HPLC) of today can meet these needs. In its analytical mode, HPLC instrumentation can be automated to the point where

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little operator involvement is necessary. In its preparative mode, multigram separations can be done routinely.

EXPERIMENTAL

Two samples of shale oil were used in these evaluations. The analytical separations were done on a tailored dual detector, Waters LC. The modifications were the use of a Rheodyne (Cotati, CA) fixed loop injector and a Rheodyne 6 port electropneumatic valve used to change the flow direction through the column. Detectors were UV at 254nm and a differential refractometer in series.

The mobile phase, HPLC grade n-Hexane, was maintained at 2.0 ml/min. The column was a 3.9mm by 30cm with a NH_2 modified support (ENERGY ANALYSIS COLUMN). Additional characterization were carried out where a high surface area silica gel (μPORASIL) column was used in series.

The preparative separations were carried out on a Waters PrepLC™ System 500A. The column used for the multigram separations in the preparative system are 57mm by 30cm. The support is a NH_2 modified silica. With columns of this diameter, sample loads of up to 8 grams have been used.

RESULTS

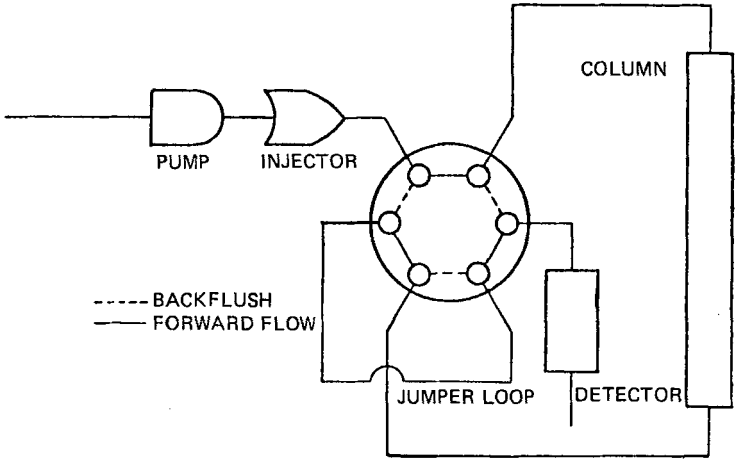
Analytical Separations

The separation of shale oil into saturates, neutral aromatics, and polar aromatics can be done across the 3.9mm ENERGY ANALYSIS COLUMN in 24 minutes using n-Hexane at 2.0 ml/min.

Approximately 0.5 grams of sample weighed to the nearest 0.1 milligram is dissolved in 20.0 ml of n-Hexane. The sample is filtered across a 0.5 micron membrane filter to remove any insolubles. These insolubles are generally classified as asphaltenes. The filtrate is loaded into the 10 microliter loop of the injector and then placed on the head of the column.

In this separation scheme, the saturates elute first. The saturate peak will contain all the normal, iso-, and cyclo-paraffins.

The olefins, normal and cyclo will also elute in this peak. Then the neutral aromatics elute. The selectivity of the column is such that all of the alkanes and alkenes, at least through cholestane, a 26 carbon saturate, will elute before benzene or an alkyl substituted benzene. The elution order of the neutral aromatics is by the number of condensed rings. When the neutral aromatics have eluted from the column, the mobile phase flow is reversed through the column. The polar aromatics will elute in a single peak. The selectivity of the column packing is such that thiophene, pyrrole, pyridine, and other heteroatom containing aromatics will elute in this envelope (Table I). A flow diagram of the six-port valve used for this column flow reversal is shown below.



This technique of column backflushing was first reported by Sautoni (1).

This technique of flow reversal through the column keeps the chromatographic equipment simple, uses a single solvent, and a single column. With an automatic injector, the system

TABLE I

Retention (k') of a variety of hydrocarbons using n-Hexane at 2.0 ml/min. across a 3.9mm NH_2 modified amine support.

hexadecane	0.10
dodecane	0.10
heptadecane	0.10
1-heptadecene	0.11
1-octene	0.12
1-octadecene	0.12
cycloheptane	0.10
pristane	0.10
cholestane	0.10
benzene	0.16
n-buytlbenzene	0.14
toluene	0.15
n-decylbenzene	0.13
mestylene	0.13
phenylundecane	0.13
biPhenyl	0.41
naphthalene	0.37
2-methylnaphthalene	0.35
2,3-dimethylnaphthalene	0.36
2,3,5-trimethylnaphthalene	0.36
acenaphthalene	0.40
acenphthyene	0.60
triphenylene	1.85
anthracene	0.83
phenanthrene	0.84
1-methylphenanthrene	0.81
fluoranthene	1.15
chrysene	2.88
benzo(a)pyrene	3.78

TABLE I (CONT'D)

ortho-cresol	11.16
phenol	11.00
2,2'bipyridine	11.23
pyridine	11.00
thiophene	13.00

The column is backflushed at k' of 5.0 and the analysis is completed at k' of 14.5.

can easily be automated. The chromatographic system uses two detectors in series, UV at 254nm is first followed by a differential refractometer. The saturated hydrocarbons are detected by the differential refractometer while those compounds with aromatic modiety are detected with greater sensitivity by UV. On the integrating recorder, the response of the UV is Pen 1 while that of the refractometer is on Pen 2. The offset of the pens gives the visual appearance that the saturates elute in the middle of the aromatic envelope, see Figures 1 and 2.

This approach was utilized for the compositional characterization of the shale oils from the two different sources (Figures 1 & 2). The hydrocarbon group composition of the two shale oils were determined to be:

	UTAH	THAILAND
Saturates	18.96 wt%	56.30 wt%
Neutral Aromatics	57.63	16.30
Polar Aromatics	23.40	27.50

The technique for quantitation utilized the approach that has been employed for crude oil (2).

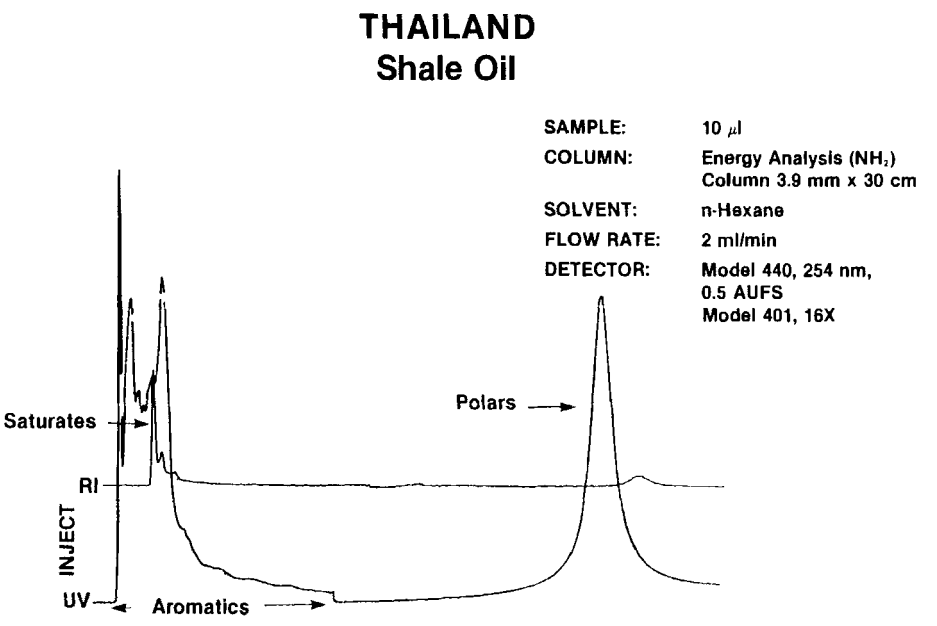


Figure 1: Thailand Shale Oil -- Hydrocarbon Group Separation.

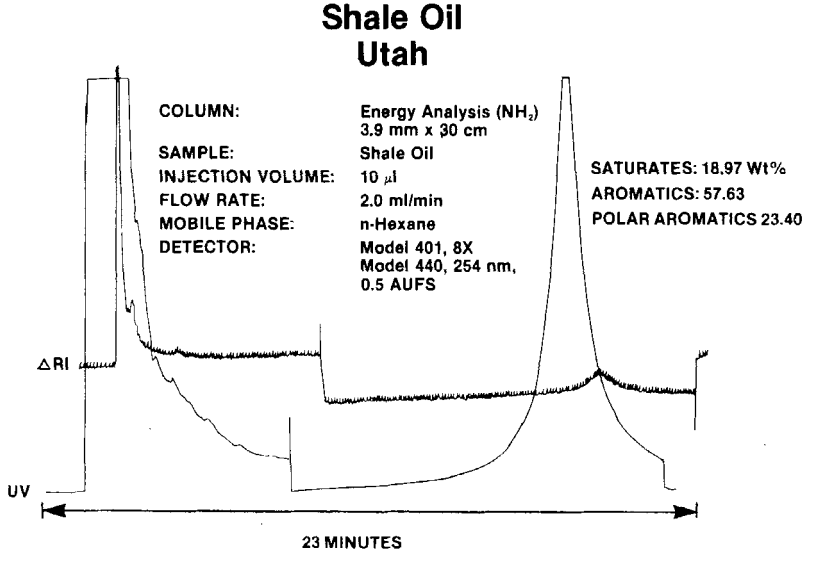


Figure 2: Utah Shale Oil -- Hydrocarbon Group Separation.

Preparative Separations

The analytical separation was scaled up so that multigram sample loads could be separated. These larger separations were done on the PrepLC™ System 500A. The column is 57mm by 30cm. The packing is a NH_2 modified silica, the same as the 3.9mm analytical column. Other than a larger diameter, the particle size of the preparative packing is a nominal 40 microns while that used in the analytical column is 10 microns. This preparative column is 200 times larger in cross-sectional area than the 3.9mm analytical column. Sample loads can be increased proportional to the cross-sectional area. If the same solvent is used at the same linear velocity, equivalent separations will be obtained in the same time frame. This translates to sample loads of up to 8 grams at a flow rate of 400 ml/min.

The preparative column is equilibrated with n-Hexane at 400 ml/min. at a pressure drop of 5 bars. The sample, up to 8 grams, is dissolved in 35-40 ml of n-Hexane. This volume is injected onto the head of the column following the manufacturer's recommendations. The saturates are collected (Figure 3 saturate collection is between #1 and #2), the aromatics are collected between #2 and #3. Instead of reversing the flow through the column, the mobile phase was stepped to dichloromethane. The polar aromatics elute with the solvent front. It is not that the flow cannot be reversed through this larger column, but by changing the mobile phase a reduction in overall solvent usage is realized. In the analytical separation, where solvent consumption is small, simplicity and automation are of prime concern. In the preparative separation, flowing at 400 ml/min. solvent consumption is of concern. Thus, the step change is solvent. The total analysis time is 6.5 minutes. After the polar aromatics have eluted from the column, it is re-equilibrated with n-Hexane, total time between injections is 10 minutes.

The fractions were recovered by evaporating the solvent to dryness. Any sample component that has a partial vapor pressure

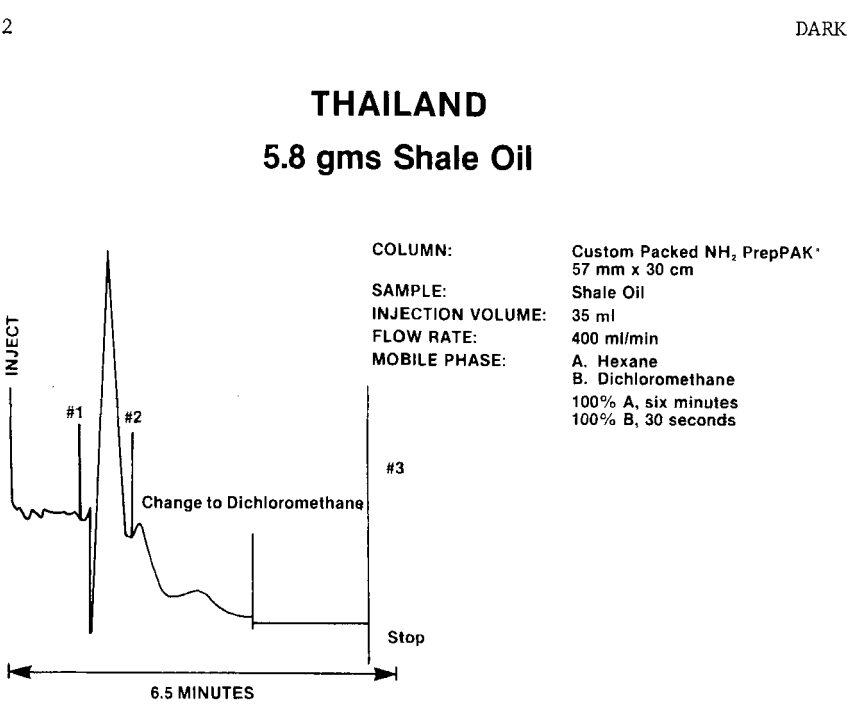


Figure 3: Thailand Shale Oil -- Preparative Hydrocarbon Group Separation.

similar to that of the solvent will be lost. After the gravimetric quantitation of the recovered fractions, they were analyzed on the 3.9mm by 30cm ENERGY ANALYSIS COLUMN (Figures 4-6). The recovered saturate fraction (Figure 4) shows response from the UV detector. This response may be due to carryover of neutral aromatics or from the olefins present in this fraction. The neutral aromatic fraction (Figure 5) shows the presence of polar aromatics. This is not due to poor chromatographic fractionation, but these polar aromatics are more soluble in the neutral aromatics than in the n-Hexane at the concentration applied to the preparative column. At the higher dilution level used in this analytical run, separation is achieved. The polar aromatic fraction is shown in Figure 6. There is sufficient material in each of these fractions so that additional characterization can be done.

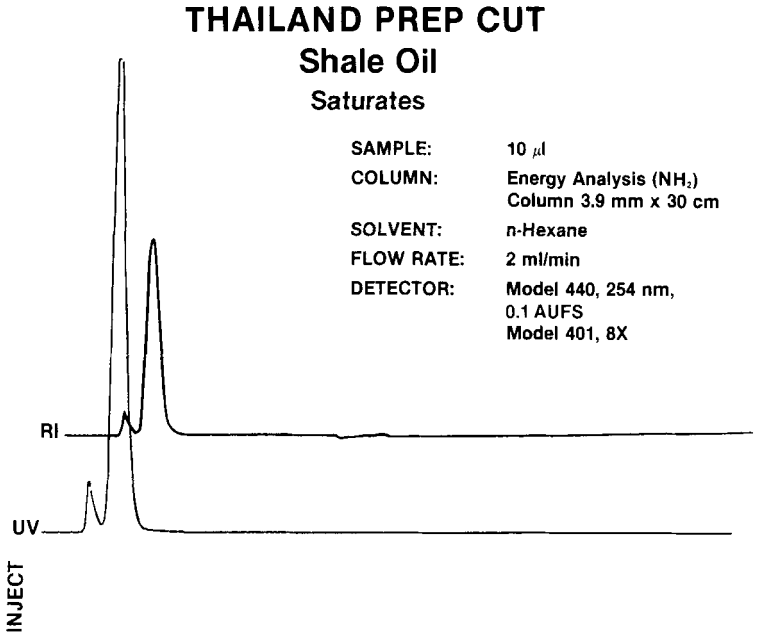


Figure 4: Thailand Shale Oil -- Saturate Fraction From Preparative Separation Analyzed Under Analytical Conditions.

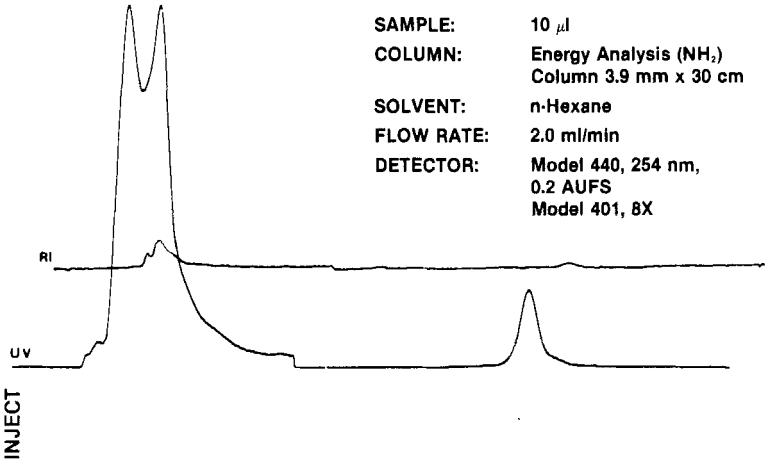


Figure 5: Thailand Shale Oil -- Aromatic Fraction from Preparative Separation Analyzed Under Analytical Conditions.

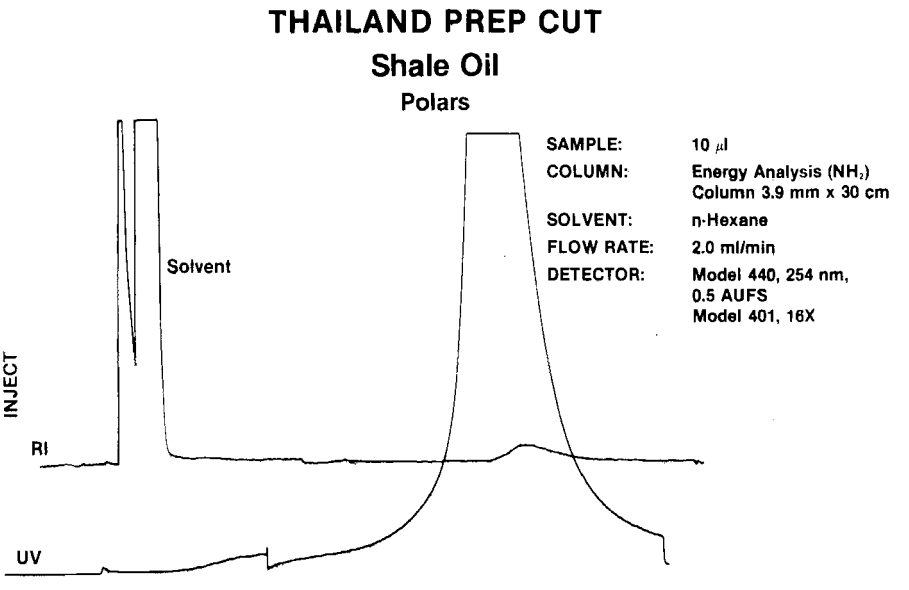


Figure 6: Thailand Shale Oil -- Polar Aromatic Fraction from Preparative Separation Analyzed Under Analytical Conditions.

Extended Separation Capabilities

The separation of saturates, neutral aromatics, and polar aromatics on the amine modified support can be carried one step further. By adding a 3.9mm by 30cm high surface area silica gel column in series with the amine column, the separation will be expanded. With these two different packings in series, the separation will now yield saturates, monoaromatics, diaromatics, three-ring aromatics, three plus ring aromatics, and the columns are backflushed to elute the polar aromatics. The backflush of the columns must be timed such that none of the polar aromatics reach the silica gel column. These heteratomic aromatics have shown very strong retention on silica. Therefore, the columns must be oriented so that the sample is injected onto the amine modified support.

The two shale oils were evaluated by this expanded separation scheme. The chromatograms, Figures 7 and 8, show the difference

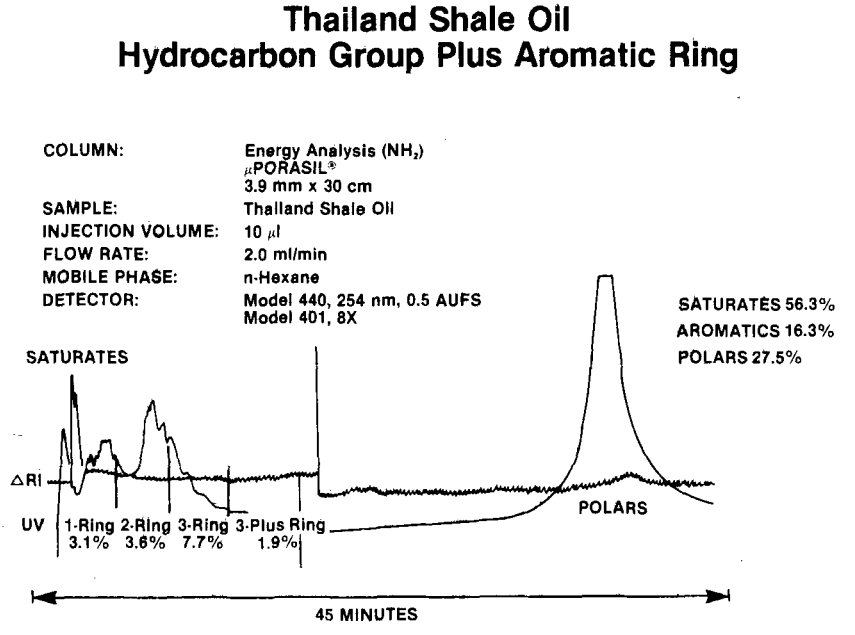


Figure 7: Thailand Shale Oil -- Hydrocarbon Group Separation with Separation of the Neutral Aromatics by Rings.

in the distribution of the neutral aromatics. The cut points of the various rings was determined by running a standard mixture of benzene, naphthalene, phenanthrene, chrysene, and perylene. The UV detector is Pen 1 and the refractometer is Pen 2 offset by 13.5mm. This gives the visual effect of the saturates eluting in the middle of the one-ring aromatics.

	UTAH Shale Oil	THAILAND Shale Oil
One Ring	7.3	3.1%
Two Ring	6.7	3.6%
Three Ring	29.0	7.7%
Three + Ring	14.7	1.9%

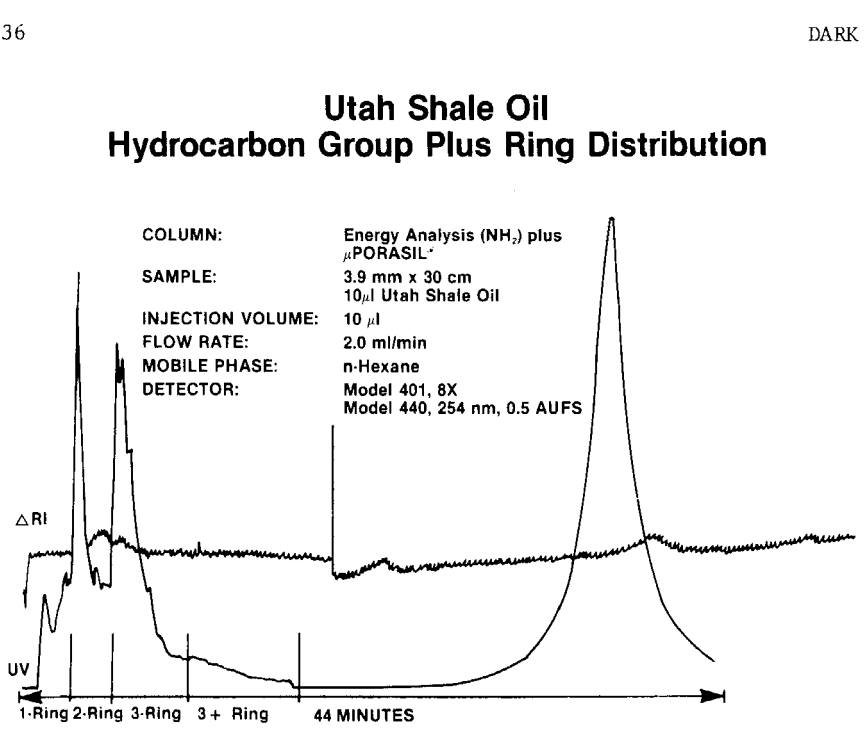


Figure 8: Utah Shale Oil -- Hydrocarbon Group Separation with Separation of the Neutral Aromatics by Rings.

Extended Preparative Capabilities

The extended analytical separation was scaled up to the multi-gram preparative separation.

Two preparative columns each 57mm by 30cm were used in series. The first column is the NH_2 modified packing while the second is a high surface area silica gel. The mobile phase is n-Hexane at 400 ml/min. as in the previous separation. The same sample work-up is used. The separation sequence should be saturates, mono-aromatics, diaromatics, three-ring aromatics, three plus ring aromatics, and then the polar aromatics. The saturates and neutral aromatics are eluted with n-Hexane while the polar aromatics will be eluted by stepping the solvent to dichloro-methane. However, the silica column must be removed from the flow stream before the polar aromatics are eluted from the NH_2

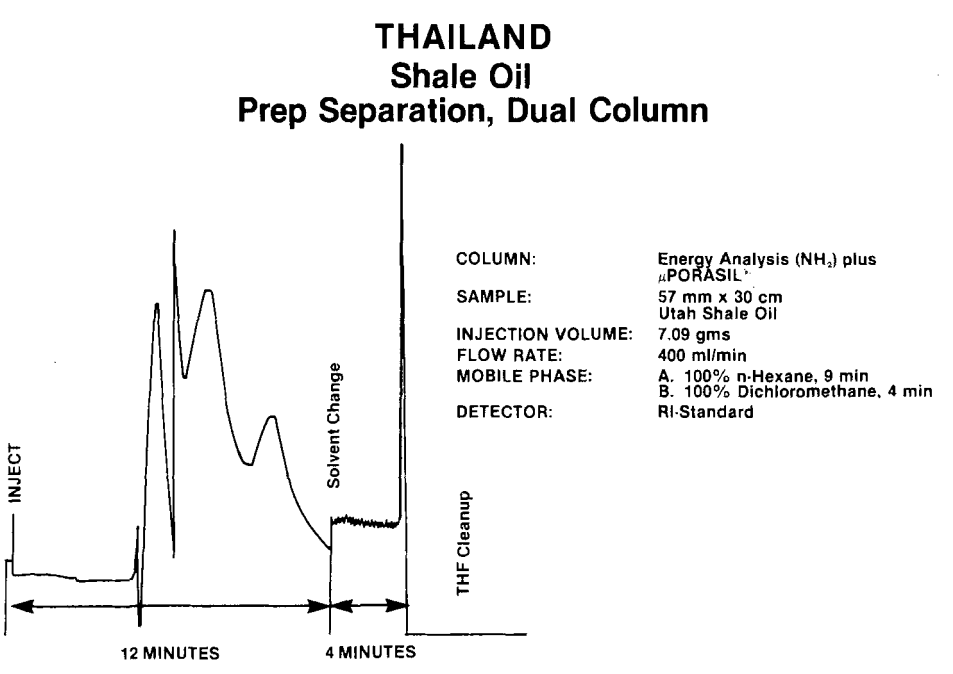


Figure 9: Thailand Shale Oil -- Preparative Separation by Hydrocarbon Group with Neutral Aromatics Separated by Rings.

packing. The polar aromatics have extremely large k's across silica with non-polar solvents. Using polar solvents to elute these polar aromatics from the silica column will lead to deactivation of the silica packing.

After the polar aromatics have been eluted from the NH_2 column, it is re-equilibrated with n-Hexane and then the two columns are placed in series. The total analysis time is 20 minutes for the separation and equilibration of the columns.

The preparative separation of the Thailand shale oil using this dual column approach is shown in Figure 9. The saturates are in the first peak, each of the other peaks were collected as neutral aromatics with increasing number of rings. The k' of cut points was predetermined by running a mixture of benzene,

napthalene, phenanthrene, chrysene, and perylene. After the neutral aromatics eluted from the columns, the silica column was removed and the solvent stepped to dichloromethane and the polar aromatics eluted.

The fractions were recovered by evaporating the solvents to dryness, with quantitation again being gravimetric. The fractions were then redissolved in n-Hexane and rechromatographed on the 3.9mm dual column analytical set-up described above (Figures 10-15). An examination of these chromatograms shows that the first fraction, saturates, contains little if any UV response and a k' that coincides with standards. The neutral aromatics fractions show peaks with increasing k' in later eluting fractions. The last eluting neutral aromatic fraction and the polar aromatic fraction show cross contamination, again, this is due to solubility at loads used in the preparative separation.

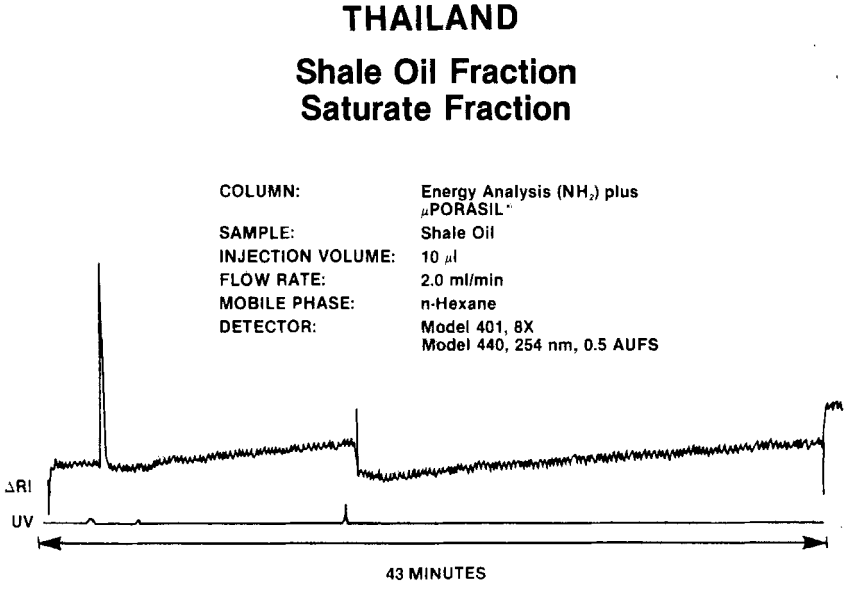


Figure 10: Thailand Shale Oil -- Saturate Fraction From Dual Column Preparative Separation Analyzed Under Analytical Conditions.

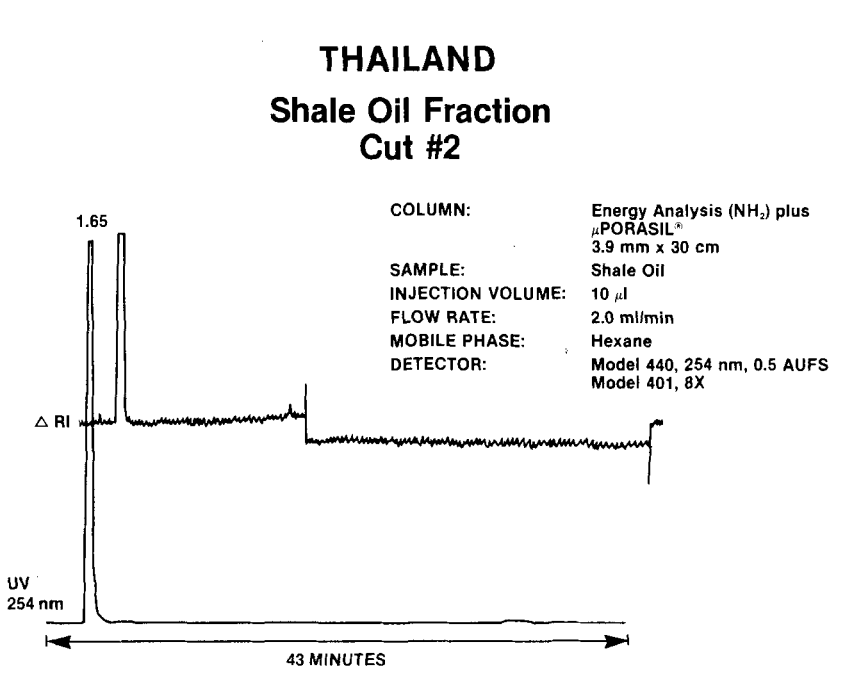


Figure 11: Thailand Shale Oil -- Cut #2 from Dual Column Preparative Separation Analyzed Under Analytical Conditions.

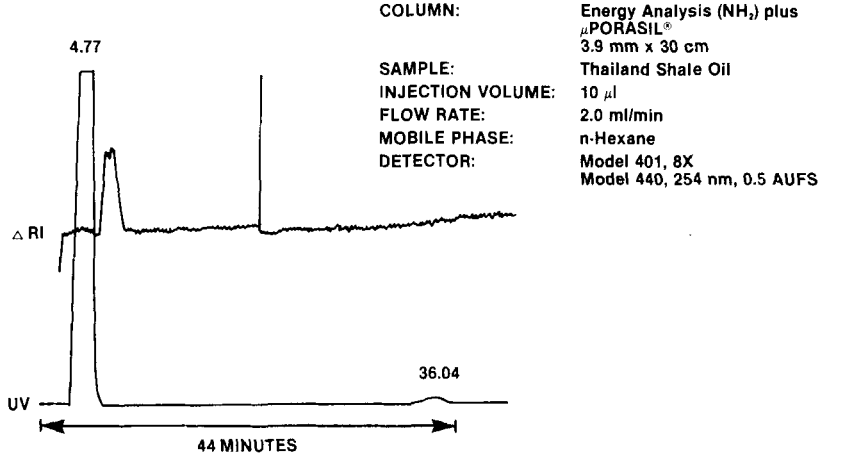


Figure 12: Thailand Shale Oil -- Cut #3 from Dual Column Preparative Separation Analyzed Under Analytical Conditions.

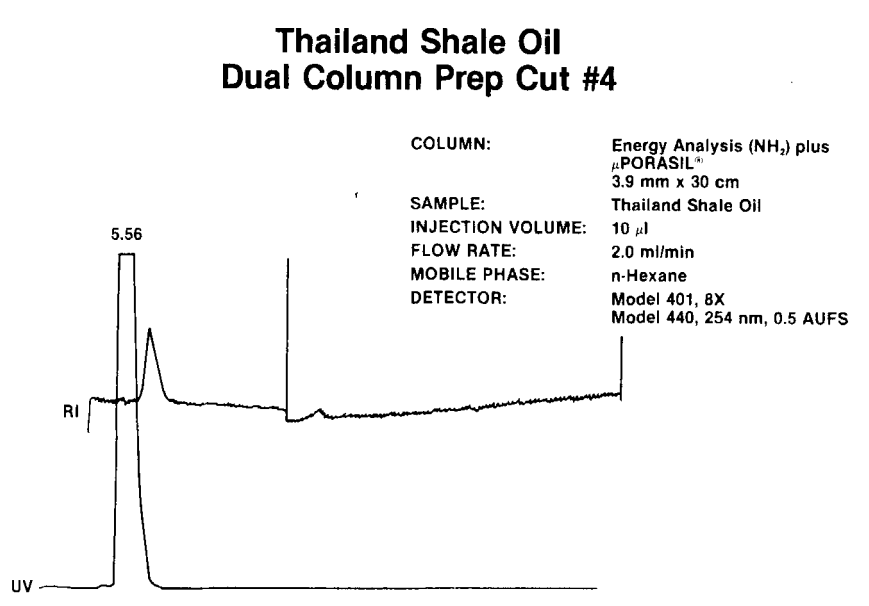


Figure 13: Thailand Shale Oil -- Cut #4 from Dual Column Preparative Separation Analyzed Under Analytical Conditions.

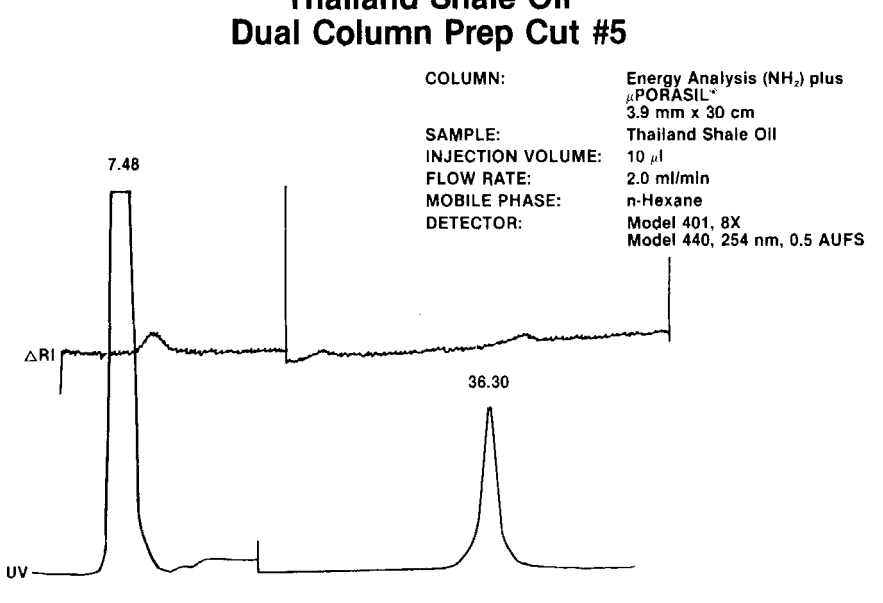


Figure 14: Thailand Shale Oil -- Cut #5 from Dual Column Preparative Separation Analyzed Under Analytical Conditions.

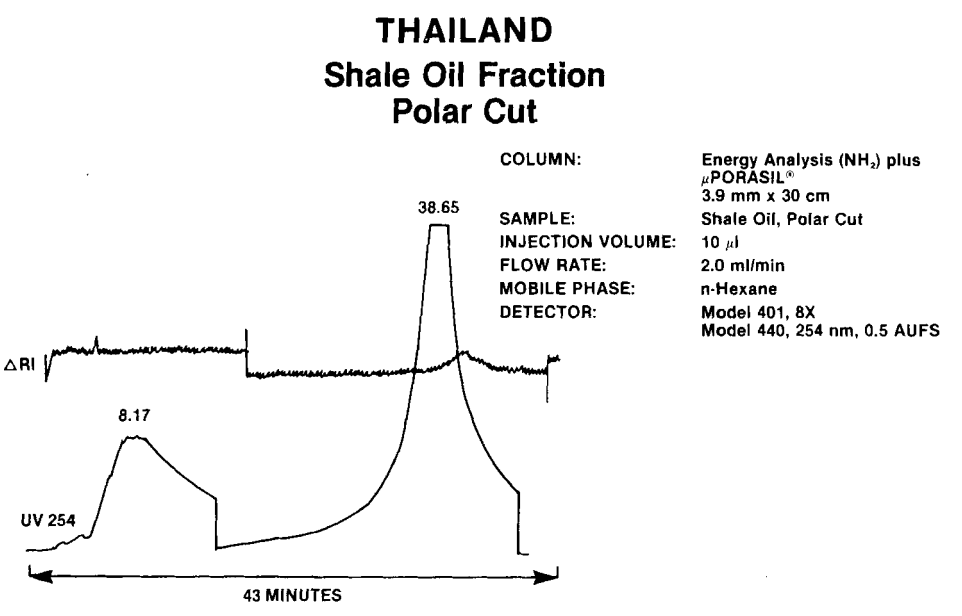


Figure 15: Thailand Shale Oil -- Polar Aromatic Cut from Dual Column Preparative Separation Analyzed Under Analytical Conditions.

A comparison of quantitation from the three separation schemes using the shale oil from Thailand is shown below. Two pooled injections across a single 57mm NH_2 column, three pooled injection across the dual 57mm columns and then the results from a single NH_2 column, 3.9mm, where detector responses were used are compared.

	ANALYTICAL	NH2	NH2-SILICA
	RUN	13.43 gm	20.62 gm
Saturates	18.97 wt.%	---	---
Aromatics	57.63	51.8 wt.%	(53.6) wt.%
1 Ring			43.7
2 Ring			5.6
3 Ring			3.0
3+ Ring			1.3
Polars	23.40	26.3	21.1
Recovery		78.0%	75.4%

Conclusions

High Performance Liquid Chromatography offers a new dimension in the separations of alternate fuels. Both preparative and fully automatable analytical systems can shorten the time required for separations. Tailored systems can provide Pilot Plant personnel with detailed and timely compositional data, shortening the decision time interval between sampling and results.

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