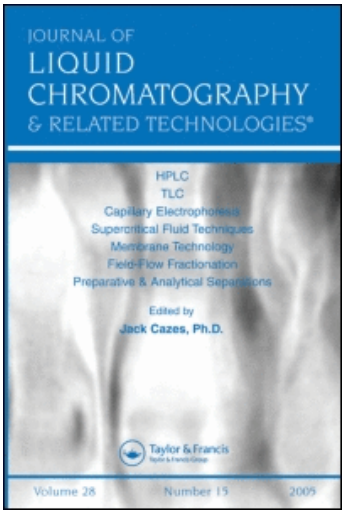

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Rapid Sara Seprations by High Performance Liqid Chromatography

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RAPID SARA SEPARATIONS BY HIGH PERFORMANCE LIQUID CHROMATOGRAPHY

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ABSTRACT

This paper presents both rapid analytical and preparative high performance liquid chromatographic (HPLC) techniques for separating liquid-fuel type materials into saturates, aromatics, resins, and asphaltenes (SARA). The preparative method, an adaptation of a technique developed by Jewell, et. al. (1, 4), significantly decreases analysis time. The analytical technique utilizes HPLC to achieve the same separations in less time.

INTRODUCTION

The separation of liquid fuels into saturates, aromatics, resins, and asphaltenes via solvent extraction and $FeCl_3$ treated clay/silica gel columns is a procedure used by the petroleum industry to monitor refining processes. It is applicable to materials boiling above 450°F. Even though several analyses via an open column procedure can be performed simultaneously, the elapsed time is several days. Utilization of a HPLC has shortened the elapsed time to 4 hours for the preparative technique and 1-1/2 hours (HPLC separation <20 minutes) for the analytical technique. The analytical technique, which utilizes response factors, permits the analysis of the entire sample and not just the portion boiling above 450°F.

EXPERIMENTAL

Apparatus

A liquid chromatograph fabricated at Gulf Science and Technology Co. was used for this study (Figures 1 & 2). It consists of an Altex Model 110 solvent pump (Altex Scientific, Inc., Berkeley, CA 94710), Water s Associates Model 401 differential refractometer (Water s Associates,

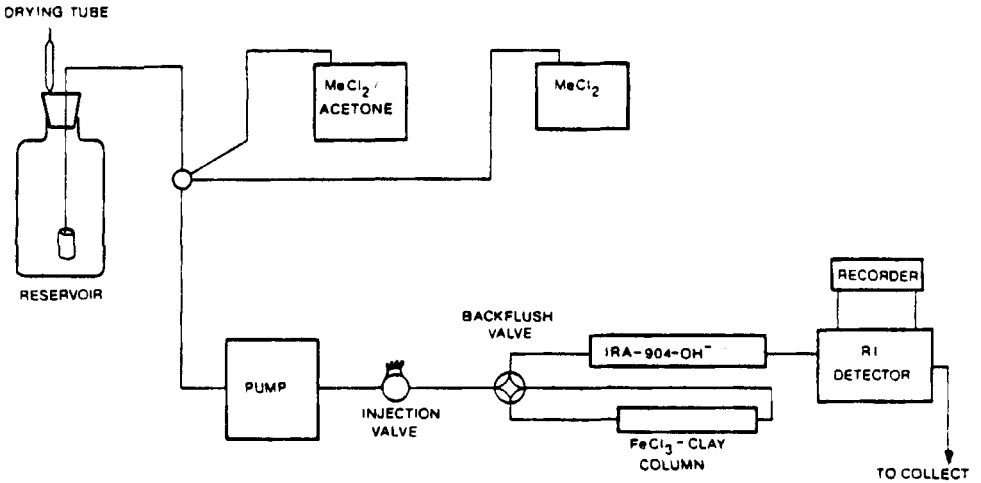


Figure 1. Preparative method set-up. For saturate and aromatic separation, a silica gel column is used in place of $FeCl_3$-Clay and IRA-904-OH^- columns.

Inc., Milford, MA 01757), Ominiscribe 4000 Recorder (Houston Instrument, Austin, TX 78753), Rheodyne injection valve (Rheodyne, Inc., Berkeley, CA 94710), equipped with 5.0 ml loop for the preparative method and a 100 µl loop for the analytical method and a four-part backflush valve (Valco Instrument Co., Inc., Houston, TX 77055). The three columns utilized for the preparative technique are: a 40.6 cm x 1.3 cm section of stainless steel tubing packed with 60-80 mesh $FeCl_3$-treated Attapulgus clay (Englehard Minerals and Chemicals Corp., Edison, NJ 08817) equipped with 5/8-inch snubbers in series with 0.7 cm x 25 cm section of stainless steel tubing packed with IRA-904-OH^- resin (Robin & Hass, Philadelphia, PA 19103) equipped with 3/8 inch snubbers, and a 40.6 cm x 1.3 cm section of stainless packed with 20-44 mesh Biosil A (Bio Rod Labs, Richmond, CA 94804) equipped with 5/8 inch snubbers.* The analytical technique utilizes a µ-Bondapak-NH_2 analytical column (Water s Associates Inc., Milford, MA 01757). Peaks are integrated by a Model 3354 B Computer (Hewlett-Packard Co., Avondale, PA 19311).

*The initial separation of the resins is done with the $FeCl_3$ clay column and IRA-904 column together. The separation of saturates and aromatics is then accomplished on the Biosil A column which is in a separate instrument.

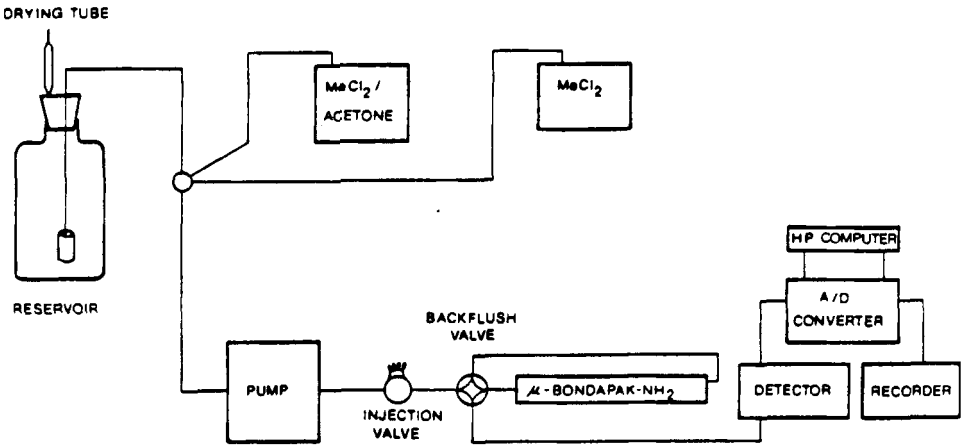


Figure 2. Analytical Instrument set-up.

Reagents

Hexane, methylene chloride, and 1/1: methylene chloride/acetone mixtures are used as mobile phases. High-purity hexane (Phillips Petroleum Co., Bartlesville, OK 74004) is satisfactory, but is dried over a 4 Å molecular sieves prior to use. HPLC grade methylene chloride and acetone (Fisher Scientific Co., Pittsburgh, PA 15219) are used as received.

The $FeCl_3$-treated Attapulgus clay is prepared as follows: cautiously add 10.0 g of anhydrous $FeCl_3$ to 10 ml of methanol, then to this solution add 50 ml of chloroform. (Both should be reagent grade.). After 1/2 hour, gravity filter through Whatman #42 filter paper into a 2 liter Erlenmeyer flask to remove the insolubles and wash with 10 ml of methanol and 100 ml of chloroform. Add 300 g of clay to the flask while swirling, then allow to set for 1/2 hour with occasional swirling. The chloroform level should be maintained approximately 1/4" over the top of the clay. The solvent is removed by vacuum filtration and the packing is dried in a hood. Next transfer the treated clay to a vacuum oven maintained at 50°C for 1/2 hour to remove final traces of solvent. The clay is then sieved to obtain only 60-80 mesh particles. This material should contain about 3% Fe, as determined by atomic absorption analysis. The IRA-904-OH resin is prepared as described elsewhere.(1)

PROCEDURE

Preparative

To a tared beaker, weigh 1.2 g of sample to the nearest 0.001 g. Add 4-5 ml of hexane and stir this mixture for approximately 5 minutes with a stirring rod to dissolve soluble material. Vacuum filter this solution through a tared 0.45 μ Millipore filter (type UH) to remove the insolubles (wash with hexane until the washings become colorless). The hexane solution is heated to 40°C and concentrated to exactly 10.00 ml under a stream of nitrogen for analysis by HPLC. The filter containing the hexane insolubles is dried at 40°C under a nitrogen blanket and weighed. If the original beaker contains undissolved materials, it is dried in the same manner as the filter and weighed. The filter containing the insolubles is transferred back to the original beaker and toluene (reagent grade) is added. The volume of toluene added is not critical but should be enough to cover the filter and to wash the sides of the beaker. This solution is filtered through another tared 0.45 μ Millipore filter and the insolubles are again washed until the washings become colorless. Dry the beaker, the original filter, and the filter with insolubles as described previously and weigh each. The asphaltene content of the sample is the difference between the weight of hexane insolubles and toluene insolubles.

The hexane solution is injected into a liquid chromatograph $FeCl_3$-treated clay/IRA-904-OH^- columns equipped with the hexane flow rate of 10 ml/min. The oils (containing saturates and aromatics) are backflushed (2) off the column after 65 seconds. Exactly 200 ml of eluent from the column is collected to ensure that all the late eluting aromatics are collected. Resins, retained by the $FeCl_3$-clay column, are eluted from the column using 200 ml of a 1/1: acetone/methylene chloride mixture. The column is then regenerated with methylene chloride and hexane sequentially. The IRA-904-OH^- resin removes any iron that is eluted with the resins. The oils are concentrated to 10.00 ml and injected onto a Biosil A column where the saturates are separated from the aromatics as described elsewhere.(3)

The solvent removal process is critical. Evaporating at too high a temperature may result in significant loss of sample. This can be prevented by: 1) initially concentrating the fraction in a tared vial to 0.5-1.0 ml using a heating block maintained at 40°C under a nitrogen purge, 2) weighing the vial containing the sample after each minute of

evaporation until the weight loss is less than 1 mg/minute. The sample weight is then recorded. This technique significantly decreases the amount of sample reported as volatiles.

Analytical

To a tared beaker, add 0.250 g of sample, weighed to the nearest 0.001 g. Sample preparation and asphaltene removal is the same as described in paragraphs 1 and 2 of the preparative technique. The hexane solution is injected into a HPLC equipped with a μ-Bondapak-NH_2 column (Figure 2) and separated into saturates, aromatics, and resins.* The peaks are integrated by a Hewlett-Packard 3354B computer using a "Zero" type method.** The hexane flow rate used is 3.0 ml/min and the refractometer is set at 16X. The elapsed time (due to removal of insolubles) using response factors obtained by injecting known concentrations of fractions from the preparative technique. Resins are backflushed off the column and determined by difference.

To date, column life has not been determined. The NH_2 column has been used for six months, at the rate of 20-30 samples per month, without difficulty. However, it is necessary to flush the column with 1:1 methylene chloride/acetone after every 20 samples, and then regenerate with methylene chloride and hexane in order to ensure repeatable retention times.

RESULTS & DISCUSSION

Model Compounds - In order to correctly identify the types of compounds eluting in each fraction, a model compound study was conducted. Model compounds were chosen on the basis of compounds normally found in coal liquids. Figure 4 divides a series of model compounds into those retained and those not retained by the $FeCl_3$-clay column. The compounds retained by the column are eluted with the resins; generally 97-99% of the resins are recoverable. Those compounds that are not retained elute with the oils and are later separated on silica gel. Figure

*A μ-Bondapak NH_2 column was chosen because of its ability to separate on the basis of polarity.

**A "Zero" type method integrates the peaks and normalizes the data to 100 area %. Data are printed out in counts and area %. The A/D sampling rate is every 0.5 sec.

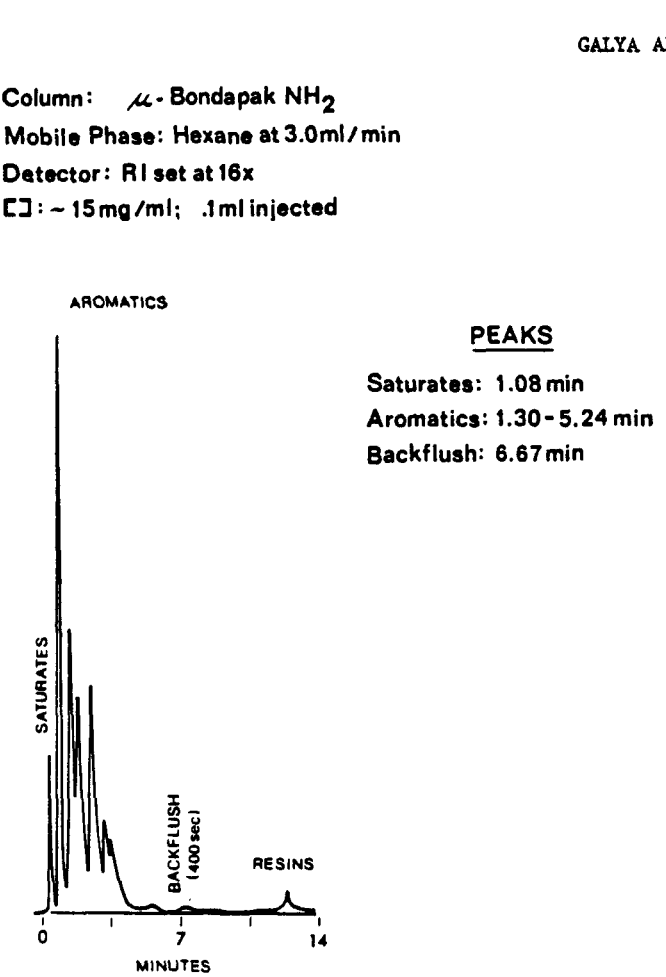


Figure 3. Chromatogram on NH_2 Column.

5 shows the fractions in which model compounds elute on the μ-Bondapak NH_2 and $FeCl_3$-clay columns. Most non-polar heteroatom species, such as thiophenes, furans and indoles elute in the aromatic fraction with both columns.

A sample of tar sands, different from that used for calibration, was fractioned by the preparative technique. These oil and resin fractions were injected into the analytical HPLC; the resin fraction was not contaminated by saturates and aromatics, but the oil fraction contained 0.5% resins.

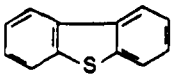
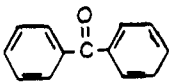
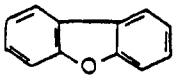
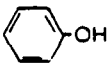
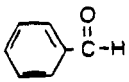
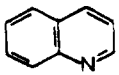
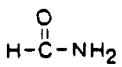
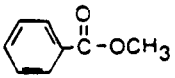
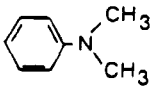
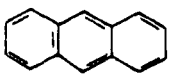
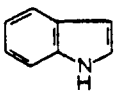
	Retention on $FeCl_3$-clay column
	dibenzothiophene — not retained
	benzophenone — retained
	dibenzofuran — not retained
	thiophene — not retained
	phenol — retained
	benzaldehyde — retained
	quinoline — retained
$R-NH_2$	amine mixture — retained
	formamide — retained
	methyl benzoate — retained
	N,N,dimethylaniline — retained
$C_4H_9-O-C_4H_9$	n-butyl ether — not retained
	anthracene — not retained
$CH_3-S-S-CH_3$	dimethyldisulfide — not retained
	benzoindole — retained

Figure 4. Model Compounds.

Data Comparison

Table 1 shows a comparison of the data obtained using the open column and preparative techniques. The deviation in the data is within

Compound	Prep SARA ($FeCl_3$-clay)	Rapid SARA (NH_2)
Dibenzothiophene	Aromatics	Aromatics
Dibenzofuran	Aromatics	Aromatics
Decalin	Saturates	Saturates
Phenol	Resins	Resins
Benzaldehyde	Resins	Resins
Isoquinoline	Resins	Resins
Quinoline		
Anthracene	Aromatics	Aromatics
Indole	Resins	Resins

Figure 5. Model Compounds.

experimental error for the open column technique. The samples shown here are actual coal liquid samples obtained from a pilot plant. Table 3 shows the data from the preparative and analytical techniques compare well.

Calibration

Calibration was accomplished by injecting known concentrations of fractions from the preparative technique into the analytical instrument, and measuring the area with the Hewlett-Packard 3354B computer. The response factors are expressed as area/concentration where concentration is expressed as mg/ml.(3) The error in determining the factors was found to be less than 1% for both the saturates and aromatics and was reproducible over the six months we have been using this technique. It is interesting to note the difference in response factors for different samples. As can be seen in Table 5, it is necessary to calibrate for each type of sample. Liquefaction conditions influence the response factors, but there is little change for different coals processed under same conditions.

Response factors are verified with pure compounds (hexadecane and naphthalene) which do not change from day-to-day.(2)

As seen in Figure 3, the aromatic fraction is separated into several components. This separation occurs mainly by ring number; this was established by injecting aromatics, such as benzene, naphthalene, anthracene, chrysene, and coronene and monitoring the retention times.

TABLE 1

Comparison of Open Column and Preparative SARA Data For Coal Liquids

	Open Column	HPLC
Sample #	X-975	X-975
Saturates: Wt. %	1.1	2.1
Aromatics: Wt. %	67.7	67.1
Resins: Wt. %	7.4	6.2
Asphaltenes: Wt. %	14.4	14.1
Insolubles: Wt. %	0.0	0.0
Volatiles: Wt. %	9.4	10.5
Sample #	X-865	X-865
Saturates: Wt. %	1.8	2.4
Aromatics: Wt. %	73.9	73.1
Resins: Wt. %	9.5	8.4
Asphaltenes: Wt. %	7.7	8.6
Insolubles: Wt. %	2.7	3.2
Volatiles: Wt. %	4.3	4.3
Sample #	X-977	X-977
Saturates: Wt. %	1.0	2.3
Aromatics: Wt. %	78.8	77.2
Resins: Wt. %	7.4	6.7
Asphaltenes: Wt. %	8.1	9.4
Insolubles: Wt. %	0.0	0.0
Volatiles: Wt. %	4.7	4.4
Sample #	X-807	X-807
Saturates: Wt. %	2.4	1.9
Aromatics: Wt. %	71.4	72.5
Resins: Wt. %	6.1	6.5
Asphaltenes: Wt. %	7.6	6.7
Insolubles: Wt. %	8.2	8.1
Volatiles: Wt. %	4.3	4.3

The backflush time of 400 seconds is based on the elution time of cororene plus 50 seconds. Because retention times and composition of aromatics differ from one sample type to another (Figures 6 and 7), automatic bunching of aromatic peaks is not possible. Consequently, each aromatic peak is integrated separately and the areas are manually added together.

Analytical Method

There were two possible approaches to the analytical method: 1) build a scaled-down version of the preparative method, 2) choose an HPLC column which would provide similar separation.

TABLE 2

Reproducability of Preparative SARA Data

For Coal Liquids

	HPLC	HPLC	HPLC
Sample #	X-975-W	X-975-W	X-975-W
Saturates: Wt. %	2.9	3.1	2.2
Aromatics: Wt. %	77.5	78.2	76.6
Resins: Wt. %	3.0	3.8	2.9
Asphaltenes: Wt. %	14.8	14.0	13.9
Insolubles: Wt. %	0.0	0.0	0.0
Volatiles: Wt. %	1.8	0.9	4.4
Sample #	X-977	X-977	
Saturates: Wt. %	2.3	1.8	
Aromatics: Wt. %	77.2	77.7	
Resins: Wt. %	6.7	6.5	
Asphaltenes: Wt. %	9.4	9.9	
Insolubles: Wt. %	0.0	0.0	
Volatiles: Wt. %	4.4	4.1	

TABLE 3

Comparison of Preparative and Analytical SARA

	Preparative	Analytical
Sample #	xx	xx
% Saturates	1.6	1.7
% Aromatics	73.6	72.5
% Resins	8.7	9.4
% Asphaltenes	4.3	4.5
% Insolubles	12.1	12.0
Sample #	yy	yy
% Saturates	2.1	2.8
% Aromatics	77.1	77.9
% Resins	7.5	6.0
% Asphaltenes	5.2	5.0
% Insolubles	8.1	8.3

The scaled-down preparative technique gave broad peaks due to bandspreading. The second choice was a μ-Bondapak NH_2 column which gave a clean separation of saturates and aromatics, and sharp peaks.

TABLE 4

Reproducibility of NH_2 Column

Sample 1 - at 1.0 ml/min

Saturates	4.4	4.4	4.5	±0.98%
Aromatics	69.8	68.5	71.1	±1.24%
Resins	9.4	10.7	8.0	±9.8%

Sample 2 - at 3.0 ml/min

Saturates	7.3	7.5	7.5	7.6	7.5	7.5	±0.85
Aromatics	55.7	56.2	55.4	55.2	56.1	55.8	±0.57
Resins	18.3	17.6	18.4	18.5	17.7	18.0	±1.8%

TABLE 5

Factors Obtained for Samples & Model Compounds

	Saturates	Aromatics
Full Range Coal Liquid I	6600	13100
Tar Sands	8000	9000
Coal Liquid II 550° - 850°F	6600	10530
Coal Liquid II 850°F+	6600	10710
Hexadecane	4450	-
Naphthalene	-	15300

Reproducibility

Both the preparative and analytical techniques gave good reproducibility (Tables 2 and 4). Table 2, third analysis of coal liquid

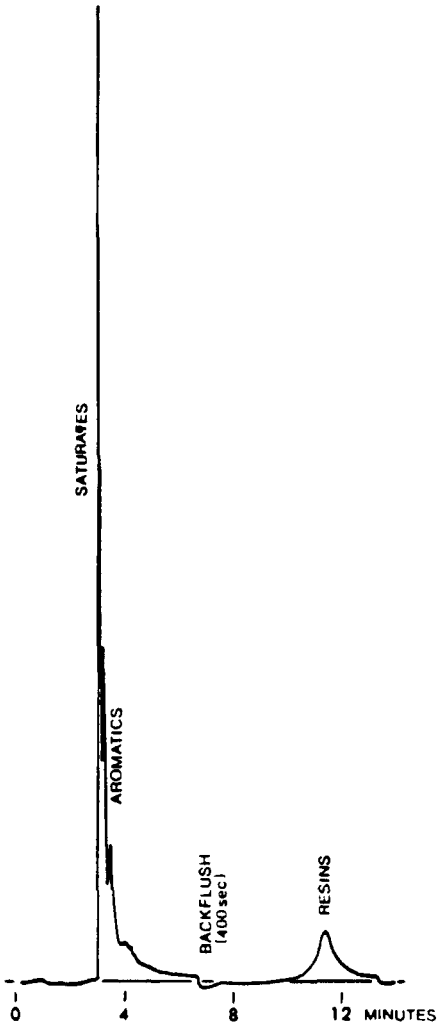


Figure 6. Chromatogram of Texas Crude Oil.

sample X-975-W, shows the largest amount of volatiles because the procedure for volatiles determination was not carefully followed. As can be seen in Table 4, the analytical data are more reproducible at a flow of 3.0 ml/min than at 1.0 ml/min, due to sharper, more easily integrated peaks.

It is necessary to run a hexane blank to determine if there is any contribution to the saturate area.

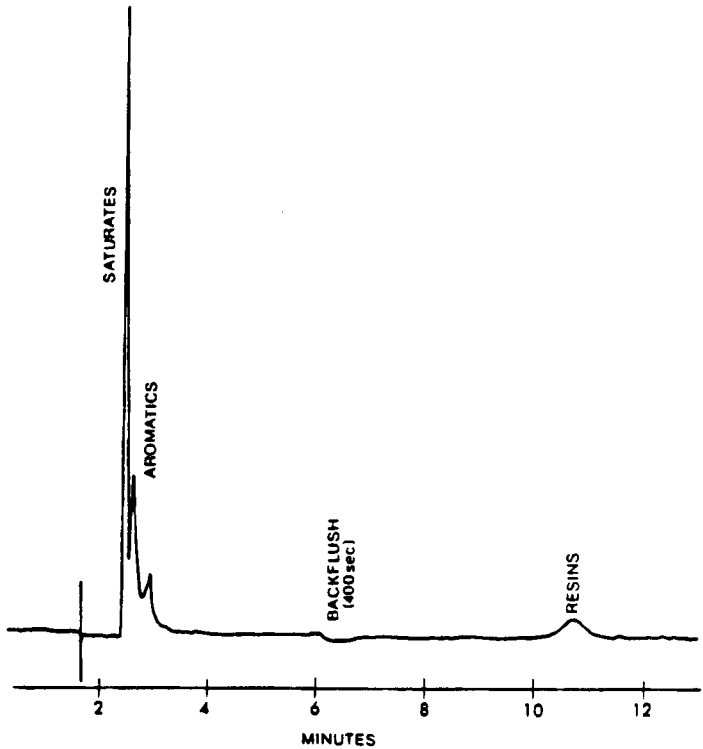


Figure 7. Chromatogram of Shale Oil (mid-distillates).

FUTURE WORK

Future work will include the development of calibration data for petroleum distillates,(3) and shale oil.

The analytical method will be modified to determine resins directly by utilizing an UV detector and a more polar solvent such as methylene chloride/tetrahydrofuran: 1/1 to ensure that all resins are eluted.

ACKNOWLEDGMENT

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