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EXISTING TECHNOLOGY TRANSFER REPORT ANALYTICAL CAPABILITIES

Appendix B

By
K. C. Tewari

June 1984

Work Performed Under Contract No. AC05-78OR03054

International Coal Refining Company
Allentown, Pennsylvania

Technical Information Center
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EXISTING TECHNOLOGY TRANSFER REPORT

ANALYTICAL CAPABILITIES

APPENDIX B

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AIR PRODUCTS AND CHEMICALS, INC.
P.O. Box 538
Allentown, Pennsylvania 18105

for the

UNITED STATES DEPARTMENT OF ENERGY
Office of Solvent-Refined Coal Products
under Contract DE-AC05-78-OR-03054

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APPENDIX B

Attachment 1

Solvent Separation Procedure A,

and Associated Development Efforts

Appendix II

Total Product

Solvent Separation Procedure

A

A) Oils - Pentane Solubles/Benzene Soluble/Pyridine Soluble

B) Asphaltenes - Pentane Insoluble/Benzene Soluble/Pyridine Soluble

C) Preasphaltenes - Pentane Insoluble/Benzene Insoluble/Pyridine Soluble

D) Residue - Pentane Insoluble/Benzene Insoluble/Pyridine Insoluble

This procedure is carried out at room temperature under nitrogen using high quality solvents. The sample may be liquid, solid or a mixture thereof, with less than 1% material boiling below (300°F). Under laboratory conditions one (1) individual with technical training can perform the analysis in one (1) day. With experience one (1) technician can handle two (2) units and complete the operation in less than eight (8) hours. A reproducibility study of the solvent separation procedure was made on a total product liquid (sample XCL-23-132PL) The results of this study are given in Table 1.

Table 1

Reproducibility of the Solvent Separation Procedure

	Mean	Standard* Deviation
oils	63.3%	1.06%
asphaltenes	8.7%	0.94%
preasphaltenes	9.7%	1.23%
residue	18.2%	0.31%

*The result of five trials.

Equipment Required:

1. Branson Model 350 Sonicator with 1/2" horn
2. Millipore 142 mm pressure filter with 1500 mL capacity #XX42-142-35 and YY-30-142-35 with 142 mm filter, 5 micron, LSWP 142-50
3. Glassware for solvent transfer lines
4. Round bottom distilling flasks - 500 mL, 250 mL, 2 each
5. Rotovapor Re 120, VWR #27582-406
6. Vacuum pump and trap
7. Nitrogen-Gas (0-20 psi adjustable), pressure filter feed

   Nitrogen-Gas (0-20 psi adjustable), rotovapor feed

   Nitrogen-liquid (1-2L), freeze sample (Dewar)
8. a) n-Pentane -

   b) Benzene -

   c) Pyridine -

   d) Methanol -

   Grade of solvent depends upon ultimate use of sample subfractions Pesticide, Distilled in Glass, or HPCL grade are acceptable.
9. Fume hood 150-200 cfm air rate exchange
10. Cooling water or heat exchanger for rotovapor condenser
11. Balance to read weights $\pm$ 0.005 grams or better with maximum load 200 grams.

Safety Features:

Solvents must be used only under the fume hood and transferred from bottle to flask by hand pump. Workers must wear protective gloves and overalls for laboratory work. Hands can be cleaned with Go-Jo waterless hand-cleaner, mild scrubbing followed by a warm water wash. All normal safety precautions must be observed during the full operation.

Sample Handling:

The sample chosen for this procedure must be representative of the process unit output. Great care must be given to the isolation of approximately 50 grams of gross product.

The sample once chosen must be kept free of air (oxygen), heat and light. Samples not ready for separation should be stored at 4°C under a blanket of nitrogen. Hot samples may be taken in 316 stainless steel bottles (DuPont #03226, 235 mL 61 x 140 mm with screw cap). Samples may be warmed to 65°C in the cans and sonicated for 15 minutes with 1/2 inch tip to induce good mixing just prior to taking a 5 gram actual work-up sample.

Procedure

The laboratory equipment is prepared in the following order:

a) Adjust and clean ultrasonic unit equipped with 1/2" horn with methylene chloride.

b) Put in place Millipore filter after taking weight of dry filter element. Ensure that all O-rings fit well with no leaks (test with n-pentane under 10 psi). Use Teflon tape (3/4") to wrap screw fittings and seals.

c) Prepare rotovapor-bath temperature at 55-60°C for n-pentane; nitrogen flow rate should just cause 1/4-1/2" dimple in liquid of 250 ml flask.

d) Cooling liquid for rotovapor condenser should be less than 10°C.

Step 1 Tare a 150 mL heavy wall Pyrex beaker, add 8 grams read to ± 0.005 grams of the desired coal-derived sample. Add approximately 100 mL of liquid nitrogen slowly to the beaker to maintain a quiet solution. Total volume of liquid nitrogen used may exceed 500 ml.

Step 2 With a Pyrex glass stirring rod (3/8"D), grind the frozen sample to a fine powder. This step requires 5-8 minutes. Fill with more liquid nitrogen to maintain at least 30 ml volume while grinding.

Step 3 Allow the liquid nitrogen to evaporate to just above the solid mixture. Add with moderate (micro-probe 1/3", power level 3) sonication 100 mL of n-pentane. Some stirring may be required - keep tools out of beaker while sonic power is on. Sonciate for 5 minutes at power level 5.

Step 4 Allow mixture to settle (1-2 minutes) decant supernatant into filter unit, refill beaker with n-pentane and sonicate again for 3-5 minutes. Allow decant liquid to filter into a 250 mL flask - do not allow filter to dry from this time onwards.

Step 5 Repeat Step 4 twice for a total of approximately 300 mL n-pentane. If catch flask fills transfer to rotovapor and begin to remove n-pentane under nitrogen at approximately 60°C. Transfer the solids with small portions (25-50 mL) of pentane.

Do not discard beaker, hold for additional transfer of solvents to filter. This assures removal of maximum amount of material and reduces loss.

Step 6 Filter the solids, adding nitrogen pressure (5-10 psi) if needed. Add new pentane via original beaker as needed for a total of approximately 2 L. This amount can be recollected from rotovapor unit during the continuous solvent removal steps.

Step 7 Continue solvent filtering (up to 2 L) until the filtrate is a very light yellow/green. At the end of the pentane extraction, with approximately 25 mL pentane in the filter, add 100 mL benzene and continue as in Step 6 for 2.5 L. The new filtrate is collected in a new 500 mL flask (tare). Continue to transfer filtrate to rotovapor - waterbath temperature 75°C. Nitrogen flow rate 1/2" dimple.

Step 8 The pentane solubles from steps 6 and 7 should be held on rotovapor for 2 minutes after the last drop of pentane has condensed in the catch flask. Remove, clean and dry outside of the flask containing the oils (reddish) and weigh. From difference on tare:

Yield of oils:----------grams

Step 9 The benzene extraction is carried out in a similar fashion as in Steps 6-8. The benzene solubles are removed from rotovapor when 10-20 mL of solution remain. The flask is swirled in liquid nitrogen to evenly coat 2/3 inner flask and freeze the solution in place. Quickly transfer flask to vacuum line (1 mm Hg) with trap and allow flask to stand unheated to freeze dry the benzene (sublime) in about 1 hour.

Yield of asphaltenes----------grams

Step 10 After the last benzene extraction begin to add pyridine and continue extraction as in steps 6-8. Remove the solvent at 90°C under 1/4-1/2" nitrogen dimple. Two liters of pyridine are required. The last wash should be pure methanol (100 mL), followed by nitrogen gas at 5 psi for 10 minutes. As the pyridine is just nearly removed (approx. 5-10 mL) stop and add 10-15 mL benzene. Swirl flask to mix contents and freeze-dry as in Step #9 for one hour. If pyridine odor remains, add 50 mL methanol and sonicate with microptip for 3 min., decant into tared Millipore filter and wash with n-pentane, allow to dry 15 minute under dry nitrogen.

Yield of preasphaltenes----------grams

Step 11 The residue will dry in-place after washing with 50 mL methanol and 50 mL methylene chloride. Stop nitrogen, gently remove filter and weigh.

Yield of residue----------grams

Step 12		
	Oils	A
	Asphaltenes	B
	Preasphaltenes	C
	Residue	D

A + B + C + D = Total recovered

Original mass of sample = MS.

MS - total recovered = net loss or gain.

If gain of weigh is observed solvent may be left in oils or asphaltenes.

If loss of weigh is observed oils have volatile matter.

Add net loss to mass of oils (A + net loss) and calculate over material recovery.

		Recovered	Corrected	%
Report:	Oils	A	A + net loss	_____
	Asphaltenes	B	B	_____
	Preasphaltenes	C	C	_____
	Residue	D	D	_____
		Total Recovered	MS	100%

It is now possible to compare samples derived during the coal conversion process with a high degree (± 1%) of reliability, and in a short amount of time. Once the classical separation has been made, the subfractions can now undergo a first level chemical characterization.

PROCESS SYSTEMS GROUP

DEVELOPMENT PROJECT REPORT

OCTOBER/NOVEMBER/DECEMBER 1979

TITLE: Energy Systems Department

PROGRAM AREA: X

PROGRAM MANAGER: J. C. Tao

87-1-X716 - PECO Demonstration Plant - Development

The GRH model has been tested with data acquired from a recent BGC gas-oil run. The model was found to be accurate in predicting light hydrocarbon yields but less effective in estimating yields of aromatics. Improvements to the model will be made when PECO operating data is available.

Screening studies on the use of GRH technology for methanol production have indicated that, in the present economic climate, GRH is not competitive with alternative processes.

87-1-X024 - Solid/Liquid Separation

A program to develop proprietary technology for the separation of ash and soluble coal products has been initiated. It is planned to install a Boll-Kirsch Candle filter at the Emmaus facility for investigative purposes during the next reporting period.

87-1-X023-02 - Coal Liquids Analysis

A coordinated approach has been established to analyze coal-derived materials generated from process studies at Trexlertown, and to prepare for cooperative SRC process modelling programs with the Joint Venture Group. A systems approach to control and minimize sample handling, increase data collection efficiency and reduce report turnaround time is the initial goal of the program. Efforts during this first quarter were focused on establishing operating needs, purchase of necessary instrumentation and personnel training.

87-1-X705 - Applications of SRC as Anode Coke

Progress during this reporting period was restricted as a result of manpower shortages. A sample of low ash solid SRC from the Lummus deashing unit at Fort Lewis was shipped to Alcoa for coking evaluation. Both APCI and Alcoa laboratories are heavily engaged in setting up the new asphaltene/preasphaltene feedstock evaluation tests. Efforts are underway to recruit a carbon chemist to work in this area.

87-1-X023-01 - Two Stage Liquefaction

A new program has been initiated with the objective of evaluating the merits of two-stage liquefaction as compared to other liquid producing technologies. Products from the LC-Fining program will be evaluated as solvents for the front end of the two-stage process. Efforts are being made to recruit personnel to man this program.

PROCESS SYSTEMS GROUP

DEVELOPMENT PROJECT REPORT

OCTOBER/NOVEMBER/DECEMBER 1979

TITLE: Coal Liquids Analysis

PROJECT NO.: 87-1-X023-02

PROJECT LEADER: F. K. Schweighardt

ABSTRACT:

An organized and centralized approach has been established to analyze coal-derived materials from process studies at Trexlertown, and to prepare for cooperative programs with the Joint Venture Group to model the Demonstration SRC-I Plant. A systems approach to control and minimize sample handling, increase data collection efficiency and reduce report turn-around time are the initial goals of the program. Efforts during this first quarter were used to establish operating needs, purchase of necessary instrumentation and training of personnel.

I. INTRODUCTION

Development of a new coal-derived liquids analysis program was initiated during this reporting period. The previous method, patterned after the method used by Pamco, suffered from poor liquid yield measurements due to an inaccurate 850°F cut point. Although other elements of the separation method were accurate, it was long and tedious to carry out. This new method depends heavily on inter-departmental cooperation [CRDD-CRSD] for servicing our present level operation in the pilot plant and experimental laboratories.

II. OBJECTIVE

The objective of this project is to set up procedures to effectively and efficiently analyze and characterize coal-derived materials from process studies at Trexlertown, and to support the Joint Venture Group SRC-I Demonstration plant program. A further objective is to coordinate the interaction of the various CPDU programs, both in-house and at Wilsonville with CRSD.

III. WORK AND RESULTS

i. Visited Pittsburgh Energy Technology Center/DOE, 30 November, to meet personnel and tour analytical facilities. Those attending were F. K. Schweignardt, W. Zubyk, T. Slager, R. Cusick, M. Oaks and J. Weber.

Discussions were centered upon correlation of simulated distillation and true boiling curves for coal-derived materials. Specific analytical data and procedures were reviewed for the determination of hydroxyl (OH) and amine (NH) groups by near infrared measurements.

ii. General visits and technical discussions were held with Catalytic, Wilsonville, 11 December; Auburn University, 9 November; and Alcoa, 9 September. These trips were used to detail analytical needs, review procedures used to characterize coal-derived materials and to establish standard laboratory practices.

iii. As a result of reviewing the needs and future programs, the analytical work-up procedure at Trexlertown was changed to reflect a more efficient and direct measure of the coal conversion processes under study. Figure 1 outlines the present approach to obtaining oils, asphaltenes, preasphaltenes and residue.

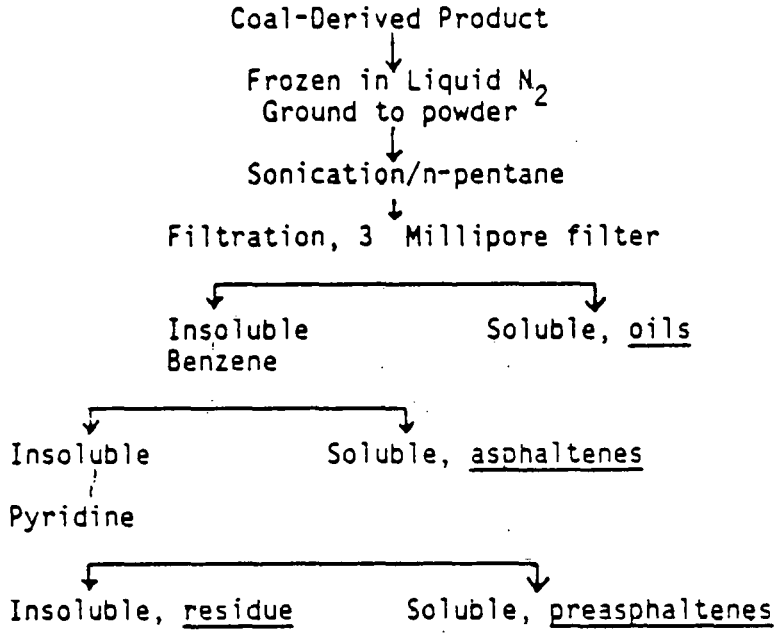


Figure 1

iv. As analytical subfractions are obtained, each must be characterized to complete material balances and reflect conversion or product improvement. Table 1 summarizes the analytical scheme proposed for each subfraction.

v. When specific analytical expertise was not available in-house university centers of excellence were contacted to assist with the analyses. Programs for analytical services have been established at:
   a) Seton Hall University - Thermogravimetric Analysis
   b) Duquesne University - Nuclear Magnetic Resonance
   c) University of Oklahoma - Mossbauer Spectra
   d) University of Nebraska - High Resolution Mass Spectra.

vi. A new coal product work-up laboratory was put into service as of November 1 to serve the process engineers of Trexlertown. With the incorporation of the new procedure, Figure 1, sample throughput increased at least three (3) fold, with an average material recovery of 98% by weight.

CONCLUSION:

i. A newly organized and chartered coal product work-up laboratory has been put into service at the Trexlertown site.

ii. A unified approach has been established to better characterize conversion products from APCI's CRST unit, and to work with the Joint Venture Group to obtain useful modeling data for the SRC Demonstration Plant.

iii. This first quarter was used effectively to develop and demonstrate cooperation between in-house analytical services, Corporation-wide, with Government laboratories, and APCI contractors to affect a common approach to coal product characterization.

TABLE I

Solvent Refined Coal Analytical Characterization Profile

SAMPLE	Elemental Analysis	Ash	Molecular	Magnetic Resonance		NIR		GC	GC/MS	HPLC		HRMS	Distillation		Metals-Minerals			Separ.
	C H O N S	Dry Wt.%	Weight, N	^{1}H	^{13}C	OH	NH			GPC	N/R		Sim	TBP	X-Ray	AA	Mossbau	Chem.
1. Whole Coal	X X X X X	X													X	X	X	
2. Recycle Solvent	X X X X X		X	X	X	X	X	X	X	X	X	X	X	X				
3. Total Product		X												X				X
4. Oils	X X X X X		X	X	X	X	X	X	X	X	X	X	X	X				X
5. Asphaltenes	X X X X X		X	X		X				X								
6. Preasphaltenes	X X X X X		X	X		X				X					X			
7. Residue		X X													X	X	X	
8. Organic Condensate	X X X X X							X										

PROCESS SYSTEMS GROUP

DEVELOPMENT PROJECT REPORT

JANUARY/FEBRUARY/MARCH 1980

TITLE: Energy Systems Department

PROGRAM AREA: X

PROGRAM MANAGER: J. C.Tao

87-1-X716 - PECO Demonstration Plant - Development

Activity during this period was restricted to essential work required in support of the facility design. Progress was made on development of the Cycsyn process simulation program and integration of Cycsyn with the mini-computer system. Work continued on compilation of the Technical Manual.

87-1-X024 - Solid/Liquid Separation

The objective of this program is to develop proprietary technology for separation of ash and insoluble organic matter from soluble coal products. The C.E. for installation of a Boll-Kirsch Candle filter at the Emmaus facility has been approved and delivery of this equipment is anticipated in the near future.

87-1-X023-02 - Coal Liquids Analysis

1) Analytical Procedure reproducibility

   The reproducibility of results obtained using the APCI Solvent Separation Procedure for analysis of coal-derived liquids has been investigated. It was observed that the reproducibility of the technique, as determined by the standard deviation in a series of five analyses, was approximately 1% when applied to analysis of a product liquid substrate.

2) Characterization of recycle solvents

   A change in the molecular composition of the phenolic fraction of a Wilsonville recycle solvent was observed over a period of one to seven weeks with the sample stored at room temperature and exposed to indirect sunlight The corresponding change in the infrared spectrum of the sample was consistent with oxidative degradation of phenolic hydroxyl groups. Clearly, careful storage of coal liquids is necessary for preservation of molecular composition.

   The use of gas chromatographic techniques for analysis of recycle solvents was also investigated in this reporting period.

87-1-X705 - Applications of SRC as Anode Coke

As a result of uncertainties in respect of our joint program with Alcoa, work on the program during this reporting period was limited to developing skills of new personnel in the laboratory and pilot plant area. A carbon chemist has been recruited to pursue this program.

PROCESS SYSTEMS GROUP
DEVELOPMENT PROJECT REPORT
JANUARY/FEBRUARY/MARCH 1980

TITLE: Coal Liquids Analysis
PROJECT NO.: 87-1-X023-02
PROJECT LEADER: F. K. Schweighardt
PRINCIPLE INVESTIGATOR: I. S. Kingsley

ABSTRACT:

A. In order to demonstrate the precision (reproducibility) of the APCI Solvent Separation Procedure it was necessary to repeat the procedure five times with a CPDU coal derived product liquid.

B. ° It was observed that the molecular composition of the phenolic fraction derived from a Wilsonville recycle solvent, V131B/190AMB changed over a period of one to seven weeks. The sample was stored at room temperature with indirect sunlight exposure during the test period.

° Multiple column chromatographic separations of a hydrogen donor solvent were performed and the reproducibility of weight fractions was determined.

° Column adsorption material in the chromatographic procedure was varied to find an optimal combination of silica and alumina for column separation of a hydrogen donor solvent into specific functional groups, saturate, aromatic, phenolic and N-bases.

° A hydrogen donor solvent (HDS) was separated into its functional group fractions and then characterized by gas chromatography (GC) and GC-simulated distillation. Several key components present in the HDS were identified.

I. INTRODUCTION

During this reporting period considerable attention has been given to two basic questions faced in developing a coal-derived product data base.

A. Development of a reproducible and sound APCI coal liquids solvent separation procedure.

B. Characterization of recycle solvents.

In the past an outline of the new method used in the CRDD coal work-up lab was presented. We now present our study of the reproducibility of this method.

Most of the activities during this period were devoted to developing solvent characterization methods. Four different aspects of this subject were investigated.

1. Storage stability of recycle solvent
2. Reproducibility of column chromotography
3. Selection of optimum adsorbants for column chromatography
4. Application of gas chromatography in the characterization of a hydrogen donor solvent.

II. OBJECTIVE

The objective of this project is to establish standard procedures to efficiently analyze and characterize coal-derived materials from process studies at Trexlertown and to support the ICRC SRC-I demonstration plant program.

III. WORK AND RESULTS

A. Reproducibility of solvent separation procedure for product liquid samples.

A product liquid sample (XCL-132PL) was separated by the APCI solvent separation procedure as shown in Figure 1, to establish a range of variation to be expected from this method. Five samples were taken from the original product liquid sample and the solvent separation procedure, outlined in the previous report, was performed on each sample. The results and error analysis are given in Table I, and show reproducibility, as determined by the standard deviation, to be approximately 1%.

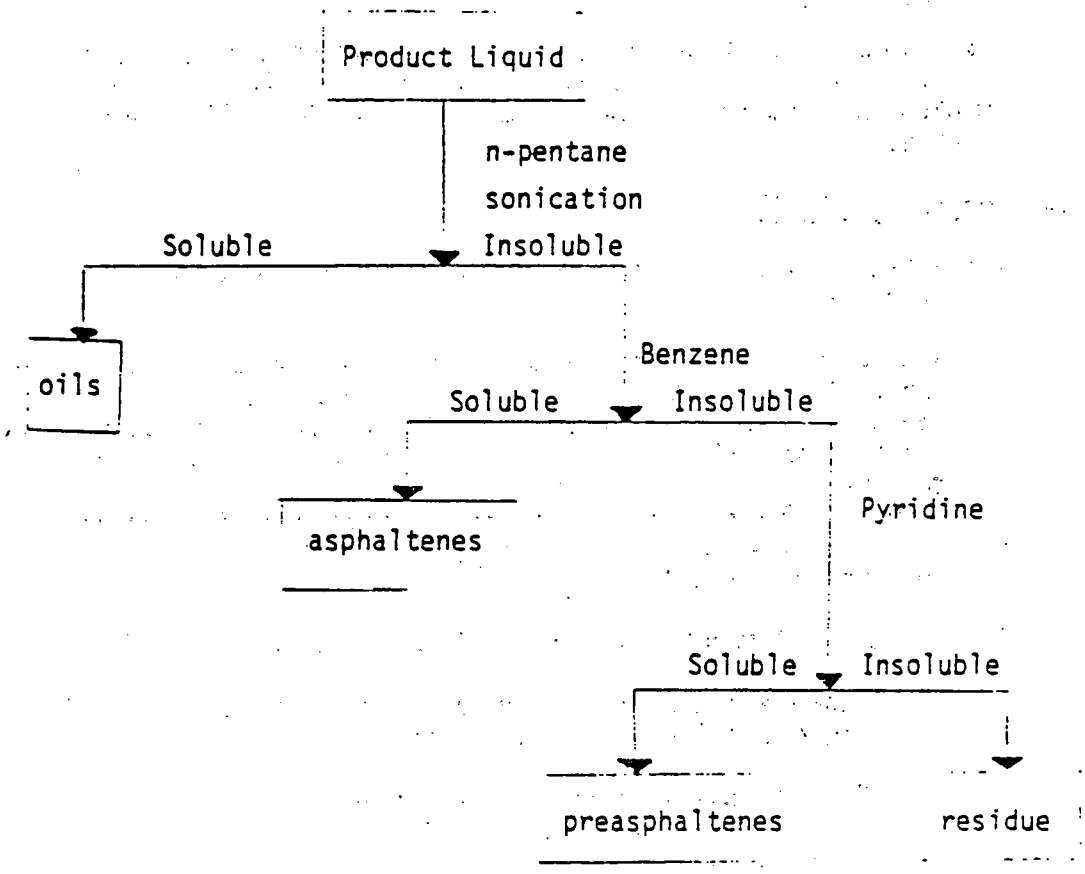
B. Selective Characterization of Recycle Solvent

1. Storage stability of the phenolic fraction of a Wilsonville recycle solvent, V1318/190AMB.

The recycle solvent was subjected to a functional group separation as outlined in Figure 2. Nitrogen base components were removed first, because they are known to irreversibly bind to silica gel used later in the procedure. As described, the saturate hydrocarbons elute first and do not respond to UV light at 320 nm. Aromatic hydrocarbons elute as a combined fraction that give a large fluorescent response. The polar fraction is last to elute and contains hydroxyl species such as phenols and alcohols.

The phenolic fraction was intentionally stored at room temperature, 25°C, in a fume hood with indirect sunlight exposure. Over the course of seven weeks the infrared (IR) spectrum of this phenolic fraction was taken as a smear on NaCl plates. After less than two weeks a small absorption peak at 1730 cm^{-1} was noted, Figure 3. This vibration absorption is indicative of carbonyl, C=O, groups of the aldehyde RHC=O and ketone $R_2C=O$ kind.

Figure 1



APCI Solvent Separation Scheme

Table I

Results of Solvent Separation Reproducibility Study

Sample # wt. in grams	1	2	3	4	5
initial sample	5.00	4.96	5.71	4.95	4.92
oils	3.13	3.12	3.60	3.03	2.97
asphaltenes	.40	.44	.48	.51	.40
preasphaltenes	.56	.41	.54	.44	.53
residue	.91	.89	1.04	.89	.92
recovered	5.00	4.86	5.66	4.87	4.82
% recovered	100	98	99	98	98
oils	62.6	64.9	63.9	62.8	62.4
asphaltenes	8.0	8.9	8.4	10.3	8.1
preasphaltenes	11.2	8.3	9.5	8.9	10.8
residue	18.2	17.9	18.2	18.0	18.7

Reproducibility of the Solvent Separation Procedure

	Mean	Standard Deviation
oils	63.3%	1.06%
asphaltenes	8.7%	0.94%
preasphaltenes	9.7%	1.23%
residue	18.2%	0.31%

Figure 4

Column Separation of a Process Solvent

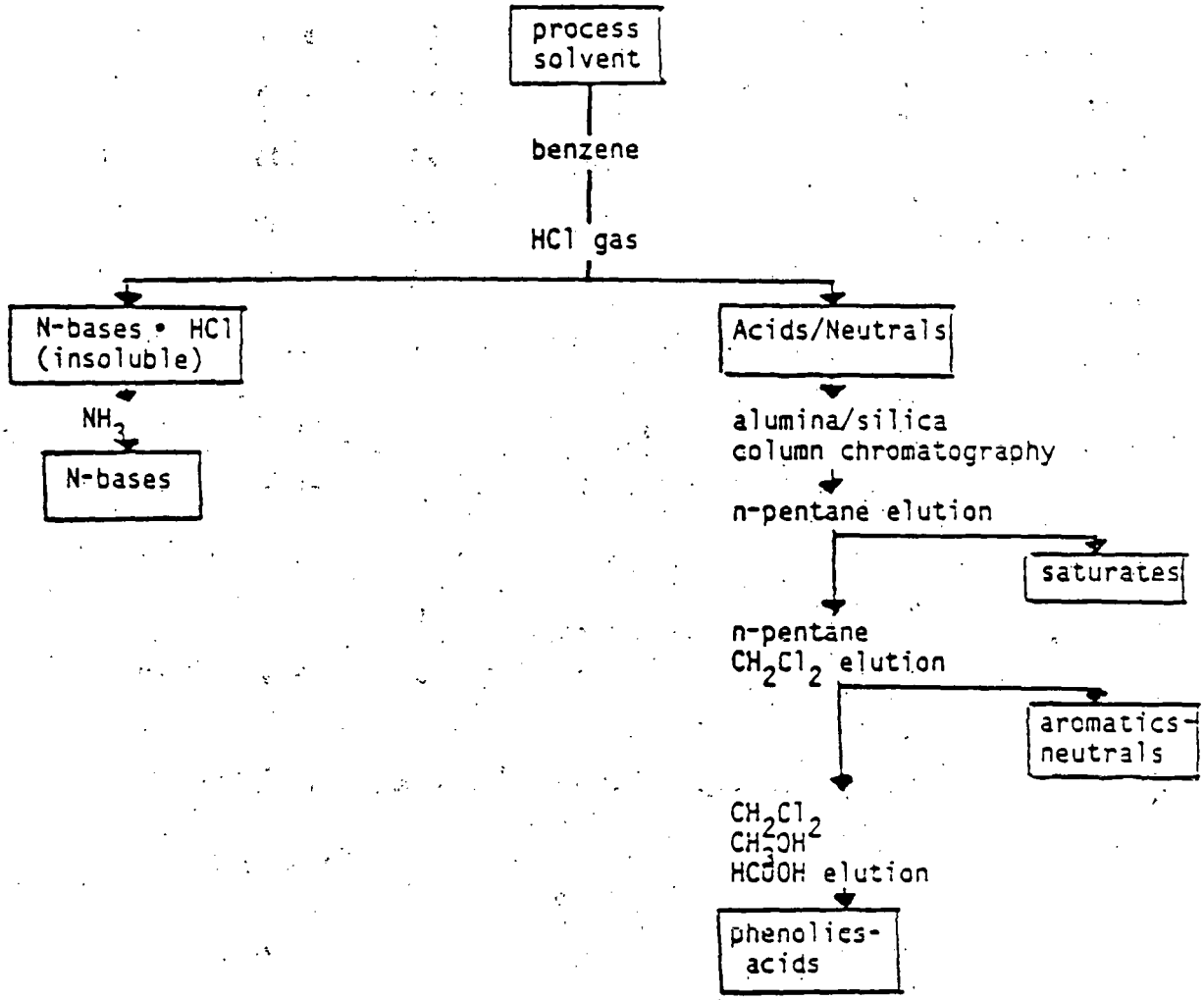
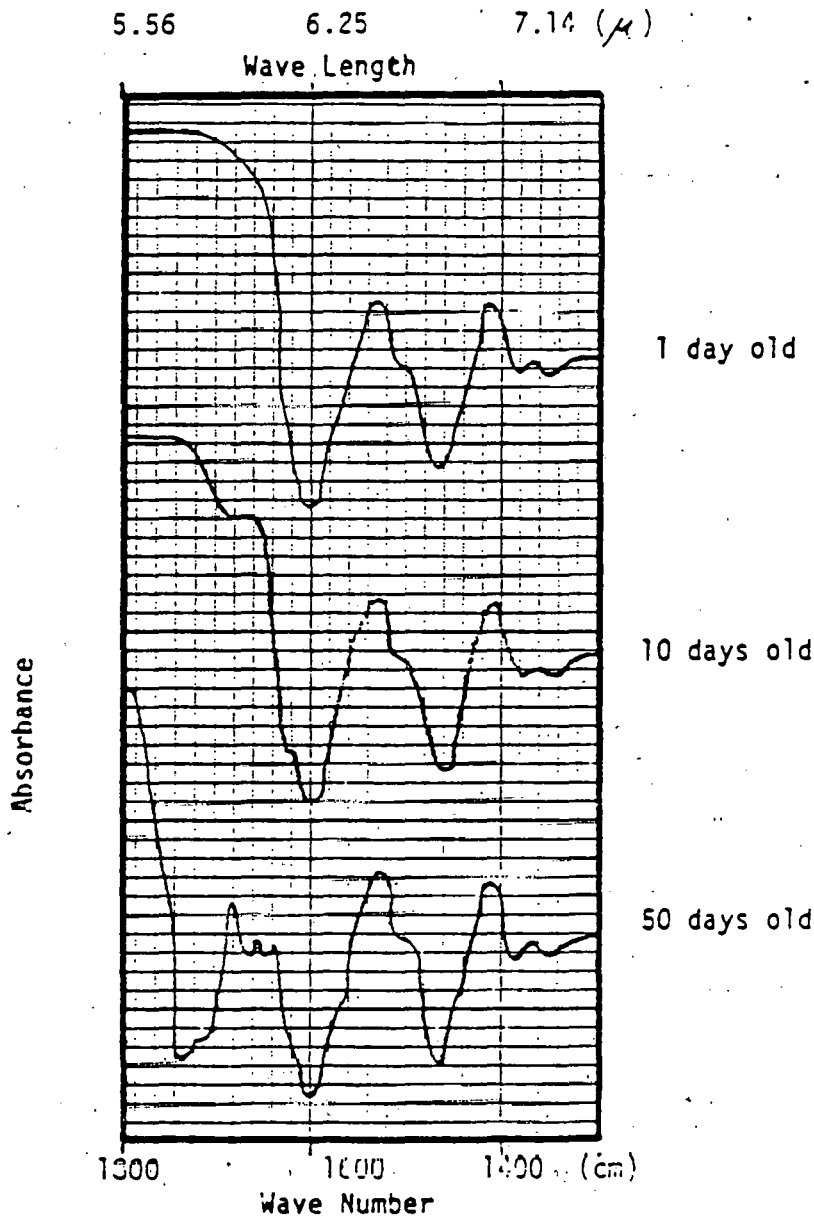


Figure 3



IR SPECTRA of phenolic fraction
(190 AMB) fresh and aged

This observation is very clear evidence that oxidation occurs with coal-derived materials and that the phenolic/hydroxyl components are very active. To confirm this observation, samples of the aged material were analyzed by ultra-high resolution mass spectrometry (HRMS) at the University of Nebraska (Michael Gross), and by combined gas chromatography-mass spectrometry (GC-MS) at Brigham Young University (Milton Lee). Both laboratories confirmed that carbonyl-containing species were present, and that dimethyl benzaldehyde (I) was a major component.

2. Reproducibility study of the column chromatographic procedure for the characterization of hydrogen donor solvents.

   A Wilsonville recycle solvent (V131B/190AMB) was separated by a mixed silica/alumina 1:1 (v/v) column into saturates, aromatics, phenolics and nitrogen bases as outlined in Figure 2. The fractions were weighed after solvent removal. Results of four different separations are given in Table II as well as the error analysis of this experiment.

3. Optimization of the column material in the column chromatographic procedure for a recycle solvent.

   Column chromatography of hydrogen donor or recycle solvent (drum #F219 WRS) was performed as outlined in Figure 2. The loading configuration of the alumina and silica absorbents in the column was varied to determine the optimal separation of the solvent into the saturate, aromatic and phenolic fractions after removal of the nitrogen bases.

   The elution scheme for each column was the same, using the same amounts of solvents to elute each fraction. The various column configurations which were used are shown in Figure 4. The intimate mixture of silica and alumina in Column V has been used in previous column separations. The results are given in Table III.

   Columns II and V gave poor total recovery probably due to excessive amounts of phenolics irreversable bound to the silica in the absorption column. Column IV showed very poor initial flowrates but gave a larger fraction of saturated compounds than the other columns. Column III would be a good column if the saturates and aromatics are not needed as two separated fractions but could be grouped as hydrocarbons. If the fraction of saturate in the recycle solvent is the most important item, column configuration IV is to be used.

Table II

Weight % Recovered by Column Separation

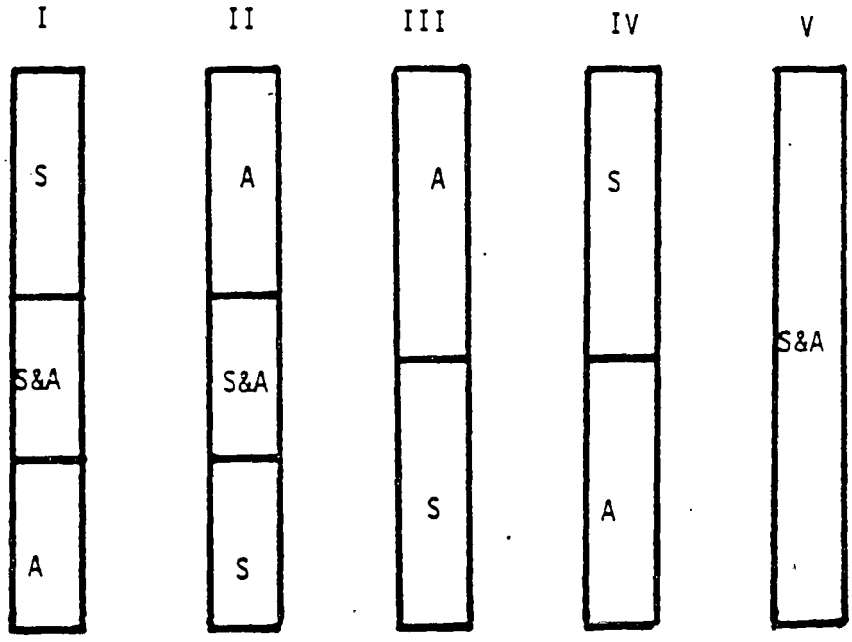
Sample #	1	2	3	4
saturates	6	8	8	7
aromatics	57	61	65	64
phenolics[1]	35	28	25	29
N-bases	2	3	3	1

[1] the results were normalized in favor of the phenolic fraction.

Reproducibility of the Column Separation

	Mean	Standard Deviation
saturates	7	0.9
aromatics	62	3.6
phenolics	29	4.2
N-bases	2	1.0

FIGURE 4



Column configuration for separation optimization using silica(S), alumina(A) and a homogeneous mixture of silica and alumina (S&A).

Table III

Results from Column Separation Optimization Study

Column #	I	II	III	IV	V[3]
% recovery	91.8	86.8	91.3	91.7	86.6
phenolics [1]	31.4	28.2	28.7	30.6	34.4
saturates	17.4	4.3	6.0	27.6[2]	12.2
aromatics	51.3	67.6	65.2	41.8	53.3
sat. & arom.*	68.7	71.9	71.2	69.4	65.5

* total hydrocarbon
1 Normalized to account for phenolics irreversible bound to silica.
2 Fraction showed contamination by aromatic fraction.
3 Column is identical to silica/alumina columns used in previous work.

4. Application of GC to Characterization of a Hydrogen Donor Solvent

A Wilsonville hydrogen donor solvent (HDS), V131B/190AMB was solvent separated into oils, asphaltenes and preasphaltenes, Figure 1, and gave 97%, 2.5% and 0.5% respectively. Column chromatography on silica/alumina, Figure 2, of the same solvent resulted in a functional group distribution that gave 7% saturates, 62% aromatics/ hydroaromatics, 29% phenolics/hydroxyl compounds and 2% nitrogen bases. The chromatographic fractions were then characterized further by gas chromatography (GC), and GC-simulated distillation.

a. Gas Chromatographic Characterization

The advantages of gas chromatographic separation over a GC-simulated distillation characterization is the enhanced resolution of individual compound peaks, so a more precise molecular profile can be assertained. The GC conditions were:

Detector	Hydrogen Flame Ionization
Liquid Phase	8% SP-2100
Solid Phase	Gas-chrom Q
Column Temperature	Programmed at +50°C for 10 min. then 5°C/min to 300°C
Sampler Induction Temp.	150°C
Carrier Gas	He
Flow Rate	30 cc/min
Column Length/Diameter	10 ft by 3/16 in. OD
Sample Size	0.9 l
Detector Temperature	310°C
Calculated Theor. Plates	2668 per meter

The chromagrams are shown in Figures 5-9. A model compound mixture was run for peak identification and relative retention time (r_t) measurements.

Figure 5a shows the chromagram for the initial HDS, Figure 5b the nitrogen bases and Figure 5c the N-base free material (precolumn). No significant peak pattern change occurred after removal of the N-bases. The N-base free material shows virtually the same chromatographic pattern as the initial HDS. This eliminates the possibility of determining the amount of N-bases in the total sample by peak quantification in the chromagram of the total HDS.

Figure 6a shows the N-base free sample (precolumn), which contains saturates, aromatics/hydroaromatics and phenolic/hydroxyl compounds. Figure 6B shows the hydrocarbon fraction (saturate and aromatic), and Figure 6c shows a model compound mixture containing aromatic and saturate. The peak identified by arrow in Figure 6a disappears after removal of the phenolic compound, arrow in Figure 6b. Therefore, this peak is indicative of the phenolic compounds. Comparing chromagrams Figure 6a with Figure 6c, compounds #7, 9, 14, 18 and 20 of the mixed model compounds are present in the precolumn material and can be identified as naphthalene, 2-methyl naphthalene, n-tridecane, dimethyl naphthalenes, phenantrene, anthracene, n-octadecane, fluoranthene and n-heneicosane and pyrene. The structures of these compounds are shown in Figure 10.

Figure 7a shows the precolumn material containing saturates, aromatics and phenolics, Figure 7b shows the isolated saturate fraction and Figure 7c shows a saturate compound model mixture. Compounds 3 and 4, n-tridecane and n-tetradecane are identified to be the two major compounds in the saturate fraction. The chromagrams also show that C_{10}-C_{29} (nonacosane), all normal paraffins, are present in decreasing amounts in the HDS.

Figure 8a shows the chromagrams of the N-base free sample, Figure 8b the aromatic fraction thereof, and Figure 8c an aromatic model compound mixture. The four major peaks in the unseparated sample are also the major peaks in the aromatic fraction and are identified from the model compound mixture chromagram as 2-methyl naphthalene, dimethyl naphthalenes, fluorene, phenanthrene and anthracene

Figure 9a shows the chromagram of the N-base free HDS, 9b the phenolic fraction and 9c the precolumn material after removal of the phenolic fraction. Figure 9b shows a very large peak, which is missing in the phenolic free fraction, as seen on Figure 6b. This peak therefor is specific for the phenolic fraction in the HDS.

Quantitative evaluation of characteristic peaks of each fraction was attempted. The peak area in the mixed chromatogram (precolumn) plus the remainder of peak areas present in the fractionated chromatogram represent the peak areas of the individual fraction in the mixed chromatogram.

Table IV shows the peaks chosen, retention times, percent peak intensities of the chromagrams and the last column is a calculation of the fraction present in the precolumn HDS material as follows:

$$C = A + A\left(1 - \frac{B}{100}\right),$$

where, A = % intensity in precolumn chromagram for a peak at r_t
B = % intensity in fraction chromagram for a peak at r_t
C = calculated % fraction present in the precolumn HDS

Figure 5

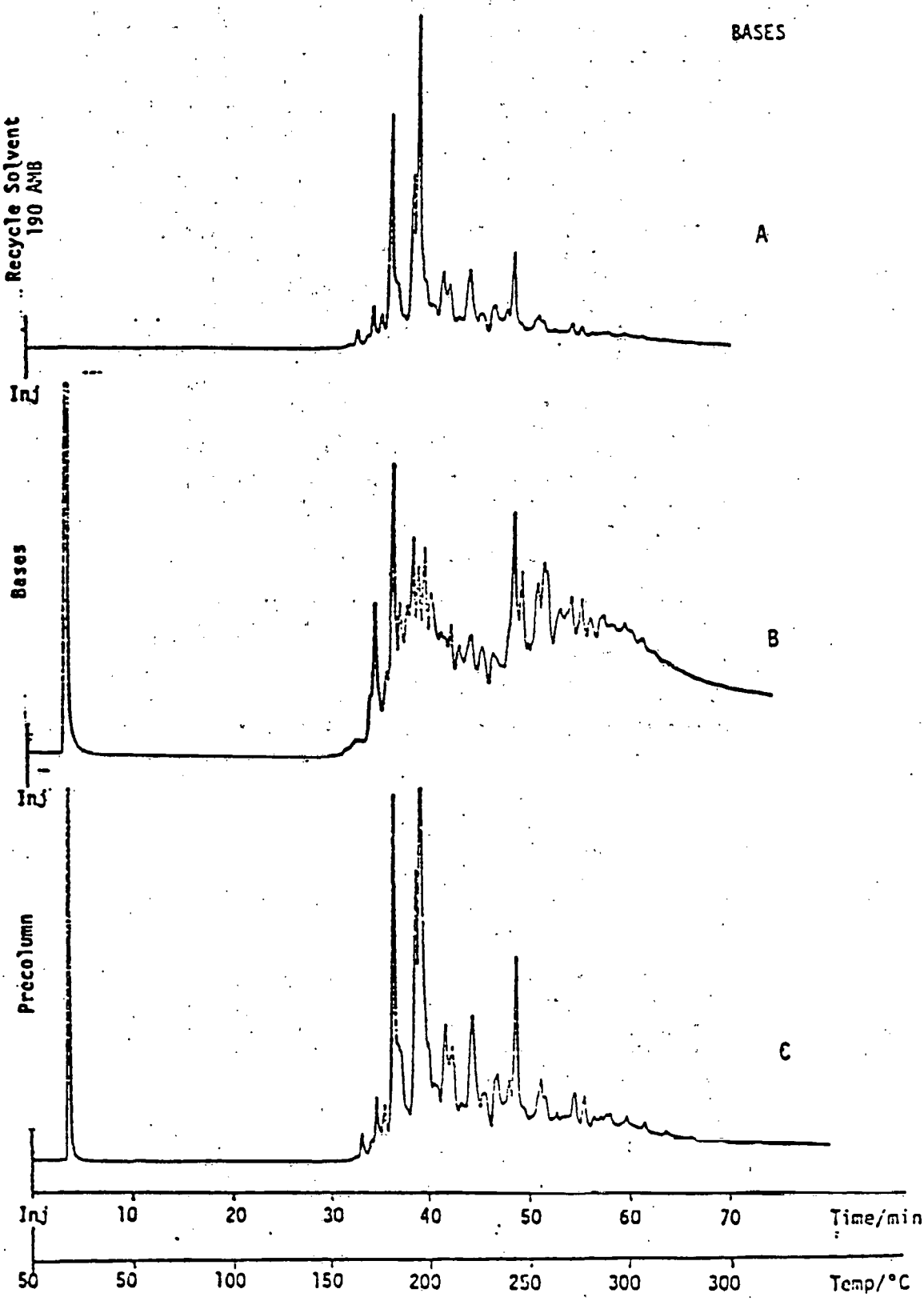

BASES
Recycle Solvent
190 AMB
A
Inj
Bases
B
Inj
Precolumn
C
Inj
10
20
30
40
50
60
70
Time/min
50
50
100
150
200
250
300
300
Temp/°C

Figure 6

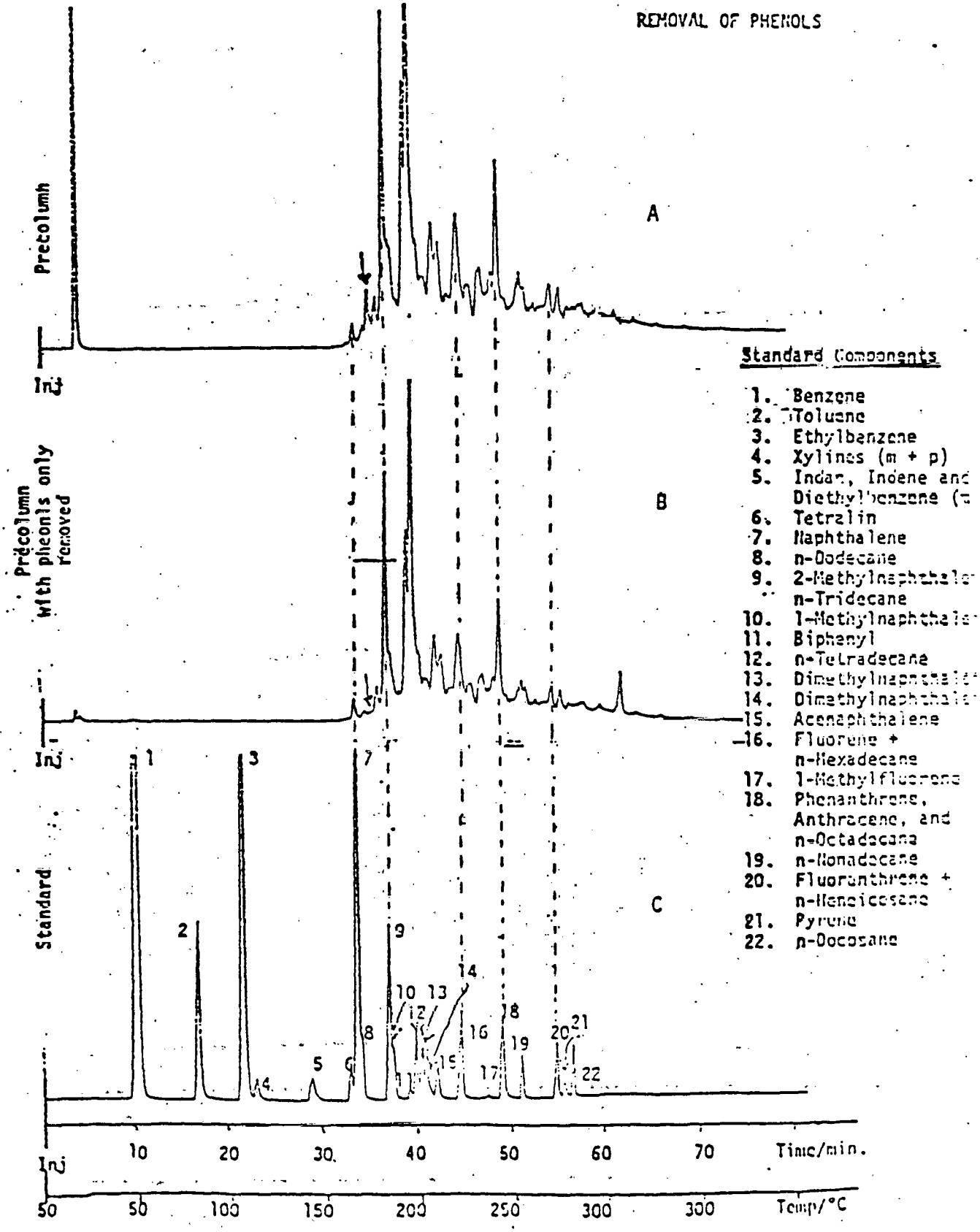
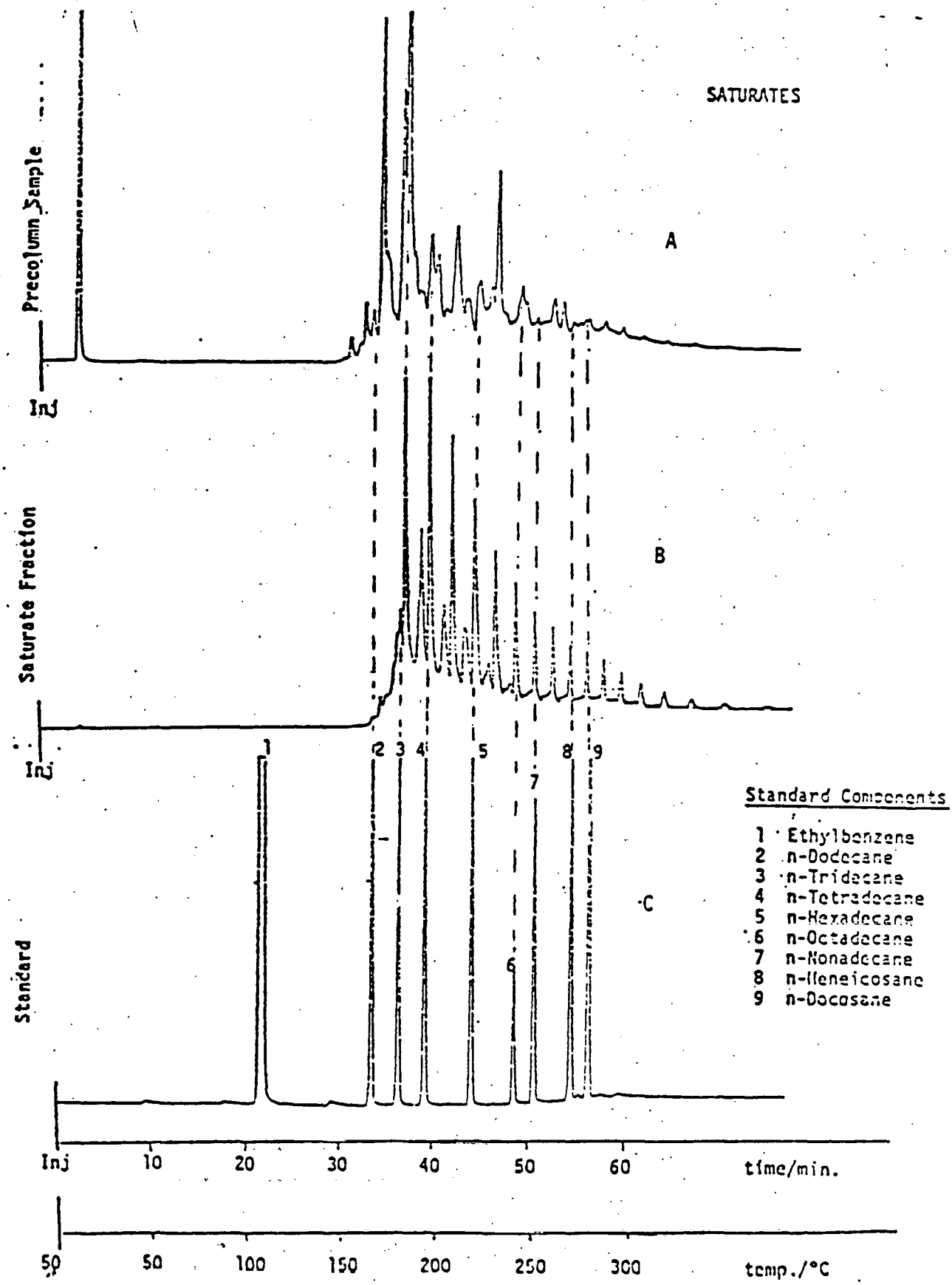

REMOVAL OF PHENOLS
Precolumn
Inj
A
Precolumn with phenols only removed
B
Standard
C
Standard Components
1. Benzene
2. Toluene
3. Ethylbenzene
4. Xylines (m + p)
5. Indan, Indene and Diethylbenzene (o -
6. Tetralin
7. Naphthalene
8. n-Dodecane
9. 2-Methylnaphthale
n-Tridecane
10. 1-Methylnaphthale
11. Biphenyl
12. n-Tetradecane
13. Dimethylnaphthale
14. Dimethylnaphthale
15. Acenaphthalene
16. Fluorene + n-Hexadecane
17. 1-Methylfluorene
18. Phenanthrene, Anthracene, and n-Octadecane
19. n-Nonadecane
20. Fluoranthrene + n-Heneicosane
21. Pyrene
22. n-Docosane
10
20
30
40
50
60
70
Time/min.
50
50
100
150
200
250
300
300
Temp/°C

Figure 7


SATURATES
Precolumn Sample
A
Inj
Saturate Fraction
B
Inj
1
2
3
4
5
6
7
8
9
Standard
C
Standard Components
1 Ethylbenzene
2 n-Dodecane
3 n-Tridecane
4 n-Tetradecane
5 n-Hexadecane
6 n-Octadecane
7 n-Nonadecane
8 n-Heneicosane
9 n-Docosane
Inj
10
20
30
40
50
60
time/min.
50
50
100
150
200
250
300
temp./°C

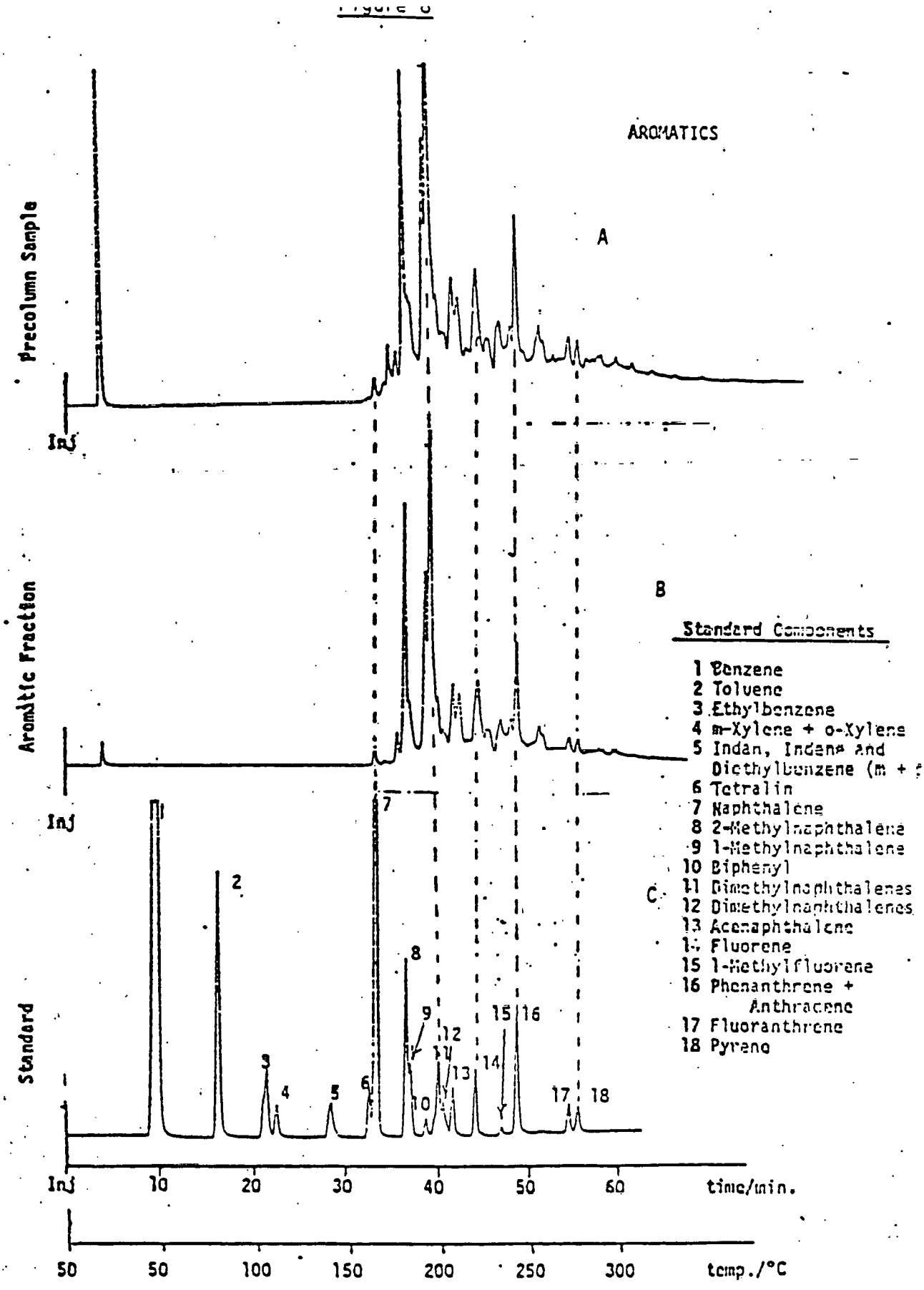

AROMATICS
Precolumn Sample
A
Inj
Aromatic Fraction
B
Inj
Standard
C
Inj
10
20
30
40
50
60
time/min.
50
50
100
150
200
250
300
temp./°C
Standard Components
1 Benzene
2 Toluene
3 Ethylbenzene
4 m-Xylene + o-Xylene
5 Indan, Indene and
Diethylbenzene (m +
6 Tetralin
7 Naphthalene
8 2-Methylnaphthalene
9 1-Methylnaphthalene
10 Biphenyl
11 Dimethylnaphthalenes
12 Dimethylnaphthalenes
13 Acenaphthalene
14 Fluorene
15 1-Methylfluorene
16 Phenanthrene +
Anthracene
17 Fluoranthrene
18 Pyrene

Figure 9

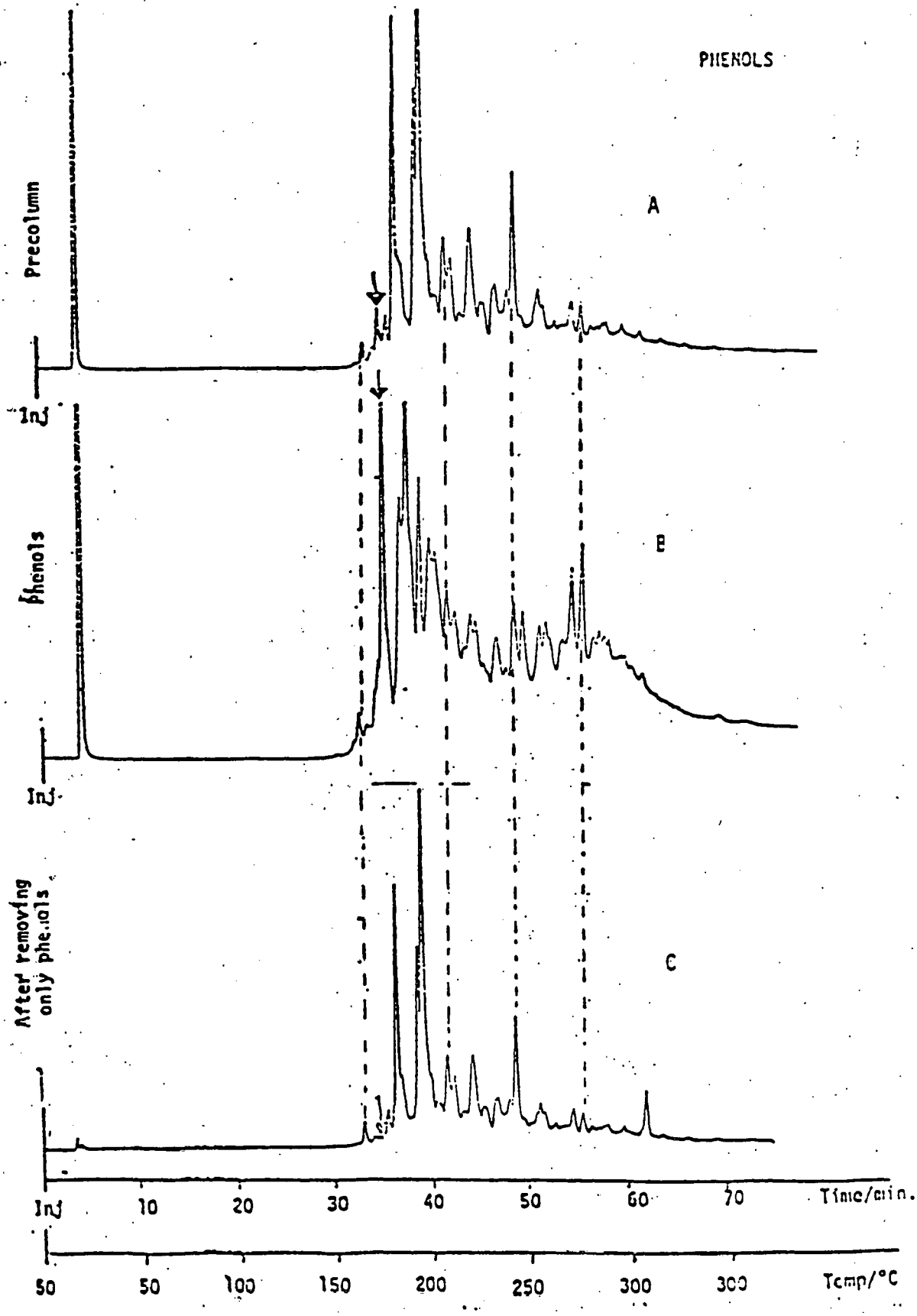
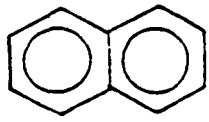
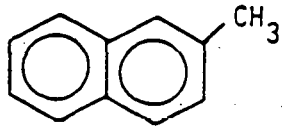

PHENOLS
Precolumn
A
Inj
Phenols
B
Inj
After removing only phenols
C
Inj
10
20
30
40
50
60
70
Time/min.
50
50
100
150
200
250
300
300
Temp/°C

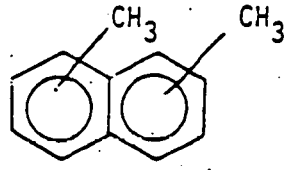
Figure 10



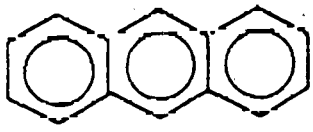
naphthalene



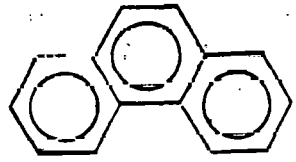
2-methyl-naphthalene



dimethyl-naphthalenes

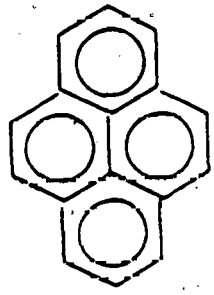


anthracene

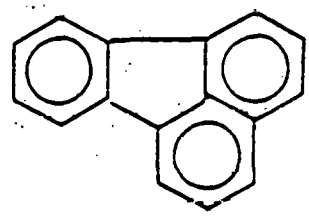


phenanthrene

fluorene



pyrene



fluoroanthene

$CH_3(CH_2)_{11}CH_3$	tridecane
$CH_3(CH_2)_{12}CH_3$	tetradecane
$CH_3(CH_2)_{16}CH_3$	octadecane
$CH_3(CH_2)_{19}CH_3$	heneicosane
$CH_3(CH_2)_{27}CH_3$	nonacosane

Comparing the GC calculated results with the actual weight fractions obtained by column separation it appears there is very little agreement in all three fractions.

b. Characterization by GC-simulated Distillation

The GC-simulated distillation was performed on the total HDS and its subfractions. The hydrocarbon chromagrams, Figure 11, show profiles very similar to those obtained by GC. The boiling ranges and % material distilled for the total HDS and its subfractions are given in Table V.

The boiling point profile are similar over the entire temperature range for the total HDS and its subfractions. It is unlikely that a temperature cut can be used to segregate one fraction from another.

IV. CONCLUSIONS

A. Reproducibility of total recoveries by the APCI solvent separation method of product liquid samples shows a standard deviation of 1%.

- Coal-derived liquids must be carefully stored under nitrogen or argon at 4°C to maintain or prolong molecular integrity. If we are to analyze the compounds from Wilsonville, Tacoma or even the Allentown Laboratories, the samples must be preserved to reduce sample oxidation.

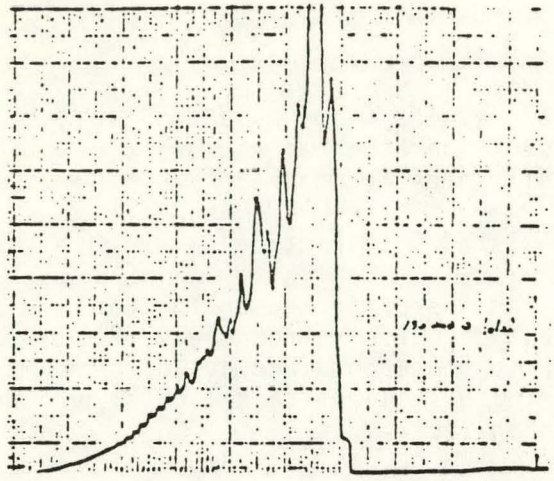
- A relatively large variation in the weight percent of recovered material from the column chromatographic separated saturates/aromatics/phenolics/N-bases indicates a need to improve the technique prior to establishing the procedure in the work-up laboratory.

- Optimization of column packings for the column separation procedure showed that a column Type III (see Figure 4) is to be used for a rapid and reliable separation of a hydrogen donor solvent into a mixed fraction of aromatics/saturates and a phenolic fraction. When the saturated fraction is required as a separate fraction of the hydrogen donor solvent, a column of Type IV (see Figure 4) is to be used.

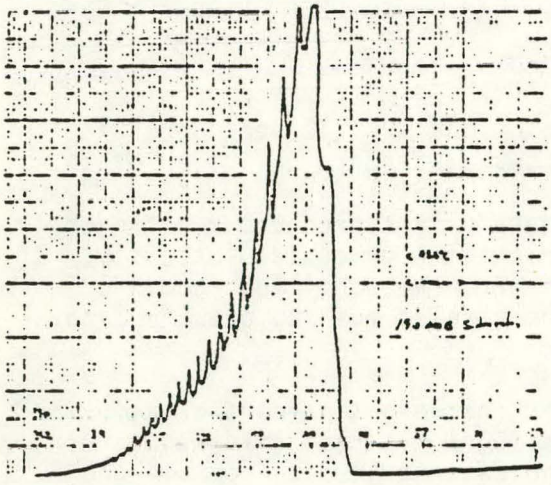
- A hydrogen donor solvent (HDS) and its functional group fractions were characterized by gas chromatography (GC) and GC-simulated distillation. Key compounds present in the HDS were identified as:

  2 methyl naphthalene
  dimethyl naphthalenes
  fluorene
  phenanthrene
  anthracene
  fluoranthene

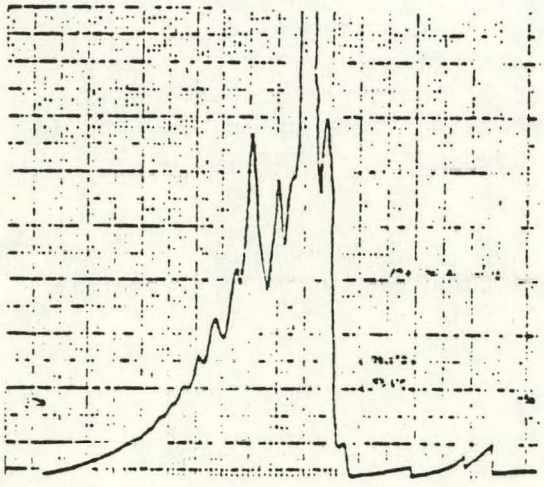
GC-Simulated Distillation
Figure 11



Recycle Solvent



Saturates



Aromatics

← Temperature

Table V

GC-Simulated Distillation [°F]

	total HDS	satur.	arom.
IBP	422	426	423
25%	486	495	486
50%	536	543	532
75%	637	625	625
95%	802	770	776
FBP	921	864	900

pyrene
n-tridecane and n-tetradecane

An attempt was made to quantify the functional group fractions directly from the chromagrams, but this failed.

Separation of the HDS into functional group fractions via temperature cuts from the GC-simulated distillation was shown futile at this point.

V. ACKNOWLEDGEMENTS

The GC experiments were designed and carried out by Ann Kamzelski, CRSD, who should be credited for her excellent work.

February 1980

Section 6

PHASE I

MONTHLY REPORT

Coal Products Analysis Laboratory

F. K. Schweighardt

The current research effort of APCI through the SRC Task Force is to develop the commercialization of solvent refined coal, SRC-I, by engineering a 6,000 ton per day demonstration plant. Irrespective of specific engineering approaches now being explored, a common need exists to develop and apply analytical techniques which will provide immediately useful information on the coal feedstocks and products formed during conversion reactions. Such techniques must provide precise (reproducible) analytical data in a reasonable timeframe to permit a host of engineering decisions to be made. These same techniques should also provide physical-chemical data to the chemist, or at least supply representative samples for more detailed analytical characterization.

Due to the inherent complexity of coal-derived materials, these products require some degree of separation to classify and quantify changes during coal conversion. An accounting of the present trends in development of a separation method is therefore in order.

Historically the conversion of coal, a macro-molecular network of polynuclear aromatic/heteroaromatic hydrocarbons, to a new chemical form was defined as the increase in benzene solubility of the product. This was because the Germans (Ca 1935) found that the original coal (bituminous) and its entrained resins were slightly soluble ($\approx$ 20%) in pyridine, and nearly insoluble (1-3%) in benzene. In the 1940-50's the degree of solubility in paraffinic solvents (pentane or hexane) was used to define the liquid end products (oils) of coal conversion. Specific distillation fractions (200-450°C) of these oils later served as recycle solvents and today have become known as the hydrogen donor solvents for coal conversion. In the late 1930's the Germans recognized that coal when heated ($\approx$450°C) for short time periods significantly increased its pyridine solubility but not its benzene solubility. Again in the 1970's this fact was rediscovered in the United States and this "new" fraction was named preasphaltenes. The degree of solubility was now used to reflect changes in the coal conversion product during various stages in a process development unit (PDU).

In a typical liquefaction process preasphaltenes are generated in the dissolver stage with only small quantities of hydrogen ($\approx$1%) consumed. Physical changes do occur in that the concentration of slurry solids decreases, viscosity increases and some thermal effects are noticed. In the reaction zone, downstream, (or still in the dissolver if recycle solvent and hydrogen conditions are sufficient) asphaltenes, benzene solubles-pentane insolubles, increase in population. Depending upon the engineering employed, which accounts for residence time, pentane soluble oils are generated along with hydrocarbon gases. As the process stream travels along, it sees a multitude of conditions, some of which may drive these products to revert (retrograde or regressive

reaction) to less soluble components. Many of these regressive reactions seem to produce pyridine insoluble components similar to the original coal -- but much less reactive.

Our separation procedure to isolate oils-asphaltenes-preasphaltenes-residue is the result of many pertabations in classical coal chemistry thought and the consequence of the present state-of-the-art technology. Our philosophy is to define each subfraction in terms of solubility in and not a precipitate from a particular solvent or solvent pair. This approach reduces co-solubility and co-precipitation effects. Each sample is treated in the following manner.

A sample of the total product stream from a process unit (100 mL) is obtained at the appropriate let-down stage and held at 4°C under a nitrogen blanket if a delay in analysis is anticipated. The sample is warmed to 50°C and sonicated (20 MHz at 200 watts) for 10 minutes to regenerate a homogeneous prime sample. Five (5) grams is removed and sent for elemental composition and ash, a second five (5) gram analytical sample is then solvent separated. The analytical sample (5g $\pm$ .005) is frozen in liquid nitrogen, ground to a course powder (100%-100 mesh) then quickly diluted with n-pentane (100 mL) and sonicated to initially extract the pentane soluble oils.

The pentane-sonication-extraction regime is repeated three times with each supernatant being decanted into a Millipore stainless steel pressure filter containing a 5 micron fluropore filter element. The 4th and 5th wash (100 mL) is used to decant all remaining solids into the filter unit. Nitrogen gas is used to inert the sample and force the solubles through the filter to be collected. While the filtrate is purged with dry nitrogen, the solvent volume

is reduced at 50°C on a Rotovapour-R. Pentane extraction (2L) is continued until just a faint yellow color remains. Benzene is next used to continue the extraction to recover the asphaltenes in a similar fashion as pentane. Nearly two liters of benzene are required. Pyridine (2-2.5L) is the final solvent for extraction to reclaim the preasphaltenes. This procedure leaves the residue (mineral matter and insoluble organics) on the filter. After back washing with methanol and methylene chloride to remove residual pyridine from the wet residue, it is then dried in-situ with nitrogen, removed and weighed to quantify the residue weight percent.

Solvents other than pentane have been used, e.g., hexanes, heptane and cyclohexane. Each gives (in the order sited) slightly more oils and therefore less asphaltenes, without greatly effecting the quantity of preasphaltenes or residue. Toluene has been substituted for benzene without major problems, but the laboratory work-up time is extended and some product changes may occur due to prolonged heating. Residual benzene on the other hand is removed from the asphaltene solution by sublimation of 4°C under 1-5mm Hg in 1-2 hours. Ethyl acetate has been used recently to isolate asphaltenes but with mixed results due to poor solvent removal.

As for the preasphaltenes, tetrahydrofuran (THF) has been substituted for pyridine but stability of ethers without peroxide inhibitors (e.g., BHT) provides an unsafe working environment. Methylene chloride and methanol (9:1) has been used with good success. The major problem is that this mixture recovers only 80-90% of the pyridine solubles. An error that could well influence kinetic measurements when coal to preasphaltene data is most important.

These results confirm that material recovery is high, $>$ 98%, and elemental analyses are fairly consistent, within experimental limits. Precision data on the solvent separation procedure is presently being evaluated.

In summary, the solvent separation provides the operating engineer with a physical-chemical probe that can quantify process changes and relate these to a well-conceived coal conversion model, and with time be used to forecast product quality assurances. Most important in developing this scheme was that the procedure be flexible in purpose, precise, ($\pm$ 2% relative), operator independent and capable of being automated for single shift data turn-around. It is our desire to provide the SRC Task Force with reliable information in a timely fashion at an exceptable cost.

The methodology described above requires one laboratory assistant 8 hours to complete, less clean-up and report preparation. To demonstrate the effectiveness of the method, the average material recovery has been 98% and elemental balances have been within experimental error limits. Experience with the method greatly reduces errors that ultimately effect engineering judgments.

For example, a total product from a coal conversion PDU was analyzed and solvent separated. Table 1 summarizes the elemental recovery data.

Table 1

Normalized Composition

Sample Name	Wt% Recovery	C	H	O[a]	N	S	Ash	$\bar{n}$Mwt[b]
Product	--	76.8	6.9	3.7	1.2	1.4	9.9	300
		[weighted elemental composition]						
Oils[c]	57.5	50.3	5.1	1.3	0.4	0.4	--	115 (200)[d]
Asphaltenes	11.9	10.1	0.8	0.6	0.2	0.2	--	48 (400)
Preasphaltenes	14.2	11.8	0.8	0.9	0.4	0.2	0.1	128 (900)
Residue	16.4	4.4	0.3	0.7	0.1	0.7	10.2	--
Summation	98.4 (100.0)	76.6	7.1	3.5	1.1	1.5	10.3	291

a) Direct determination

b) Vapor pressure osmometry, 27°C in methylene chloride, 4 pts extrapolated to infinite dilution to give number average molecular weight.

c) Material loss adjusted to oils as volitiles removed during work-up.

d) $\bar{n}$Mwt of each fraction.

Attachment 2

Wilsonville Solvent Separation Procedure

Appendix IV

Solvent Fractionation of Solvent Refined Coal For Characterization

1. Scope

This method is designed to characterize high molecular weight bituminous materials by separating into three group classifications, using solvents as the media. Since results will vary according to the conditions of solvent treatment, the procedure is quite detailed and must be closely followed. The method has been developed primarily to characterize coal extracts.

2. Principle

Coal extracts are separated by solvent fractionation into the following three high molecular weight fractions:

A. Benzene Insolubles -- that fraction of the solvent refined coal (SRC) that is insoluble in benzene at its atmospheric boiling point.

B. Asphaltenes -- the fraction of the benzene-soluble SRC insoluble at room temperature in a mixture of 100 parts of pentane and 9 parts of benzene when the ratio of the liquid mixture to the weight of benzene solubles is 109.

C. Oil -- the benzene-soluble, pentane-soluble fraction of the SRC.

3. Apparatus Required

(1) Alundum thimbles, 45 mm x 127 mm size, round bottom RA 98 type
(2) Soxhlet extractor
(3) Beaker A, a 600 mL Griffin beaker
(4) Beaker B, a 100 mL Berzelius beaker
(5) Beaker C, a 800 mL Griffin beaker
(6) Buchner funnel, with fritted disc, medium porosity, 150 mL capacity
(7) Wide mouth, 4 oz. sample bottle

4. Reagents

(1) Benzene, reagent grade
(2) Pentane, practical grade
(3) Celite 545, Anal. filter aid

5. Procedure

A. Separation of the Benzene Insoluble Fraction

(1) Grind approximately 10 grams of solvent refined coal sample (SRC) to minus 100 mesh and place in 1 oz. bottle.

(2) Dry the SRC sample in oven at 105°C for 1 hour. At the same time dry an alundum thimble (1) containing 1-2 grams of celite at 105° for 1 hour.

(3) Remove both to desiccator and allow to cool to room temperature.

(4) Weigh thimble containing celite and record on calculation sheet at (2) and (5).

(5) Place 1-3 grams of SRC in thimble and weigh. Record at (1) on calculation sheet (Note A). Subtract (2) from (1) on calculation sheet and record at (3). This is the weight of sample.

(6) Mix celite and SRC as well as possible by rolling and tapping carefully.

(7) Place thimble in extraction apparatus.

(8) Put 3 boiling stones and approximately 250 mL benzene in 500 mL flask. Assemble apparatus as shown in Figure 1.

(9) Set powerstat at approximately 80.1°C, 80 volts and turn on heat. Check carefully for overflow of thimble and plugging in capillary at bottom of extractor as soon as reflux starts.

(10) At end of four hours stop extraction, remove thimble, allow to drain in beaker. Check for precipitate on outside of thimble. If present, remove by washing with benzene and transfer washings back into thimble.

(11) Stir material in thimble with small spatula. Replace thimble in extractor and continue extraction.

(12) Repeat steps (10) and (11) at 8 hours, 12 hours, 16 hours, and 20 hours. Benzene should now be coming through clear; if still cloudy, continue 4-hour runs.

(13) Allow extractor to cool and drain.

(14) Remove thimble and let stand in air until visibly dry.

(15) Place thimble in vacuum oven and dry with at least 29 inches of mercury, vacuum, and 100°C for 4 hours.

(16) Remove, place in desiccator to cool. Weigh and record at (4) on calculation sheet. Subtract (5) and (4) and record at (6). This is the weight of Benzene Insoluble Fraction.

B. Separation of Benzene Soluble, Pentane Insoluble (Asphaltene) Fraction

(17) Transfer carefully all the contents of the 500 mL flask into Beaker A using fresh benzene to rinse out flask. Discard the boiling stones at this time.

(18) Evaporate this solution to approximately 50 mL on steam bath.

(19) Evaporate as much as possible; add to 600 mL beaker containing pentane vary as little to wash as possible.

(20) Stir Beaker C for 5 minutes and let stand at least one-half hour.

(21) Weigh the clean, dry filter paper, and record on calculation sheet at appropriate place.

(22) Filter contents of Beaker C through the Buchner funnel into a filter flask with suction.

(23) Add 5 mL benzene to Beaker C to dissolve any holdup. Add 50 mL more pentane to beaker while stirring. Pour into funnel.

(24) After filtration, wash the asphaltenes on funnel with fresh pentane and stir with spatula. Continue until washings come through clear.

(25) Continue filtration until visibly dry. Place funnel in vacuum oven at 29 inches of mercury (vacuum) and 100°C for 4 hours.

(26) Remove from oven. Place in desiccator until cool.

(27) Weigh and record at (7) on calculation sheet. Then (7)-(8) equals line (9), weight of asphaltenes.

C. Separation of Benzene Soluble, Pentane Soluble (or oil) Fraction

(28) Transfer pentane filtrate from filtering flask to a large beaker, 600 or 800 mL, and evaporate on steam bath.

(29) When volume is down to approximately 50 mL, transfer with rinsing to a tared (lined (11)) wide mouth, 4 oz. sample bottle.

(30) Place in heated vacuum desiccator at 29 inches of Hg, vacuum, and 100°C for 4 hours. Weigh and record in appropriate places on calculation sheet.

Solvent Fractionation of Extracts

Data Sheet

		A	B
1.	Weight of thimble and celite and sample	_____	_____
2.	Weight of thimble and celite	_____	_____
3.	Sample weight	_____	_____
4.	Weight of thimble and celite and benzene insoluble material	_____	_____
5.	Weight of thimble and celite	_____	_____
6.	Benzene insolubles	_____	_____
7.	Filter paper insolubles	_____	_____
8.	Filter paper	_____	_____
9.	Weight of asphaltenes	_____	_____
10.	Beaker and oil	_____	_____
11.	Beaker weight	_____	_____
12.	Oil	_____	_____

	A	B	
$\frac{6}{3} \times 100 =$	_____	_____	% benzene insolubles
$\frac{9}{3} \times 100 =$	_____	_____	% asphaltenes
$\frac{12}{3} \times 100 =$	_____	_____	% oil

% ash = _____

% UC = _____

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Attachment 3

Distillation Separation Procedure D

Appendix I

Total Product

Distillation Separation

Procedure D

A) Oils - Material distillable from IBP to 850°F.

B) SRC - Pyridine soluble portion of distillation bottoms.

C) Residue - Pyridine insoluble portion of distillation bottom.

D) SRC - Oils/asphaltenes/preasphaltenes are determined by Procedure W. A five (5) gram sample of the SRC is recovered from the pyridine solubles and replaces the total product as the starting material.

Distillation: A 300 gram total product liquid sample is removed from the holding can after heating to 60°C and thorough mixing. Great care must be taken to obtain a well-mixed sample.

The sample is then distilled in a 1" x 6" vacuum jacketed distillation unit packed with podbielniak heli-pak high efficiency packing. The total plates as determined by Pod's data book indicate 15 at total full reflux. A reflux ratio of 10:1 at 550°F. Fractions were collected at IBP to 420°F, and 420 to 550°F under 100 mm Hg, and 550-end point (850°F) under 0.5 mm Hg. The pot temperature was 650°F at final end point.

The distillation bottoms were pyridine extracted to yield the SRC and residue.

The SRC was then solvent separated by Procedure W to give SRC-oils, asphaltenes, and preasphaltenes.

New Distillation Workup Procedure

R. Cusick

A new method for separating CPDU process samples is being developed. CRDD is currently using a solvent separation scheme in which the entire pilot plant sample is extracted into pentane to remove the oil fraction. How well this oil extraction method relates to a distillation method is uncertain. Therefore, a method to separate the process samples by distillation is being developed as an alternative method.

In the earlier method used by CRDD samples were distilled to a 850°F endpoint (corrected). Unfortunately there seemed to be considerable uncertainty in the final cut point. In the method we are developing, the distillate materials that will be distilled off up to a 850°F cut point will be compared by simulated distillation to get absolute yields plus an understanding of the cut points themselves.

During the method developement period several distillations on a standard process mixture from the pilot plant was distilled. During the distillation three cuts were removed:

IBP-420°F
420-550°F
550-850°F

Simulated distillations were made on each sample (Table 1).

Starting with a single CPDU material the reproducibility for the distillations is shown by comparing Run #2 and #3. The amount of 420-850°F material was 65.3 and 63.3 wt.%, respectively. The 550°F cut points for all of the runs were quite reproducible. The 550°F cut point was consistently around the 96% point in the simulated distillation except for Run #5.

The 850°F cut point varied between 719 and 751°F. We had long realized that the cut point of the lab method differed significantly from the plant distillations. When the 550-850 cut from a prior distillation was added back to the total sample as we had practiced in our earlier workup method, a different result was observed as shown in Run #4.

By having the heavy cut present, the end point seemed to increase although the yield of 550-850°F material decreased.

When the solids are removed from the 550-850 diluted sample, even less yield of 550-850 material was observed as shown in Run #5. Therefore, to practice the dilution method seems to complicate the overall distillations. We will begin analyzing samples routinely using the procedure practiced in Runs #2 and #3.

METHOD DEVELOPMENT PROGRAM FOR PRODUCT WORK-UP EX SRC PILOT PLANT

FEED: BLEND OF BCL 22-50 PL AND XCL 23-189 PL

...MBER NUMBER	WGT. % INT-420%	SIM DIST	WGT. % 420-550°F	SIM DIST	WGT. % 550-850°F	SIM DIST	WGT. % 850-BTMS.	NO. SOLVENT RECYCLE TO STILL & YIELD	REMARKS
	1.6		27.1		38.2		31.2	(0)	15 TP 10: 1 RR at 4: + 550°F. TTO :
st								420 - 850 65.3	final cut point
				396		520°F			
0°F				11.0%					
0				96.0%		7%			
5%				548°F		751°F			300 G Chg.
6%				552°F		757°F			No diluent
7%				558		764°F			Added
8%				568		773°F			
9%				579		788°F			
P				592		800°F	Liq. Temp.		
11 Cut						772	650°		
	2.2		27.1		36.2		33.8	(0)	Same As Above
				399°F		516°F		420 - 850	
0				12.0%				63.3	
0				96.0%		9%			
5%				546°F		728°F			
6%				549°F		735°F			
7%				555°F		742°F			
8%				564°F		752°F			
9%				577°F		767°F			
P				592°F		779°F	Liq. Temp.		
1 Cut						758°F	588°F		
	3.2		28.0		32.0		36.6	(1)	Same As Above
t.									except 212 G of
				400°F		526°F		420 - 850	550-final cut po
0				9.0%				60.0	ex run 2 & 3 sol
0				96.0%		6.0%		60.0 93.3	added to chg.
5%				547		744°F		64.3	
6%				550°F		752°F		Loss 6.7%	Solvent removed
7%				556°F		759°F			per Kayhart.
8%				565°F		769°F			
9%				576°F		786°F			
P				587°F		802°F	Liq. Temp.		
1 Cut						820°F	620°F		
	2.6		28.3		27.9		40.8	(2)	Same as above
t.								420 - 850	except solids
				402		524°F		56.2	not removed.
				10.0					
				93.0		7.0%		56.2 87.4	
				555		719°F		64.3	
				559		724°F		Loss 12.6%	
				565		732°F			
				574		742°F			
				585		759°F			
				599		775°F	Liq. Temp.		
Cut						770°F	600°F		

KS: Actual liquid temperatures are reached during a short period at end of distillation.

Pressure increases from 0.4-0.5 to 1.0-1.1mm running time on distillation - 9 hrs. average.

Actual 775°F
SIM DIST 97.5% @ 775°F

Merwin Oakes
3-21-80

Linwood Analytical Activities

PHYSICAL TESTING - R. Cusick

Product Workup Distillations

XCL-21 - 314/315 PL Completed

XCL-23 - 51/52 PL Completed

XCL-23 - 188/189 PL Discontinued

Set Up Still #937

6" hipod column

15 theoretical plates

charged	300g (as received)		Reflux ratio
Cuts:	Int.	420	10/1
	420	550	10/1
	550	850	Total take off
	850	Btms.	----
Pressure:	Int.	420	100 mm
	420	550	100 mm
	550	850	0.3/0.5 mm

Runs on above still at stated conditions.

Run #1 BCL-22 - 50 PL & XCL-23 - 189 PL Blend

#2 BCL-22 - 50 PL & XCL-23 - 189 PL Blend

#3 BCL-22 - 50 PL & XCL-23 - 189 PL Blend

#4 BCL-22 - 50 PL & XCL-23 - 189 PL Blend

#5 BCL-22 - 50 PL & XCL-23 - 189 PL Blend

#6 BCL-22 - 50 PL & XCL-23 - 189 PL Blend

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Attachment 4

Solvent Separation

Modified Wilsonville Procedure W

Appendix III

Total Product

Solvent Separation

Modified Wilsonville Procedure

W

A) Oils - Soluble material in pentane-benzene (10:1) during the precipitation of the benzene soluble asphaltene.

B) Asphaltenes - Soluble material in benzene and insoluble by precipitation in pentane-benzene (10:1).

C) Preasphaltenes - Benzene insoluble-pyridine soluble material by solvent extraction/filtration.

D) Residue - Pyridine insolubles.

Equipment Required: Same as that listed for Procedure A.

Safety Features: As described for Procedure A.

Sample Handling: As described for Procedure A.

Procedure

The laboratory equipment is prepared in the following manner:

a) Adjust and clean ultrasonic unit equipped with 1/2" horn with methylene chloride.

b) Put in place Millipore filter after taking weight of dry filter element. Ensure that all O-rings fit well with no leaks (test with n-pentane under 10 psi). Use Teflon tape (3/4") to wrap screw fittings and seals.

c) Prepare rotovapor-bath temperature at 55-60°C for n-pentane; nitrogen flow rate should just cause 1/4-1/2" dimple in liquid of 250 ml flask.

d) Cooling liquid for rotovapor condenser should be less than 10°C.

Step 1 Tare a 150 mL pyrex beaker, add 5 grams read to ± 0.005 grams of the desired total coal-derived product. Add approximately 100 mL benzene and sonicate 10 minutes with the 1/2" horn at power level 7.

Step 2 Tare filter element and prepare filter unit. Pour supernatant benzene soluble into filter and catch in tared 1 L receiving flask.

Step 3 Add 100 mL portions of benzene and sonicate 2-4 minutes to rapidly extract benzene solubles. Repeat this step 4 times. Each supernatant is passed through filter and recovered.

Step 4 At the 5th wash pour all beaker contents into filter and rinse beaker with 100-200 ml benzene in 50 mL portion.

Step 5 Continue benzene extraction via filter apparatus for 2.5 L, or until slight color remains - 3.5 L.

Step 6 The benzene insolubles are extracted with 3 L of dry pyridine that has been warmed to 60°C. Catch in a tared flask.

Step 7 The pyridine insolubles are washed with 200 mL methanol, and 100 mL methylene chloride followed by a nitrogen flush for 15-20 minutes to remove excess solvent. The filter is removed, weighed and residue recovered.

Step 8 The pyridine solubles are recovered for pyridine on a rotovapor RE under nitrogen gas, 1/2" dimple, at 90-100°C waterbath temperature. Preasphaltenes are recovered after being washed with 200 mL methanol and dried.

Step 9 The benzene solubles are reduced in volume of benzene to approximately 50 mL. A 1 L beaker is filled with 500 mL n-pentane and placed ready to be sonicated, 1/2" horn.

Step 10 The concentrated benzene solubles are decanted into the n-pentane while the sonic power is at 3. The original flask may be washed with 10 mL benzene to remove any material and washed with n-pentane, 50 mL.

Step 11 The oils are recovered by filtering the mixture created in Step 10 through a 5 millipore filter. The insolubles are washed with 500-1000 mL pentane. Oils are finally recovered by rotovap under nitrogen at 60°C. To ensure benzene removal flask must be rotating 5-10 minutes past the last drop of material condensing. Check by GC for NMR for benzene removal.

Step 12 Asphaltenes may be recovered from the filter, or better washed out with 250 mL benzene. Benzene is removed by rotovap and nitrogen flow at 75°C to just 10-20 mL. The tared flask is then frozen in liquid nitrogen and the benzene sublimed under vacuum (1 mm Hg) for 1-2 hours.

Losses are due to removal of light ends from oils or transfer error. If transfer error can be reduced by experience the loss may be assigned to the oils to complete the material recovery.

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Attachment 5

Statistical Comparison of

Three Solvent Separation Procedures

PROCESS SYSTEMS GROUP

DEVELOPMENT PROJECT REPORT

APRIL/MAY/JUNE 1980

TITLE: Energy Systems Department

PROGRAM AREA: X

PROGRAM MANAGER: J. C. Tao

87-1-X716 - PECO Demonstration Plant - Development

Support of the Marcus Hook project continued throughout this reporting period. The programming for CYCSYN simulation of the overall facility was completed and decisions were made on the minicomputer scanning frequencies, storage, transmission and reporting requirements. Writeups for the Technical Manual were issued. The development plan and budget are under review.

87-1-X024 - Solid/Liquid Separation

It is anticipated that Dr. Doohee Kang will be available to assume responsibility for this project in first quarter FY '81, assuming that the program continues to be funded. The Boll-Kirsch candle filter is now on-site at the Emmaus facility and installation will proceed shortly. Efforts are underway to procure the necessary laboratory equipment and supplies to facilitate start-up in early FY '81. It is felt that alternative laboratory facilities will be required in the longer term as the program develops.

87-1-X023-02 - Coal Liquids Analysis

Activity during this reporting period concerned the comparison of three analytical procedures - conventional distillation and two solvent extraction techniques - used to fractionate coal-derived liquid products. The results indicate that, although a simple elemental analysis does not reveal appreciable differences between the fractions produced by each procedure, a more detailed investigation of the chemical and physical properties of the materials indicates appreciable dissimilarity. It was also found that prolonged exposure of coal liquids to relatively high temperatures during the distillation procedure effects changes in molecular composition and boiling range of the starting material.

87-1-X705 - Applications of SRC as Anode Coke

A petrographic laboratory for the optical characterization of coals and carbon products is being set up in Allentown Labs. Sample preparation equipment and a reflected light microscope photometer equipped for photomicrography will be purchased in due course. Evaluation of apparatus for small-scale carbonization of coking feedstocks is underway.

PROCESS SYSTEMS GROUP

DEVELOPMENT PROJECT REPORT

APRIL/MAY/JUNE 1980

TITLE: Coal Liquids Analysis

PROJECT NO: 87-1-X023-02

PROJECT LEADER: F. K. Schweighardt

PRINCIPAL INVESTIGATOR: I. S. Kingsley

I. OBJECTIVE

The objective of this project is to establish standard procedures to characterize and analyze coal-derived materials from process studies at Trexlertown and to support the ICRC SRC-I demonstration plant program.

II. DESCRIPTION OF WORK

Activity during this reporting period concerned the statistical comparison of three analytical procedures that can be used to fractionate a total coal-derived liquid. Selection of the procedures was based upon methods currently practiced that can best simulate the separation of the Wilsonville pilot plant product stream, i.e., distillation to recover recycle solvent and solvent extraction to recover solvent refined coal from residue.

III. RESULTS SUMMARY

The results of our investigation show that each procedure produces subfractions that are individually different into themselves - oils/distillate - asphaltenes - preasphaltenes - SRC oils - residue. In comparing similar subfractions we find many more differences than similarities. The similarities in elemental compositions may be attributed to the precision of the methods employed as well as to the continuum of molecular species present in coal-derived materials. The continuum of composition in particular makes a clean cut-point nearly impossible without high efficiency procedures/equipment.

Differences are apparent both on the molecular level and the overall subfraction level. We observe that the number average molecular weights for the distillate is less than the solvent separated oils, and that fractionation Procedure A using only n-pentane, gave oils of smaller molecular weight than those produced from Procedure W where n-pentane:benzene (10:1) was used. This can be attributed to larger molecular species being co-solubilized with the addition of benzene. The preasphaltene molecular weight is greatest for the distillation procedure. We can attribute this to possible repolymerization of oils + asphaltenes during the prolonged (6-10 hours) heating of the total sample. Refractive index measurements also confirm that the oils/distillate from each procedure are different and agree to the same order as the molecular weight.

Gas chromatography used for both simulated distillation and molecular profiles for identification show that the distillate contains more light (IBP-420°F) material but does not achieve an endpoint of 850°F. In comparing the solvent separated oils, both procedures produced materials that gave higher boiling points but could not duplicate the boiling range of an authentic continuously distilled recycle solvent from the Wilsonville pilot plant. A forced high temperature distillation was conducted and it gave an endpoint only 40°F less than the recycle solvent, and the distillate yield increased from 66 to 72%. The heavy distillate fraction (550-850°F) was the only fraction to increase. Gas chromatography has shown that the oil material left behind by our distillation, i.e., the oil associated with the SRC, contains mostly large 3 and 4 ring polynuclear aromatic. The composition of this SRC oil is less polar than either the oils or the asphaltenes.

Nuclear magnetic resonance has provided some structural information on the oils and distillate subfractions. Our calculations indicated an average ring size of two and that nearly one-third of the available ring sites were alkyl substituted, while approximately 1-2% of the sites had hydroxyl groups (phenols) attached. An additional 1% of the available ring sites occurred as ether oxygens. The hydroaromatic character of the oils was similar for the distillate and Procedure A, while the oils from Procedure W were slightly less hydroaromatic in nature.

In general, the distillation procedure gave a distillate that was chemically and physically reproducible, but a bottoms that may have undergone repolymerization as evident from the analytical characterization. The distillation procedure can produce a reasonable oil product that approximates to a Wilsonville recycle solvent. It should be noted that our starting sample is generated in a 50 lb/day CPDU and not the pilot plant. The degree of conversion and severity for this sample may be less than that achieveable elsewhere.

The solvent separated preasphaltenes and residue were (chemically) very similar, giving the same recovered value and ash content, while the oils and asphaltenes exhibited different chemical and physical properties. The differences, as discussed, are attributed to the type of solvent used to isolate them.

Our recommendations would be to distill the total product liquid in such a manner as to reduce repolymerization (lower pressure) and to isolate the gross pyridine solubles by ultrafiltration followed by Procedure W to reclaim the total SRC and to improve the relative distribution of asphaltenes/preasphaltenes. This would serve to increase the apparent precision of the method.

The formal report is available through CRDD on request from the authors.

PROCESS SYSTEMS GROUP

DEVELOPMENT PROJECT REPORT

APRIL/MAY/JUNE 1980

TITLE: Coal Liquids Analysis

PROJECT NO.: 87-1-X023-02

PROJECT LEADER: F. K. Schweighardt

PRINCIPAL INVESTIGATOR: I. S. Kingsley

ABSTRACT:

The third quarter was devoted to evaluation of three analytical procedures for laboratory reproducibility and comparison of the resulting fractions for differences in molecular composition. Procedures were selected on the basis that the method be currently practiced, and that the fractions best simulate the separation of the Wilsonville pilot plant product stream, i.e., distillation to recover recycle solvent and solvent extraction to recover solvent refined coal from residue. As a model we chose the recycle solvent from the Wilsonville pilot plant that is continuously distilled to give a near 850°F end-point. By using simulated distillation and other analytical techniques we compared each solvent defined oil or batch distillate to the model recycle solvent.

The results of our investigation show that each procedure produces five fractions that are chemically and physically different - oils/distillate - asphaltenes - preasphaltenes - SRC oils - residue. In comparing the fractions from each procedure we find many more differences than similarities. The similarities in elemental composition may be attributed to the precision of the elemental analysis (CHONS) methods employed as well as to the continuum of molecular

species present in coal-derived materials. The continuum of composition in particular makes clean cut-points nearly impossible without greatly increasing the efficiency of the procedures and equipment.

Differences are apparent both on the molecular level and the overall fraction level. We observe that the number average molecular weight for the distillate is less than that for solvent separated oils, and that the pentane soluble oils from Procedure A had a smaller molecular weight than Procedure W oils which were soluble in n-pentane: benzene (10:1). This can be attributed to larger molecular species being co-solubilized with the addition of benzene. Increase in refractive index measurements confirm that the oils/ distillate from each procedure are different and also confirm the observed increase in molecular weight. The preasphaltene fraction recovered from the distillation procedure had a higher molecular weight than the preasphaltenes recovered from the solvent fractionation procedures. We can attribute this to possible repolymerization of oils - asphaltenes - preasphaltenes during the prolonged (3-6 hours) heating of the total sample.

In general, the distillation procedure gave a reproducible distillate yield, but a bottoms (850°F+) that may have undergone repolymerization as evident from our analytical characterization. The distillation procedure can produce an oil product that nearly resembles a Wilsonville recycle solvent, if special heating conditions are used.

The solvent separated preasphaltenes and residues were similar giving nearly identical yield and ash content, while the oils and asphaltenes exhibited different chemical and physical properties. The differences, as discussed, are attributed to the solvent composition used to isolate them.

It must be kept in mind that our starting sample is generated in a 50 lb/day CPDU and not a six ton per day pilot plant. The degree of conversion and severity experienced by our sample may be different than that achievable elsewhere.

Table of Abbreviations

mg = milligram
mL = milliliter
μL = microliter
L = liter
°C = degrees celsius
°F = degress fahrenheit
cm = centimeter
nm = nanometer
mm = millimeter
D = diameter
OH = hydroxyl group
NH
= amine group
NH_2
β = beta
α = alpha
σ = sigma
MHz = megaherz
IBP = initial boiling point
cfm = cubic feet per minute
psi = pounds per square inch
Hg = mercury
$\bar{n}$Mwt = number average molecular weight
C = carbon
H = hydrogen
O = oxygen
N = nitrogen
S = sulfur
SD = standard deviation
ppm = parts per million
L = light ends IBP-420°F

K = middle distillate 420-550°F

D = heavy ends 550°F-FBP

Asphalt. = asphaltenes

Preasphalt. = preasphaltenes

atm = atmosphere, 14.7 psi

LHSV = superficial liquid hourly space velocity

wt = weight

CSTR = continuously stirred tank reactor

CPDU = Coal Process Development Unit

I. INTRODUCTION

The third quarter was devoted to evaluation of three analytical procedures for laboratory reproducibility and comparison of the resulting fractions for differences in molecular composition. The three procedures were selected on the basis that their fractions could best represent the product streams as they will be isolated in the commercial SRC demonstration plant. The results of this investigation will help us to establish a standard procedure to separate coal-derived material and permit us to relate liquefaction behavior in our process development units with the Wilsonville pilot plant and ultimately to the commercial scale plant.

II. PROJECT OBJECTIVE

The objective of the overall project is to establish analytical procedures to effectively characterize coal-derived materials from process studies at Trexlertown that will relate directly to materials derived from the commercial SRC plant. This program supports the International Coal Refining Company SRC demonstration plant program. Other objectives are to coordinate the interaction of the various CRDD-CPDU programs with CRSD staff, to interact with Wilsonville pilot plant staff and to join their activities with CRDD.

III. Sample Selection

Selection of the prime sample for this study was made to best represent a total coal liquefaction product (liquids, solids, and mineral matter) and not a subfraction (distillation overhead or underflow). The sample, XCL-23-169, was generated in the CRDD-CPDU from the conditions listed below:

XCL-23-169 Process Conditions

Hydrogen pressure	170 atm (2500 psi)
Temperature	454°C (850°F)
LHSV	2.0 $hr.^{-1}$
Hydrogen	2.2 wt.% slurry
Feed	30% Pyro Ky. #9 coal
Solvent	70% Wilsonville process solvent

IV. Separation Procedures

The three procedures chosen for evaluation, D (distillation), A (Air Products) and W (Wilsonville), are outlined in schemes I-III. The details of each are given in Appendices I, II, and III. Each procedure was discussed with the technical staff two weeks in advance to familiarize each person with the details of the laboratory operation. To gain experience with the three procedures, product liquid samples taken from earlier times in the same run (XCL-23) were used.*

Procedure D: Because distillation will be the primary means by which recycle solvent and other coal-derived liquids will be separated from the SRC-I demonstration plant product stream, it is important to be able to duplicate that process step in the laboratory for quality control. At the Wilsonville pilot plant a continuous distillation unit removes the -850°F liquids so that the bottoms may enter the solids separations unit, presently a Kerr-McGee critical solvent deasher.

*The time of analysis is defined as the overall elapsed time to set-up, carry out and report the analytical results.

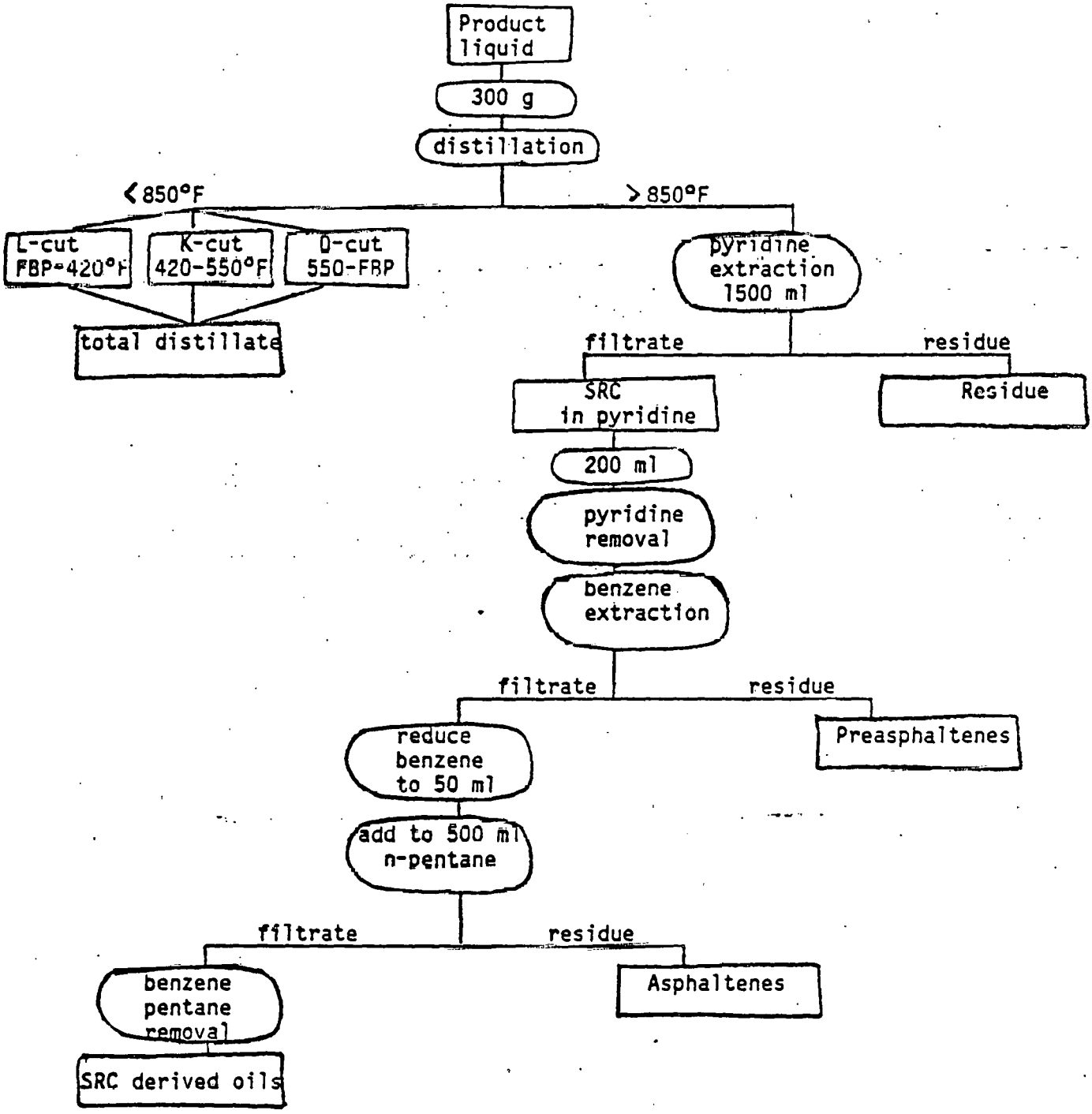
In the Wilsonville laboratory batch distillation high vacuum (.5 mm Hg) is used to remove the liquid products. The resulting bottoms are extracted with cresol to isolate unconverted residue/minerals (cresol insolubles) from the converted product, SRC. SRC is then solvent separated to isolate SRC-oils, asphaltenes and preasphaltenes by Soxhlet extraction. The solvent separation procedure as performed at Wilsonville is given in Appendix IV.

As performed at Wilsonville the entire procedure takes 4-5 days and a material balance is achieved by calculating the preasphaltenes by difference.

We have modified the Wilsonville procedures to achieve a direct measure of each fraction for material balance and decreased the laboratory time by using ultrafiltration and sonication in place of Soxhlet extraction. The procedure we adopted involves a flash distillation of 300 gram of the total product liquid taking cuts IBP-420°F and 420-550°F under 100 mm Hg, and 550 to ~850°F end-point at 0.5 mm Hg. The bottoms are pyridine extracted to give the soluble SRC with rejection of the insoluble organic matter (IOM) and mineral matter. The SRC is freed from pyridine and extracted with benzene by ultrasonic agitation and filtered through a 5 micron Millipore filter. Benzene insolubles on the filter are recovered as preasphaltenes. Asphaltenes are obtained by precipitating them from 50 mL of benzene in 500 mL n-pentane. The oils are therefore the n-pentane:benzene (10:1) solubles that are recovered by removing the solvent mixture by rotovap under nitrogen at 70°C. As described in Scheme I and detailed in Appendix I and III the distillation/separation procedure requires a total of 22 man-hours.

The batch distillate portion, IBP-850°F, will be compared to the Wilsonville recycle solvent obtained via continuous distillation and the solvent separated oils to be described.

Scheme I. Product Liquid Separation Procedure D

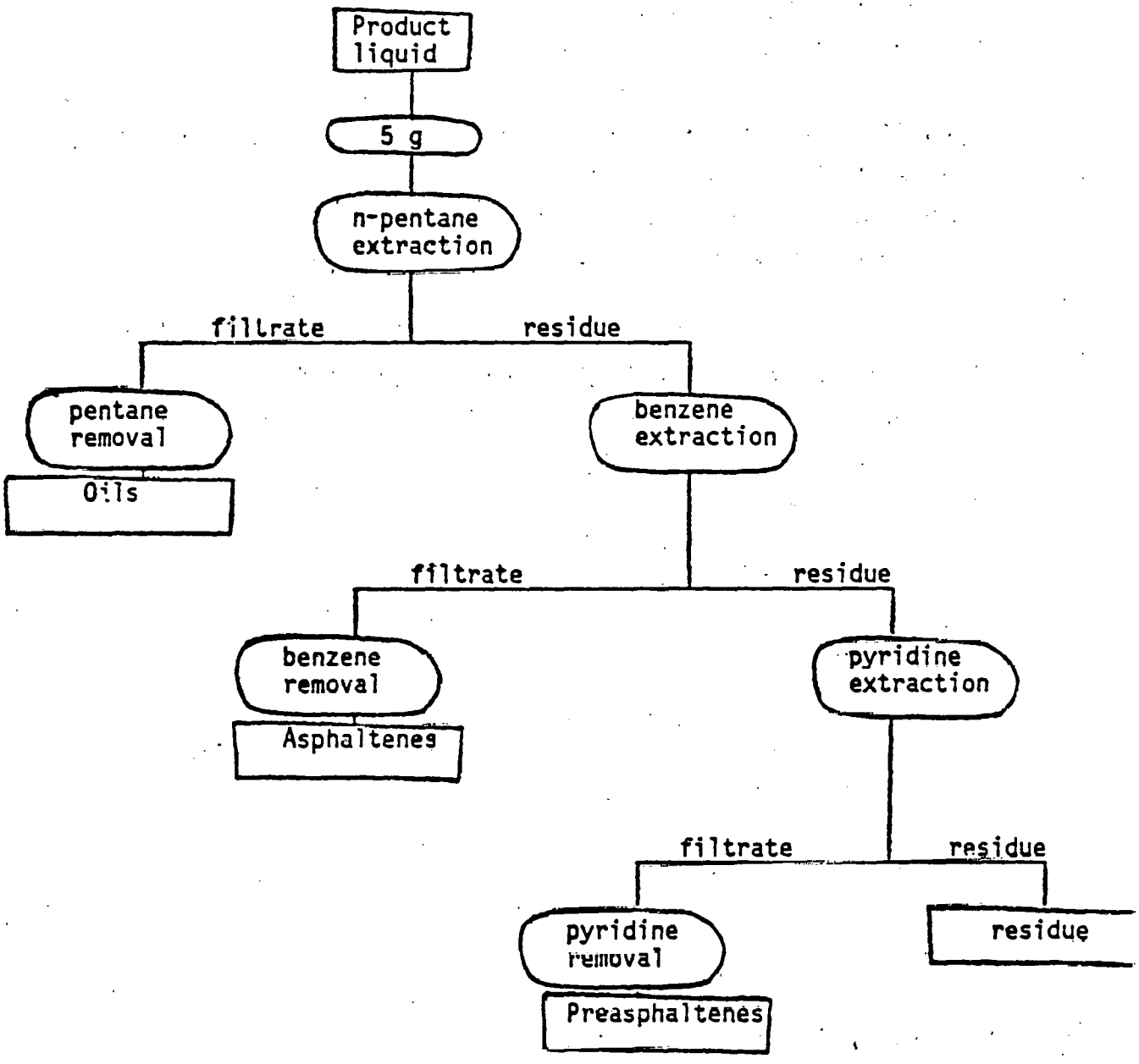


Procedure A: Another approach to coal product separation is the isolation of the oils, asphaltenes, preasphaltenes, and residue as various solubility classes without prior distillation. The total product is handled directly and fractions are isolated in sequences as soluble in and not as a precipitate from a particular solvent or solvent pair to reduce co-solubility and co-precipitation effects.

Procedure A is considerably different than Procedure D and attempts to simulate in quantity and composition the continuously distilled recycle solvent from Wilsonville or the batch distilled material (Procedure D). Scheme II outlines the procedure and Appendix II details the laboratory work-up. In general 5-8 grams of the total product is frozen in liquid nitrogen to achieve a homogenous sample that can be crushed to a fine powder in the inert atmosphere. Pentane is added to solubilize the oils and ultrasonic agitation is used to extract the oil from any solid matrix. The pentane solubles are filtered away using a five micron Millipore filter unit. Extraction and sonication with addition of n-pentane are continued in 500 mL portions until the filtrate is clear, 2-3 liter. Once the oils have been removed benzene is used to extract the asphaltenes. Pyridine is subsequently used to extract preasphaltenes in a similar fashion. Solvents are removed under nitrogen and fractions weighed for direct material recovery. This procedure requires 10-12 hours to perform.

Procedure W: The separation procedure commonly practiced at the Wilsonville pilot plant, Method #34550-3 referenced to Consolidation Coal Company Procedure #44 (12/30/59), Appendix IV, requires that the starting sample be a distillation bottoms free of cresol insoluble matter. In the operation at the Wilsonville pilot plant samples taken at plant site V110 (distillation feed) are first laboratory vacuum distilled to achieve an 850°F end point. These distillation bottoms are cresol extracted in a Soxhlet and the solubles are freed of cresol by distillation to give the starting material (SRC) for their solvent characterization. This procedure requires 3-4 days to complete.

Scheme II. Product Liquid Separation Procedure A

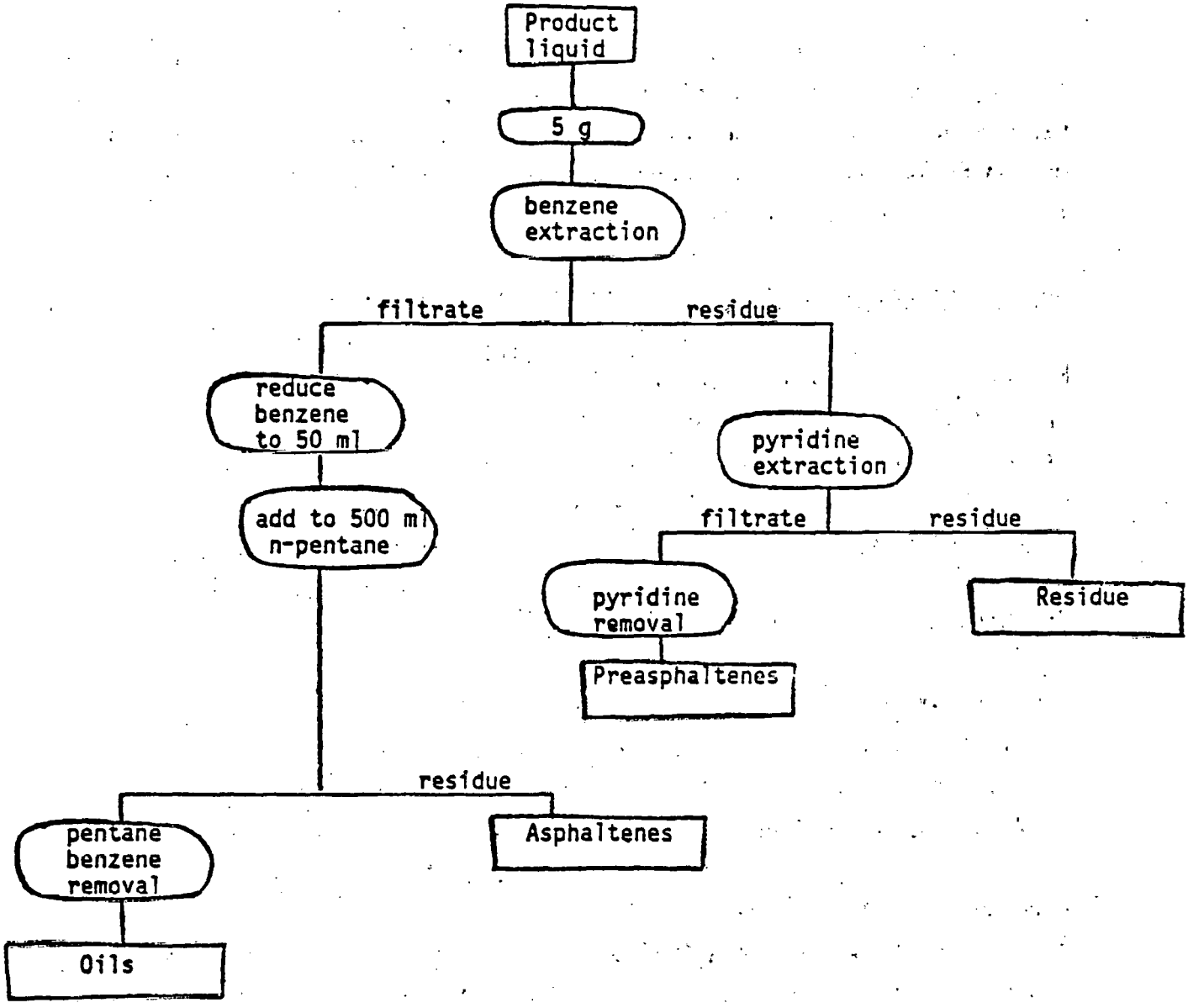


Because this procedure involves extensive Soxhlet extraction and not all materials are directly recovered and weighed we have chosen to substitute for this method as outlined in Appendix III, Scheme III. The total product is used as the starting material and we have substituted ultrasonic extraction/micro-filtration for Soxhlet extraction. In this manner we can reduce the overall separation time to approximately 10-12 hours, maintain the fraction distribution as found by Soxhlet extraction, and provide a high degree of reproducibility. Because this procedure uses benzene to solubilize the material and then precipitates the asphaltenes from a mixture of n-pentane:benzene (10:1) the chemical composition of the oils and asphaltenes may show significant differences when compared to the oil fraction of Procedure A.

Procedures D, W and A just described each provide operationally defined fractions that may be different in their chemical composition as well as the quantity of fractions recovered.* This investigation will attempt to compare the physical-chemical nature of fractions from each procedure. From this information we will decide upon the best analytical approach that will quantitatively relate to specific SRC demonstration plant product streams. We further wish to provide a flexible procedure that can be used in the CRDD-CPDU program that would quantitatively relate changes in the total coal-derived product as a function of change in process temperature, hydrogen pressure, residence time, coal:solvent feed ratio, added mineral matter or catalyst content.

*By operationally defined we mean that the order of analysis used in each procedure effects the distribution of components. For example, oils may be a distillate, a pentane soluble material, or a material first soluble in benzene that remains in solution when an excess of pentane is added.

Scheme III. Product Liquid Separation Procedure W.



Details of Analytical Workup

Product Analyses

- Elemental Analyses - Huffman Laboratories, Wheatridge, Colorado.

Direct determination was made on a micro (3-10 mg) scale for each element, carbon, hydrogen, oxygen, nitrogen, and sulfur. Duplicate determinations were requested for carbon, hydrogen and sulfur. Ash values were carried out on 50-100 mg samples according to ASTM (D-482) procedure, with temperature conditions for dry ash, 750°C.

- Number Average Molecular Weight - Huffman Laboratories.

Molecular weights were determined in methylene chloride or pyridine (preasphaltenes) at four concentrations in the range 1-10 mg/mL at 27°C or 50°C by vapor pressure osmometry (VPO). The reported number average molecular weights are extrapolated to infinite dilution to remove or reduce intermolecular interactions, e.g., hydrogen bonding.

- Functional Groups (OH, NH, NH_2) - APCI-CRSD.

A method was designed to quantitatively measure, by near infrared spectroscopy, the amount of OH, NH and NH_2 functional groups present in a sample of material soluble in methylene chloride (typically SRC liquefaction products) by comparison to reference materials.

A weighed amount of sample is dissolved in 10 mL of methylene chloride, transferred to a 1 cm path cell and measured by near infrared spectrophotometry. The molar absorbance of the OH, NH and NH_2 functional groups are measured at the wavelength maximum of OH (~2790 nm), NH (~2885 nm) and NH_2 (~2950 nm). Since the molar absorbance of each functional group in heterogeneous samples, such as SRC liquefaction products, is the average of many compounds containing one or more of the above functional groups, the peak maximum and the absorbance of any functional group is the average of all compounds having that one functional group. For the purpose of

this test the absorbance of each functional group at the wavelength maximum is assumed to be equal to that of β-naphthol (OH), carbazole (NH) or 1-aminonaphthalene (NH_2). These compounds are used as standard reference materials to estimate the weight percent of O as OH, N as NH and N and NH_2.

By comparing the NIR intensity of a sample to that of standard compounds, β-naphthol for OH and carbazole for NH, we find the example in Figure 1 has 1.44% OH and 0.17% NH. This sample contains 2.62% oxygen and 0.66% nitrogen by elemental analysis. By simple calculation we determine that 55% of the oxygen in the oils exists as hydroxyl, while only 26% of the nitrogen exists as NH. The other oxygen form (45%) is represented by cyclic ethers, and the other nitrogen form (74%) by pyridine-like, -N=, structures.

- Nuclear Magnetic Resonance - CRSD

Proton ('H) magnetic resonance spectra were taken at 60 MHz as 10% solutions in deuterated methylene chloride (CD_2Cl_2) at 35°C.

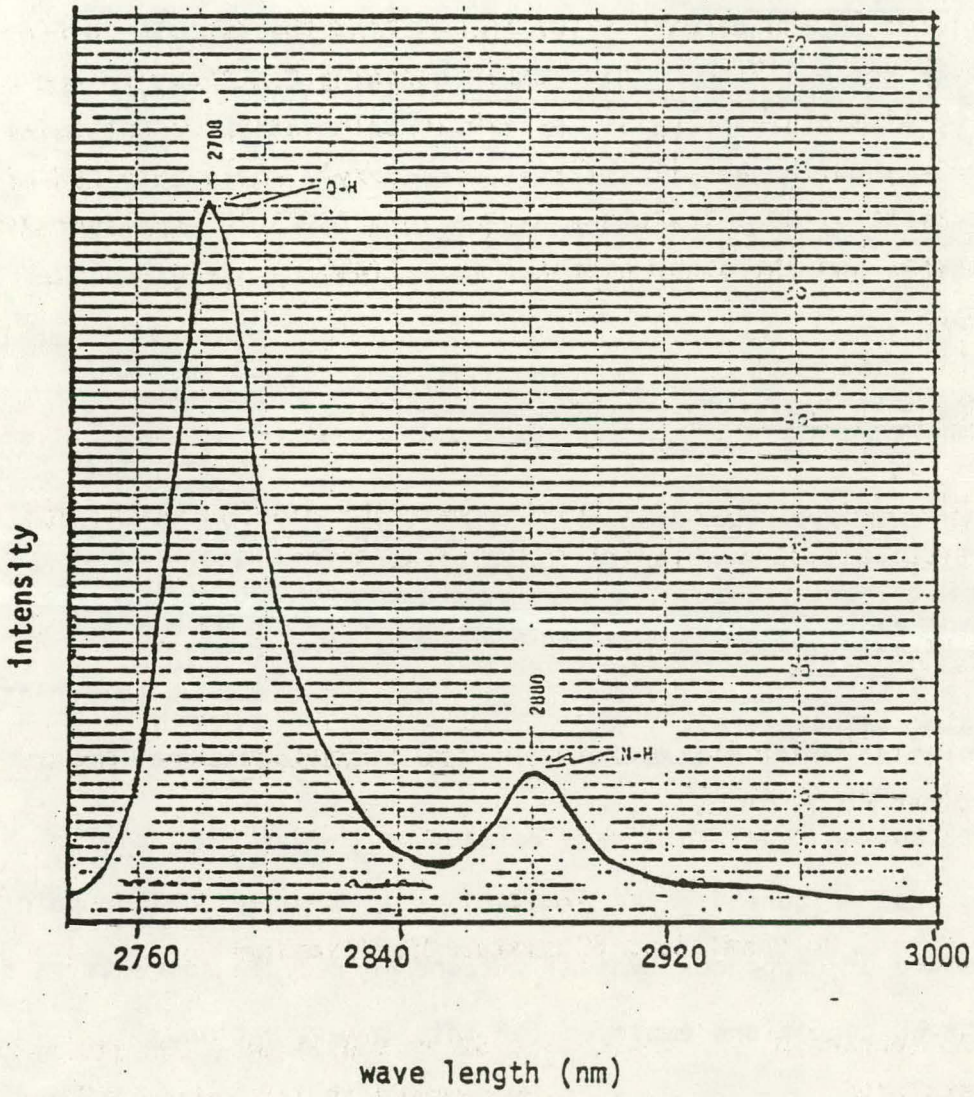
- Simulated Distillation - CRSD

Simulated distillation was measured by gas chromatography. The conditions used are given in Table 1.

Table 1
GC Conditions Simulated Distillation

Column length/ID	40.67 cm x 6.35 mm (1.33 ft. x 1/4")
Temperature	Programmed at 11°C/min - 30°C to +380°C
Detector	Thermal conductivity
Carrier Gas	Helium
Flow Rate	50 mL/min
Sample Size	2 µL
Column Packing	Methyl silicon
Solid Phase	10% UCW 98
Liquid Phase	80/100 mesh arom-P-acid wash

Figure 1 Near Infrared scan of an oils-sample obtained by product-liquid separation procedure A.



A typical example of a standard aliphatic hydrocarbon (C_5-C_{40}) mixture used for calibrating the simulated distillation curve is given in Figure 2. Figure 3 represents a typical simulated distillation GC profile, while Table 2 lists the weight percent distilled as a function of temperature for a typical pentane soluble oil.

- Gas Chromatography - CRSD

The gas chromatographic separations were performed using the conditions below.

The gas chromatographic conditions were:

Detector	Hydrogen Flame Ionization
Liquid Phase	8% SP-2100
Solid Phase	Gas-chrom Q
Column Temperature	Programmed at +50°C for 10 min. then 5°C/min to 300°C
Sample Induction Temperature	150°C
Carrier Gas	Helium
Flow Rate	30 mL/min
Column Length/Diameter	4.07 m x 4.8 mm OD (10 ft x 3/16")
Sample Size	0.9 µL (microliter)
Detector Temperature	310°C
Calculated Theor. Plates	2668 per meter

The retention times (Rt) were related to the boiling point of the respective compounds. Figure 4 gives a relationship between boiling point and structure of compounds typically found in recycle solvents as determined by the GC conditions employed for this investigation.

- Refractive Index - Huffman Laboratories.

Refractive index was determined as either transmittance or reflectance of light by the neat sample at 30°C. The values are precise to three significant figures to the right of decimal. Both reflectance and transmittance

Figure 2. Simulated distillation chromatogram of a C_5 to C_{40} aliphatic hydrocarbon calibration mixture.

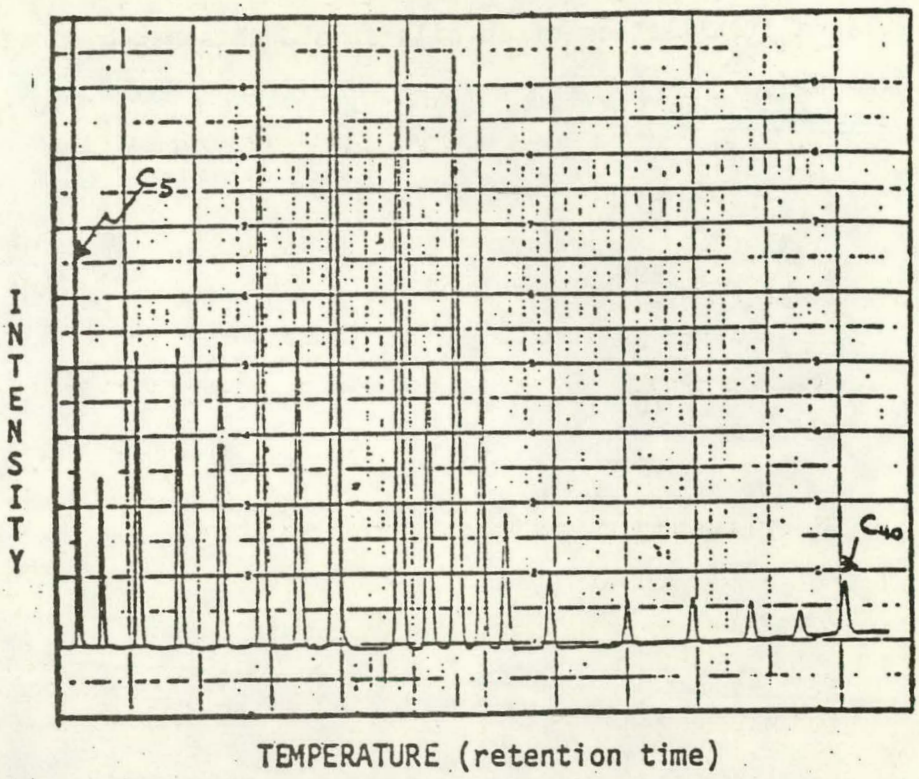


Figure 3. Simulated distillation chromatogram of a pentane-soluble-oils sample obtained by product liquid sparation procedure A.

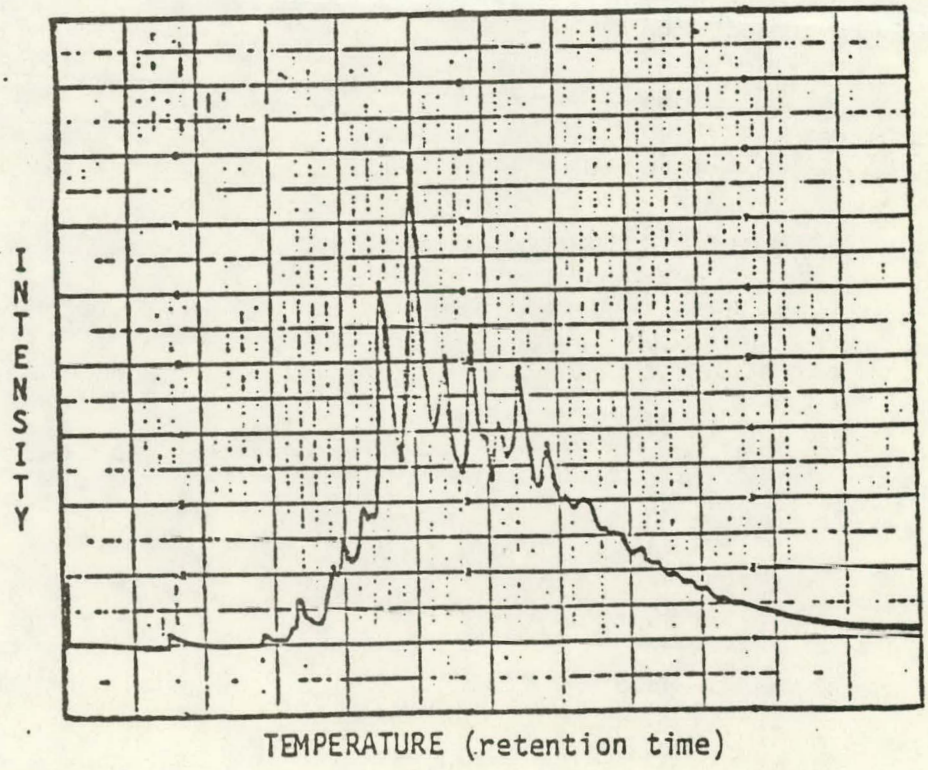


Table 2

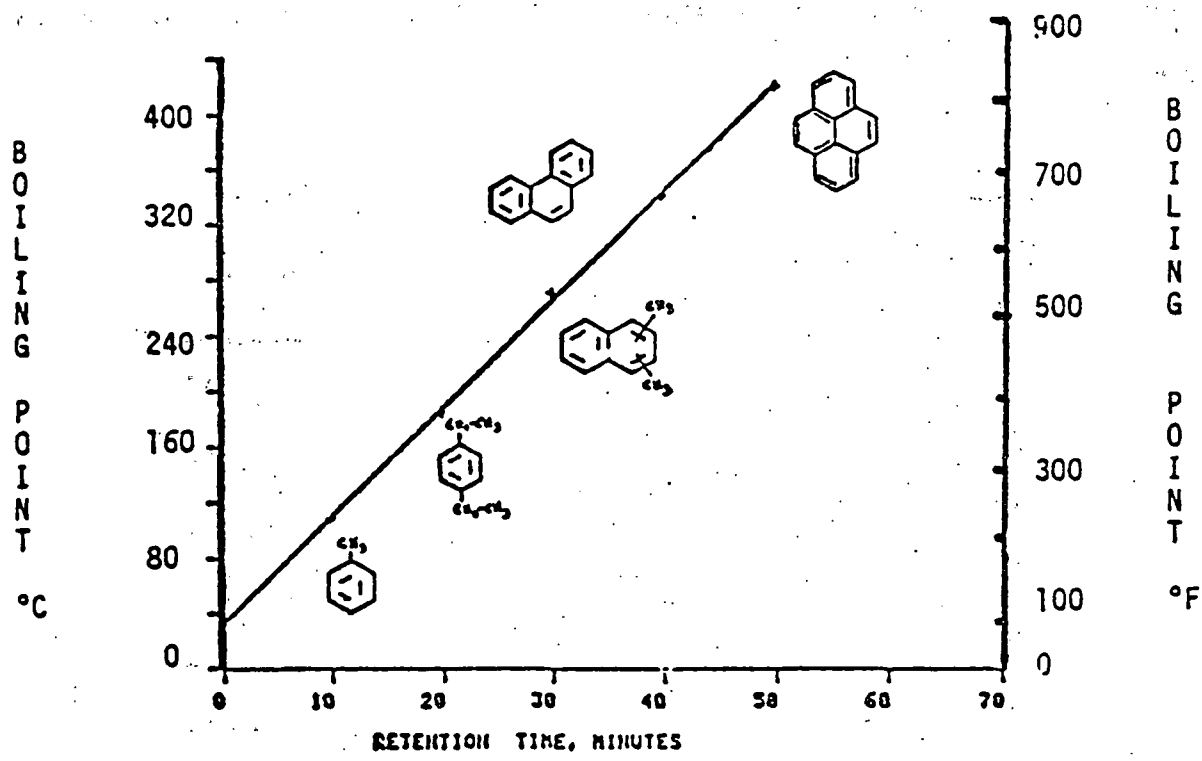
Simulated distillation of an oils-sample obtained by product liquid separation

Procedure A

% Off	Temp. °F
IBP*	359
5	415
10	445
15	457
20	473
25	486
30	493
35	506
40	522
45	538
50	555
55	571
60	592
65	610
70	631
75	653
80	682
85	715
90	758
95	832
99.5	999
100	1040

IBP* = .5%

Figure 4. Standard curve of gas-chromatographic retention time versus boiling point of polynuclear aromatic hydrocarbons found in coal liquids.



were used due to the opaqueness of some of the oils/ distillates. Refractive index provides an indication of composition and in particular the degree of conjugation such as found in polynuclear aromatic hydrocarbons.

V. RESULTS AND DISCUSSION

The results of this investigation will be presented as a series of comparisons between the three methods of separation, A, W and D. Data are all average values of at least 3 trials in each case. When more than three values were used it is noted on the table or figure.

During the course of the investigation no data points were omitted, unless a laboratory error occurred while performing the procedure. When such an error, e.g., lost sample, was reported the entire sample separation was repeated. Errors in subsequent elemental or nmr analysis for example, while harder to judge as being outside two values, were repeated once to allow it to fall within 10% of the other values. If the repeated value was not within 10%, the values were averaged as received.

In every case possible the technician who started an analysis completed it to maintain constant human bias in laboratory technique. Analyses were timed but no effort was made to stress rapid work-up to the technical staff.

Definition of fractions used in this study are:

1. The yield of solvent refined coal (SRC) will be defined as distillation bottoms (>850°F) that are pyridine soluble, while the solvent separation Procedures A and W will define SRC as the sum of asphaltenes and preasphaltenes.

2. Oils that are associated with the SRC (SRC-oils) will be reported separately (see Figure 5d). For Procedure D the SRC-oils are the bottoms material soluble in 10:1 pentane:benzene. SRC-oils from Procedure A are defined as the material soluble in 10:1 pentane:benzene from the asphaltenes. The value obtained from Procedure A is used for Procedure W.

3. The distillation Procedure D generates three subfractions of the total distillate (a) IBP-420°F, light ends; (b) 420-550°F, middle distillate; and (c) 550°-end point, heavy ends.

- Product Liquid Separations

A summary of the fraction yields for each separation of the total liquid/solid product is given in Figures 5a-c. Results are the average of three trials with material losses adjusted by normalization for Method D (loss average 2.5%) or by adding the total loss which presumably are light ends to the pentane soluble oils for both Method A (loss average 1.5%) and Method W (loss average 5%).

The oil yields are about 6% greater for the solvent separated procedures than the distillate. In order to determine if the distillation procedure was getting the full distillate as overhead we carried out a fourth distillation. In this case the entire unit was heat traced up to the distilling head and the end-point was determined when the 0.5 mm Hg vacuum broke due to decomposition and reached 2.0 mm. The yield of distillate increased from 66 to 72% with a simulated distillation end point 50°F higher than the three distillation average.

Sampling a coal-derived product for analytical characterization is a very difficult task due to the presence of mineral matter, suspended organic matter and liquid. Our sampling techniques involved two levels of sample withdrawal; (a) 300 gram from a 4 liter container, and (b) 5-8 gram from a 100 mL glass container. To test our sampling for each procedure a 5 gram sample was removed prior to running each procedure by each of four technicians. This gave us nine (9) independent samples from two containers - three from 4 liter and 6 from 100 mL containers.

Elemental analysis, Figure 6a-b, was run on each sample. We found that the ash content varied most at the 300 gram size. This is not unexpected due to the difficulty in mixing a 4 L container.

Weight percent distribution of the products.
Each is an average of three complete separations.

Figure 5a

Product Liquid Separation
Procedure D

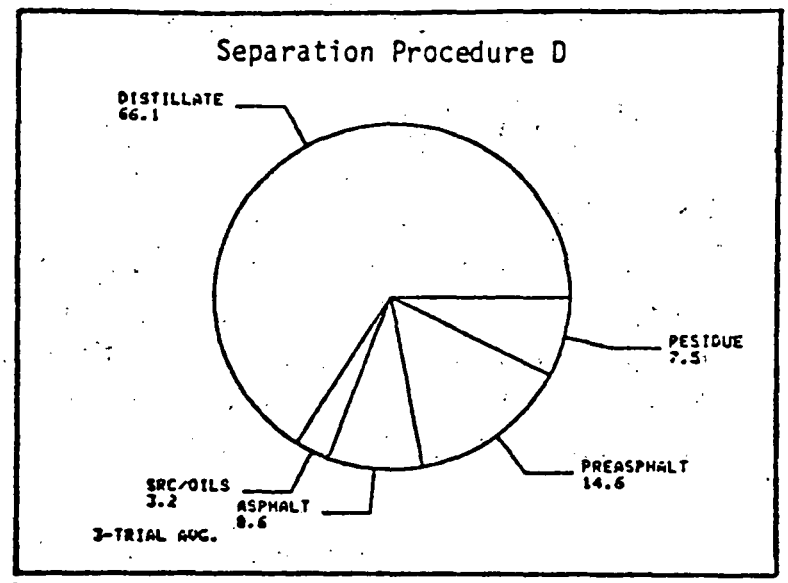


Figure 5b

Product Liquid Separation
Procedure A

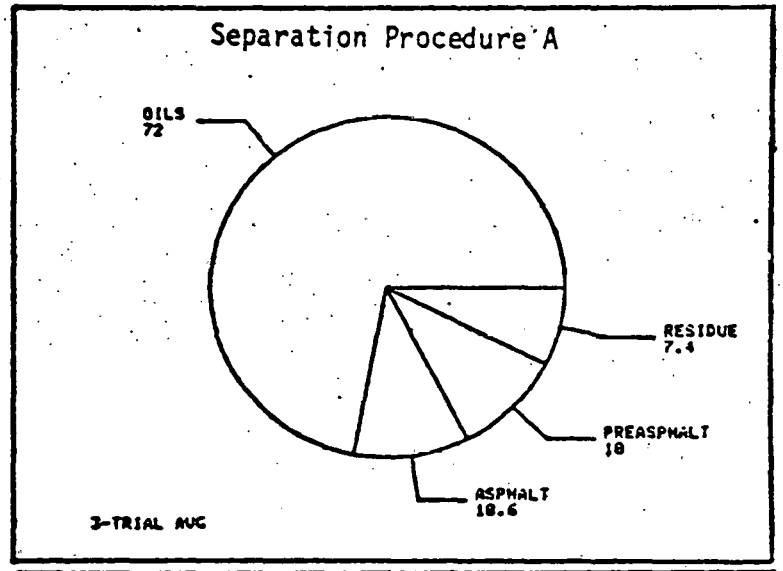


Figure 5c

Product Liquid Separation
Procedure W

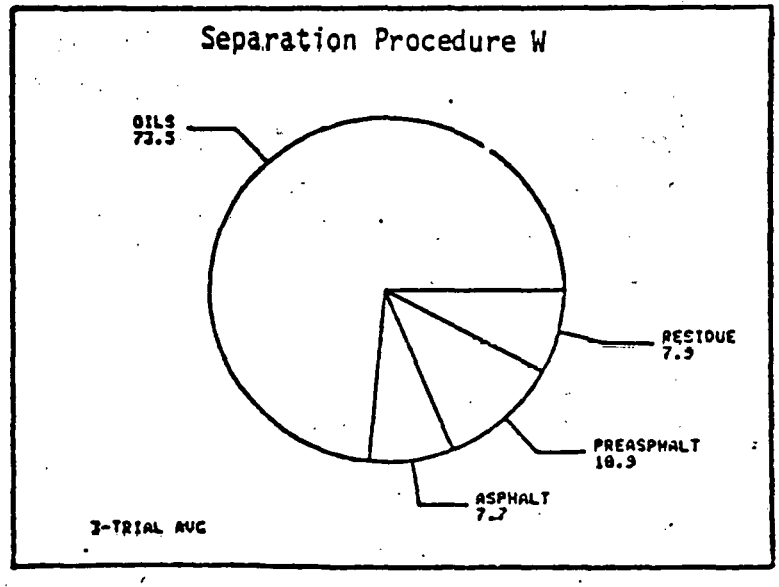
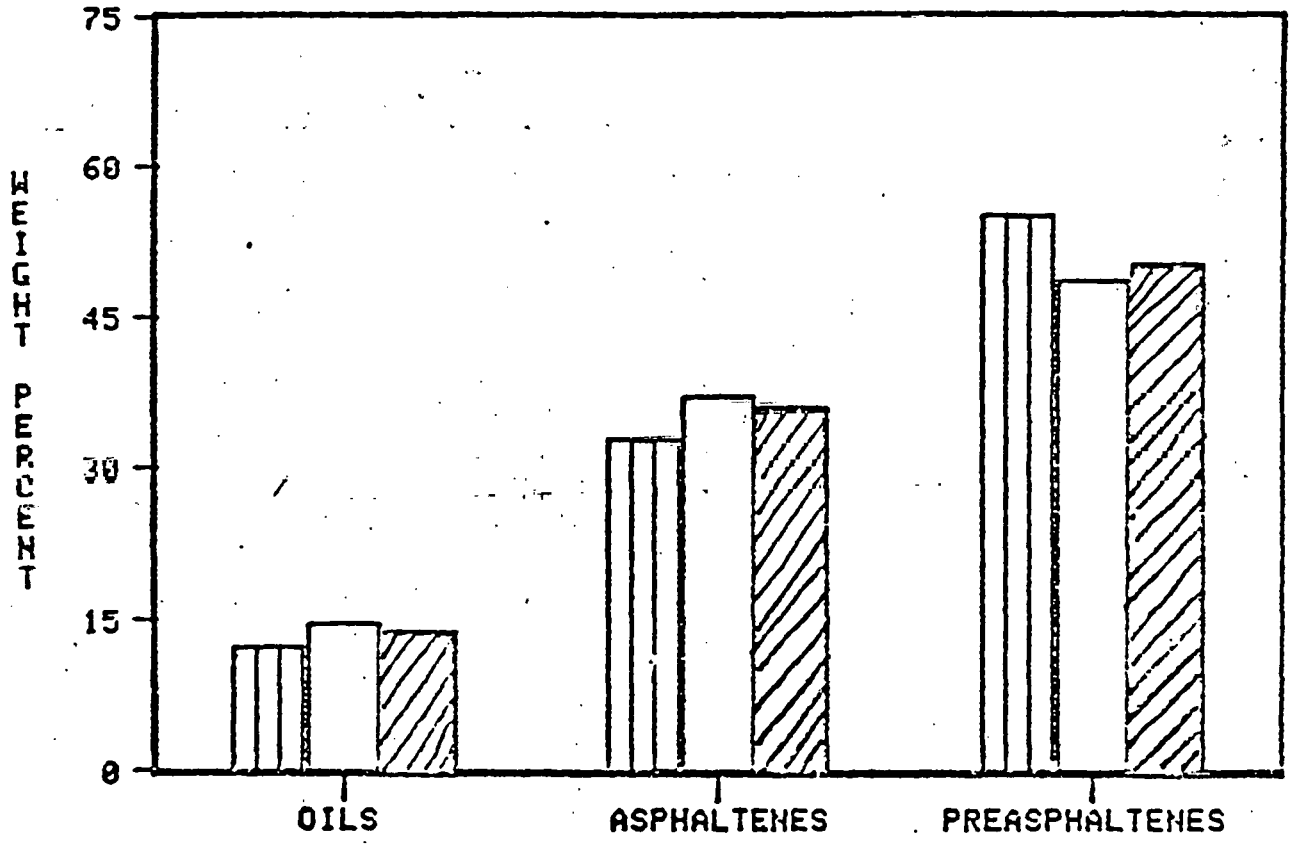


Figure 5d. Weight percent distribution of oils/distillate, aspnaltenes ana preaspnaltenes in tne SRC.



SRC FRACTION CALC.

Figure 6a

Comparison of the total starting product XCL23-169PL elemental and ash composition after normalization. The results are an average of nine samplings.

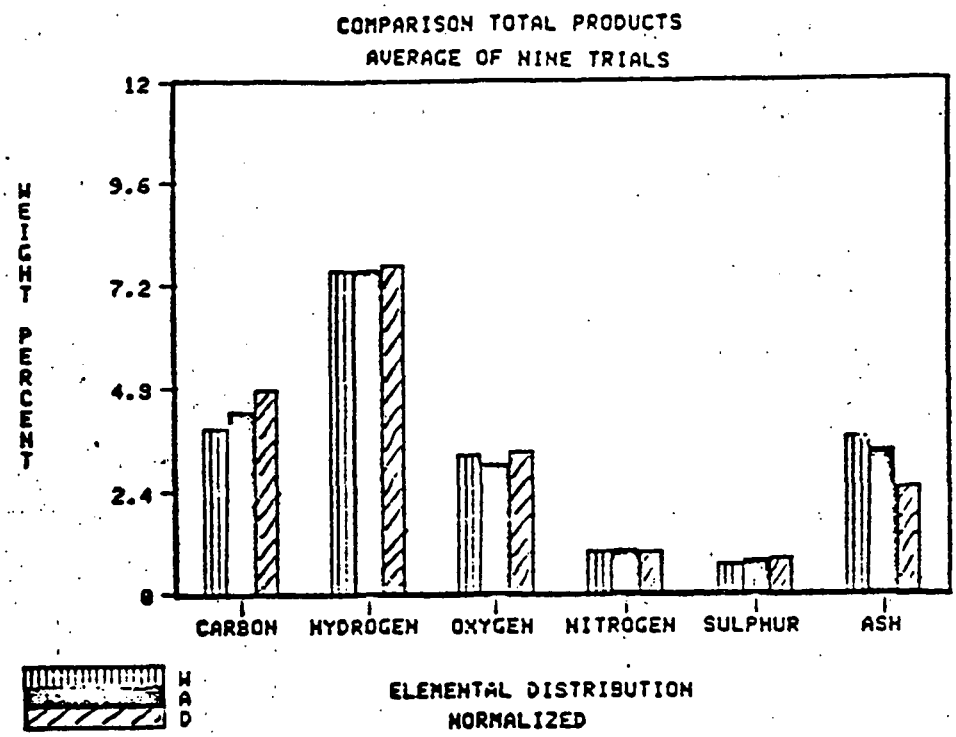
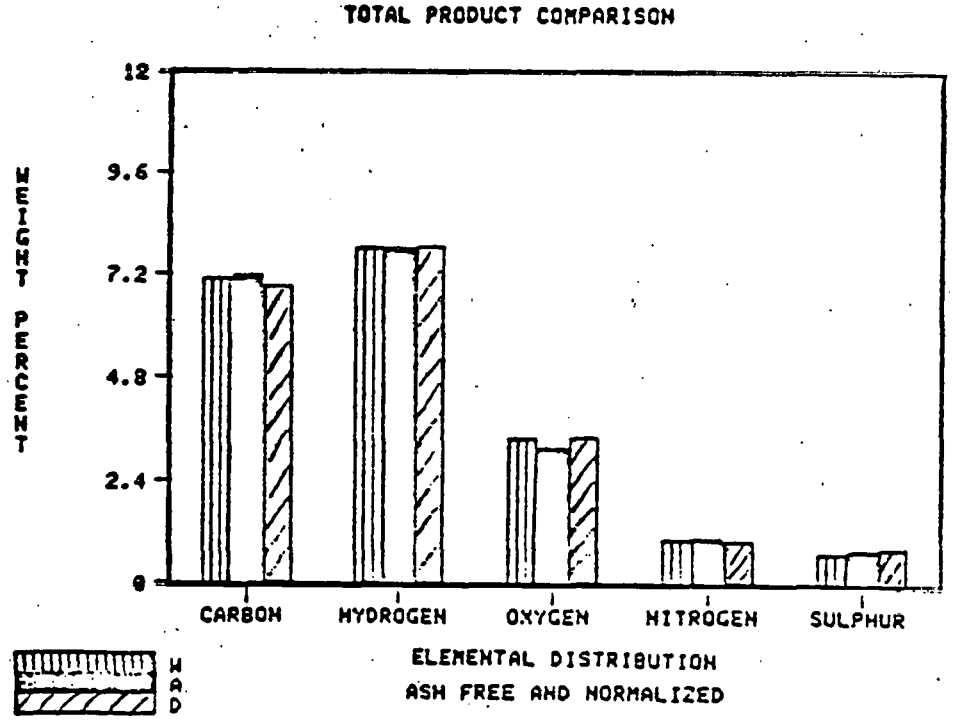


Figure 6b

Comparison as in Figure 6a of the calculated ash free results as an average of nine samplings.



It is interesting to find that when the elemental data is presented as ash free, Figure 6b, the distribution of CHONS is nearly identical. This may indicate that there is non-selective adsorption of soluble organic material on residue matter in the total product. We may assume that the relative distribution of oils-asphaltenes-preasphaltenes should be unaffected by poor sampling, but the weight percent of the residue fraction and resulting ash value would be in error.

The yield of preasphaltenes (Figure 5a-c) was found to be significantly greater from the distillation procedure (14.6%) than from either solvent extraction (10-11%). This is the first indication that prolonged heating during distillation may have caused an apparent repolymerization of oils and/or asphaltenes to form preasphaltenes.

The major product in SRC-I liquefaction is a solid that can be defined in terms of the distribution of SRC-oils, asphaltenes and preasphaltenes. The relative amounts of these components reflects the process that created it, and the process can be controlled to vary the proportion of components to give the desired SRC product.

The quantity of SRC-oils represent the depth and/or efficiency of the distillation and solids removal steps. If the distillation temperature or vacuum is increased, less SRC-oils remain. For the demonstration plant 5-10% oils are necessary in the SRC to achieve a good fluid phase for transport after distillation but prior to Critical Solvent Deashing. The SRC-oils are also important as a component of the SRC because the quality of the SRC, e.g. softening point, can be controlled with the oils content.

Chemically these SRC-oils are less polar than the distillate, are mostly 3-4 and 5 ring polynuclear aromatics, and have a number average molecular weight near 300. When isolated the SRC-oils appear as a heavy varnish with a slight aromatic odor.

SRC asphaltenes and preasphaltenes provide detailed information as to the coal liquefaction process. Asphaltenes have been found with molecular weights from 350-700, and preasphaltenes exhibit molecular weights from 800-3000. The range of molecular weight, heteratom content and carbon aromaticity of asphaltenes and preasphaltenes reflect the degree of liquefaction severity.

It is therefore important that the procedure to isolate and define these components does not change their distribution in the process.

Figure 5d gives the distribution of SRC/oils-asphaltenes-preasphaltenes in the SRC from the CPDU sample XCL-23-169 as determined by each of the three separation procedures, D, A, and W. The most oils and asphaltenes are found by Procedure A and the least by Procedure W. The yield of preasphaltenes was greatest by Procedure D and least by Procedure A. These differences correspond to changes that may have been generated as a result of the separation procedure on the total product. Batch distillation exposes the product to high temperatures (>600-650°F) for longer time (3-6 hours) than does continuous distillation (<1 hour). Repolymerization may have resulted and changed the relative composition of the asphaltenes and preasphaltenes.

Thus far we may summarize our observations:

- Oils will distill.
- Asphaltenes and preasphaltenes will not distill.
- Pentane soluble oils are nearly equivalent to a distillate.
- Batch distillation heating may cause repolymerization.

We will now define in detail the chemical characterization of each fraction from each procedure.

Table 2a summarizes the mean and standard deviation of the fractions for each separation method. Once the technical staff gained experience with a method the major sources of error were associated with poor mixing prior to sampling, and poor sampling for subsequent analytical characterization, such as for ash.

Table 2a

Means and Standard Deviations of Weight Percent (three trial average) for Each Fraction Obtained by the Three Separation Procedures

		Mean	SD
Method D	distillate	66.1	0.6
	SRC derived oils	3.2	1.2
	asphaltenes	8.6	0.5
	preasphaltenes	14.6	1.6
	residue	7.5	1.7
Method A	oils	72.0	1.4
	asphaltenes	10.6	0.9
	preasphaltenes	10.0	1.3
	residue	7.4	0.4
Method W	oils	73.5	0.2
	asphaltenes	7.7	0.9
	preasphaltenes	10.9	1.2
	residue	7.9	0.2

- Elemental Analysis

Each sample and fraction was submitted for elemental analysis. The total product liquid was sampled nine times and each aliquot analyzed. Figure 6a and b give the normalized and ash free elemental composition, respectively. Sampling of the total product caused significant error in ash content, yet the elemental distribution was unaffected.

Figure 7a,b,c compare the elemental distributions found in each fraction within individual procedures and contrasts them against the other. Notice that the trend in elemental composition in going from oils to asphaltenes, preasphaltenes and finally to residue within each procedure is nearly identical to that of the other two procedures, e.g., carbon and hydrogen decrease while oxygen, nitrogen, and sulfur increase. The absolute weight percents of the elements in each fraction are compared in Figures 8a,b,c,d.

Here we observe slight differences in the elemental distribution. The distillate/oils show the greatest similarity in elemental composition except for the oxygen content which is higher in the distillate. The functional group distribution of this oxygen will be discussed later.

The asphaltenes and preasphaltenes show definite trends in their elemental composition with an increase in carbon and a decrease in oxygen content comparing Method W vs. Method A vs. Method D. The elemental hydrogen distribution is nearly identical in all three cases. The data are presented as ash free because the preasphaltenes derived from the distillation Procedure D contained mineral matter. On the average the "as received" elemental data gave the same trends for the oils and asphaltenes where no ash was present.

The distribution of sulfur and nitrogen in nearly all fractions is uneventful.

Figure 7

Elemental analysis results after normalization for ash-free composition., obtained on the subfractions of the three separation procedures.

:gure 7a

Separation Procedure D

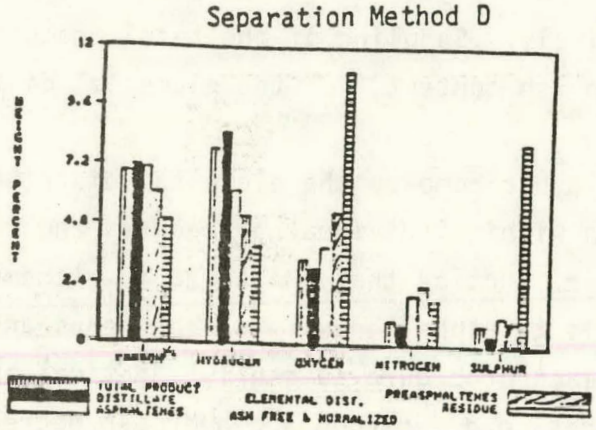


Figure 7b

Separation Procedure A

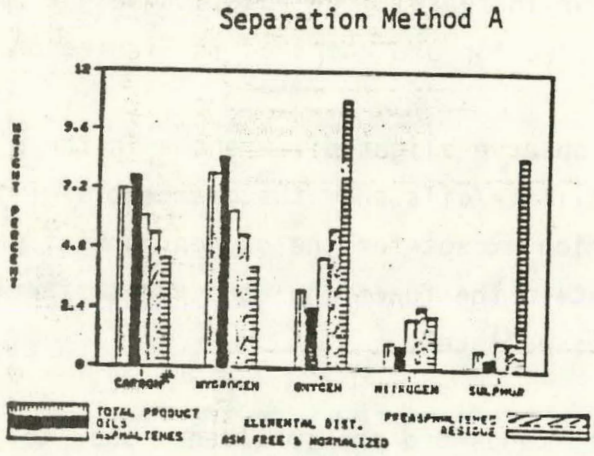
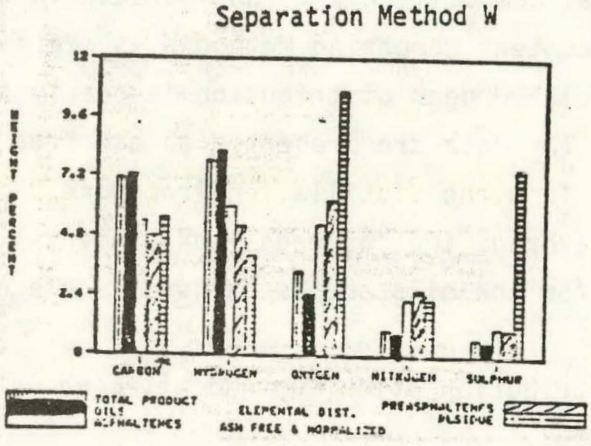


Figure 7c

Separation Procedure W



* The ordinate for weight percent carbon starts at 80 for all fractions except the residue where it represents 70 weight%.

Figure 8

Comparison of oils (a), asphaltenes (b), preasphaltenes (c) and residue (d) for their elemental distribution as a function of the separation procedure employed. (three trial average)

Figure 8a

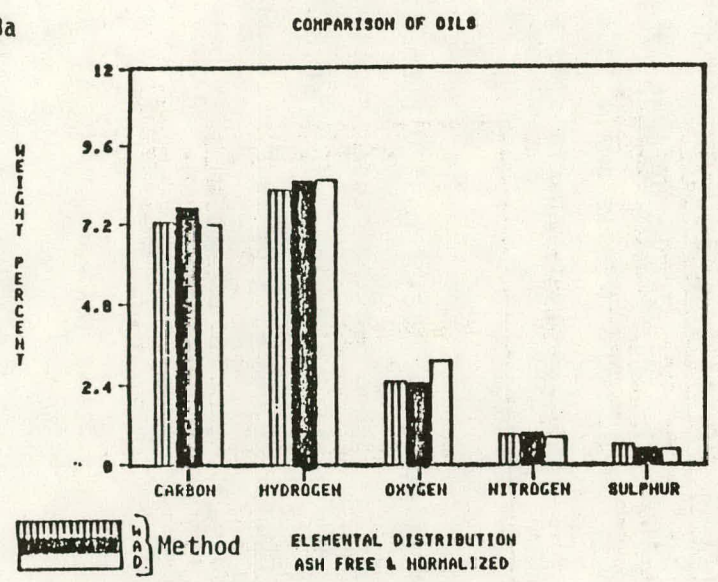


Figure 8b

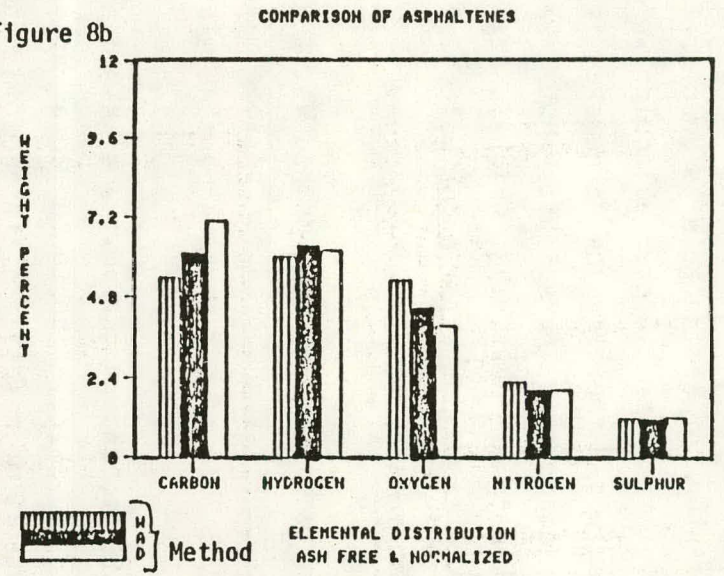


Figure 8c

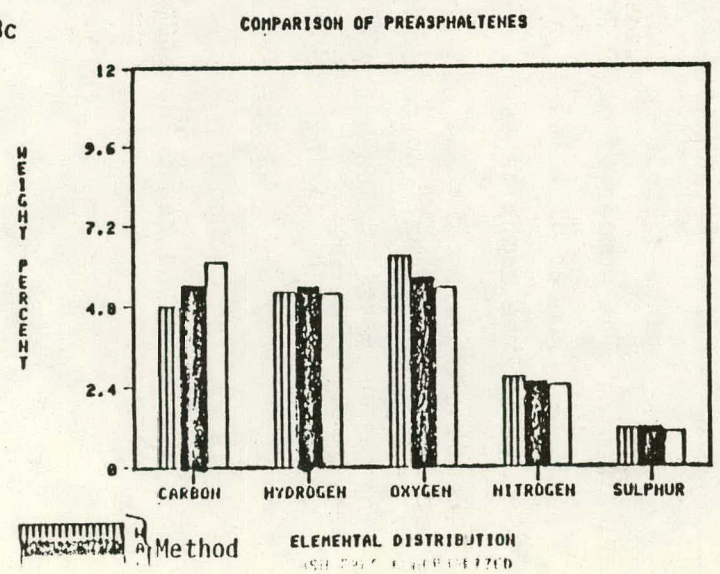
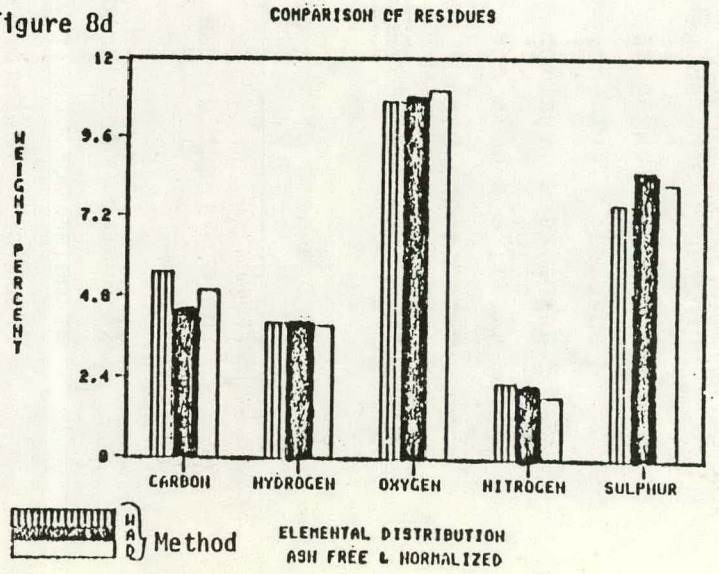


Figure 8d



- Molecular Weight

Figure 9 gives the number average molecular weight profiles for each fraction compared by the method of isolation. The trends are interesting and can be explained. Procedure W gave an oil with the highest molecular weight, 210. This may be due to the use of ~10% benzene in the solvent mixture of Procedure W to recover the oils, thereby allowing co-solubilization of higher molecular weight species. These compounds would therefore be taken away from the asphaltene fraction and accordingly increase its $\bar{n}$Mwt. We find the distillate oils having the lowest $\bar{n}$Mwt, 190, which is not surprising because the higher boiling compounds with larger molecular weights were left in the bottoms as SRC-oils.

In the case of the asphaltenes we find that Method W's fraction has the greatest $\bar{n}$Mwt. This confirms the transfer of some material to the oil fraction due to the use of the benzene-pentane mixture.

It must be considered that to change the $\bar{n}$Mwt a significant number of moles must be transferred in relation to the total moles in the fraction. Therefore, the 3% of material difference in Method W and Method A asphaltenes (7.7 vs. 10.6%) adds about 4% to the oils, but makes a 25-30% difference in the final weight percent of asphaltenes. The number of moles transferred to the oils is small, but the number of moles of higher molecular weight materials left behind in the asphaltenes is now much larger.

Preasphaltene molecular weight shows the biggest difference for the distillation bottoms. If prolonged heating caused repolymerization - but not coking -the number average molecular weight should increase rapidly. We observe a change of nearly 1000 mass units in the $\bar{n}$Mwt for Method D preasphaltene. The error of analysis is between 5-10% in the range 200-3000 Mwt.

Figure 9

Comparison of the molecular weight profiles of oils/distillate, asphaltenes, preasphaltenes and SRC as a function of the separation procedure employed. (three trial average)

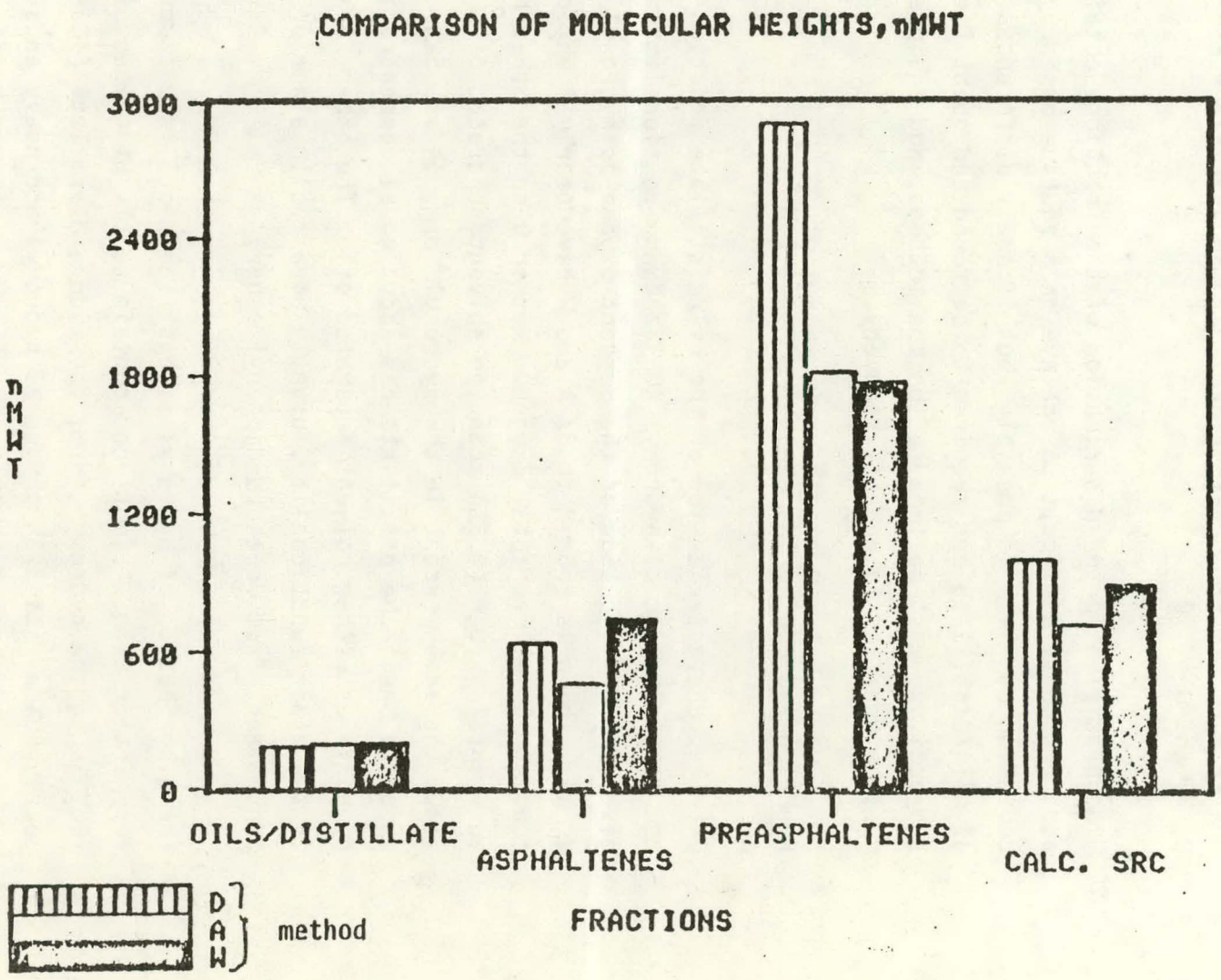


Table 4 summarizes the overall weight percent recovery and elemental distribution for all fractions and gives the calculated mean with a standard deviation. In general elemental analysis can achieve the following in overall precision for a typical coal-derived material C:87±0.4; H:8±.2; O:3±.3; N:2±.2 and S:1±.1. Duplicate analyses on the same sample by the same technician can achieve a precision for C, H, and O of ±0.2.

High precision in the distribution of the fractions obtained from each method is difficult to achieve on a routine basis. A standard deviation of ±1-2% is possible, but if small differences in yield of oils/distillate are required to be found and quantified, less subjectivity must be imparted on the methods, and equipment design must be modified to enhance recovery.

- Functional Groups (-OH, -NH)

Detailed characterization of the oil/distillate fraction included the determination of hydroxyl (OH) and NH functionalities. Table 5 gives the distribution of the percent oxygen as hydroxyl and nitrogen as NH. The oils from Methods A and W have nearly identical hydroxyl content as well as total oxygen. Method D on the other hand has more total oxygen (2.8%) than the solvent separated oils (2.4%) but about the same percent in the hydroxyl form, 54 vs. 52%. On an absolute basis the distillate has about equal concentration of hydroxyl as either solvent separated oil. The other form of oxygen is the ether functionality, usually as a cyclic ether or as a contaminant from Dowtherm-diphenyl ether.

The distribution of hydroxyl amongst the distillate fractions is very interesting. Light ends contain nearly 6% oxygen of which ~60% is in the hydroxyl form, the middle distillate (420-550°F) has nearly 60% of its 3.3% oxygen as hydroxyl and heavy ends (550-850°F) have nearly half of their 1.9% oxygen as hydroxyl. Figure 10 gives the weight distribution of the distillation fractions. From the

Table 4

	Method	Carbon Mean	Carbon SD*	Hydrogen Mean	Hydrogen SD*	Oxygen Mean	Oxygen SD*	Nitrogen Mean	Nitrogen SD*	Sulfur Mean	Sulfur SD*	Ash** Mean	Ash** SD*
Oils	D	87.2	0.3	8.5	0.1	3.1	0.4	0.8	0.1	0.4	0.1		
	A	87.7	0.2	8.5	0.2	2.4	0.1	0.9	0.4	0.5	0.1		
	W	87.2	0.2	8.2	0.1	2.5	0.2	0.9	0.1	0.6	0.1		
Asphaltenes	D	87.1	1.5	6.2	0.4	3.9	1.1	2.0	0.2	1.2	0.1		
	A	86.1	0.5	6.3	0.1	4.4	0.3	2.0	0.1	1.1	0.1		
	W	85.4	0.1	6.0	0.1	5.3	0.1	2.3	0.1	1.2	0.1		
Preasphaltenes	D	86.1	0.4	5.2	0.1	5.3	0.5	2.4	0.1	1.0	0.1	1.4***	--
	A	85.4	0.4	5.4	0.2	5.6	0.3	2.5	0.1	1.1	0.1	--	--
	W	84.8	0.3	5.2	0.2	6.3	0.5	2.6	0.2	1.1	0.1	--	--
Residue	D	75.0	1.3	3.9	0.1	11.1	1.2	1.8	0.4	8.2	0.6	3.0	.2
	A	74.4	0.4	4.0	0.2	10.9	0.6	2.1	0.1	8.6	0.2	4.2	.1
	W	75.5	0.4	4.0	0.1	10.7	0.4	2.2	0.2	7.6	0.4	4.3	.1

Mean and standard deviation of normalized ash-free elemental analyses for each separation fraction. The results are an average of three trials and may not add up to 100%. The standard deviation is related to the mean by the following definition:

*In any unimodal distribution, which is reasonably symmetrical about its average two thirds of the distribution, lies less than one standard deviation away from the mean; and 95% of the distribution lies less than two standard deviations away from the mean.

**Normalized ash content of total product (three trial average)

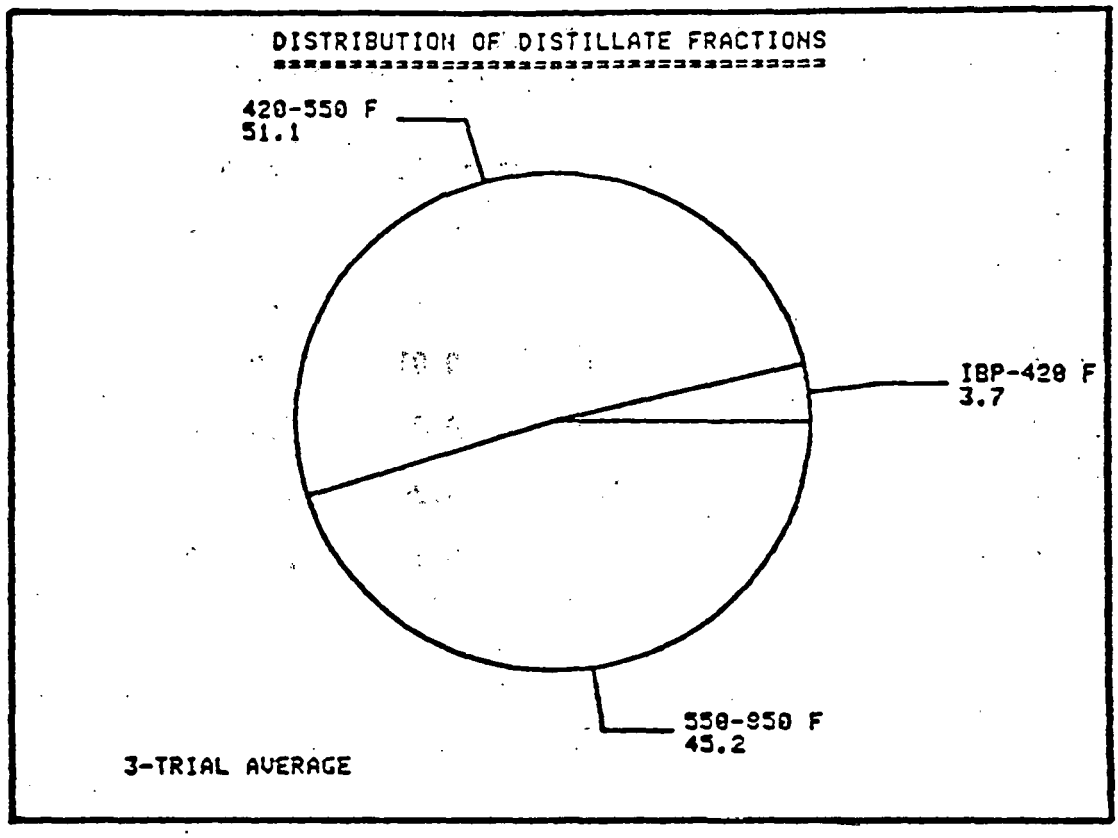
***Ash was found due to poor filtering. Add this value to residue (D) for 4.4% total ash.

Table 5

Distribution of Functional Groups as
Determined by Near Infrared Measurements

Fraction	Wt.% Function Gp.		Ele. Wt.%		% Oxygen
	OH	NH	O	N	as OH
Total Distillate (Method D)	1.5	0.1	2.8	.8	54
L/IBP-420°F	3.5	0.01	5.9	.5	59
K/420-550°F	1.9	0.02	3.3	.6	58
D/550-850°F	0.9	0.20	1.9	.9	49
Oils (Method A)	1.3	0.1	2.4	.9	52

Figure 10. Distribution of distillate fractions on a weight percent basis.



APCI-CPDU the total product does not contain more than 5% light ends, most of which are removed in the primary condenser with water.

- NMR Analysis for Structural Parameters

Proton magnetic resonance was used to determine the distribution of structural hydrogen in each fraction of oils/distillate. Samples were dissolved in deuterated methylene chloride (CD_2Cl_2) as 10% solutions to minimize intermolecular interactions. Spectra were taken at ~35°C at 60 MHz and the tallest peak set at 70% full chart expansion. After each spectrum was recorded it was integrated to provide the following areas: aliphatic proton (0-2 ppm) (H_{al}); alpha hydrogen (H_α) to aromatic rings (2-4 ppm); and aromatic (6-9 ppm) hydrogen (H_{ar}). Table 6a summarizes the proton nmr data as received.

To determine the differences in average structure of the molecules in each oil/distillate fraction the nmr data along with the sample's elemental distribution (C, H, O, N & S), functional group assignment (% O as OH) and the assignment of first approximations to certain key NMR parameters were entered into a computer program. The program, modified by H. L. Retcofsky and F. K. Schweighardt, is based upon the Brown and Ladner equations for calculating aromaticity of organic mixtures from proton magnetic resonance data. Table 6b summarizes the results of those calculations. The aromaticity, fa ('H), relates the fraction of carbons in benzene (aromatic) rings. A value of .6 would indicate 60% of the carbons are associated in aromatic rings. An example of a typical structure would be diethyl benzene with 6 aromatic carbons and 4 aliphatic carbons.

The value of σ (sigma) indicates the percentage of sites on such aromatic rings that are not substituted by hydrogen nor are part of adjacent aromatic rings. In diethyl benzene two of six sites have substituents, therefore σ = 33%. The higher the value of σ the greater is the substitution. If during a process run splitting of

Table 6a

Structural Parameters

derived from proton magnetic resonance (NMR)

for the oils/distillate obtained by the three separation methods

	D	A	W
H_{ar}	32.3	33.8	32.2
H_{α}	29.8	29.8	31.1
H_{al}	37.1	35.5	35.3
H_{OH}	0.9	0.9	1.4*

H_{ar} = percent hydrogen attached to aromatic ring carbon

H_{α} = percent hydrogen attached to carbon one bond removed from aromatic ring carbon

H_{al} = percent hydrogen that is either two carbon atoms removed from an aromatic ring or of aliphatic/alicyclic structure

H_{OH} = percent hydrogen in hydroxyl functional groups

* The hydroxyl value was estimated to be the same as that of the A-oil fraction.

Table 6b

Calculated structural parameters for the

oils/distillate obtained by the three separation methods

	D	A	W
fa ('H)	.61	.62	.64
σ	34.6	33.1	38.1
H_{ar}/C_{ar}	.92	.95	.89
X Best	2.0	2.0	1.8

fa 'H = fraction of carbon aromaticity $\frac{C_{ar}}{C_{total}}$ as calculated from proton magnetic resonance data

σ = percent of substitution of the aromatic system, i.e., the fraction of available aromatic edge atoms that is occupied by substituents

H_{ar}/C_{ar} = the atomic hydrogen to carbon ratio of the hypothetical unsubstituted aromatic nucleus

X_{Best} = number of hydrogen attached to α carbon

alkyl groups off of rings were evident, σ would decrease rapidly, while if hydrogenation of multi-ring system were taking place, σ would increase, such as when napthalene becomes tetralin. The value of H_{ar}/C_{ar} is a general guide to the kind of structure present. If benzene were the prime unsubstituted structure $H_{ar}/C_{ar} = 6/6 = 1$, while if napthalene were the structure $H_{ar}/C_{ar} = 8/10 = .8$, and phenanthrene would give 14/10 = 0.7. Our data show that Procedure D and A oils have more two ring structures, while Procedure W oils contain more 3 ring or higher structures. This is reasonable in light of the use of 10% benzene in pentane to recover the oils which would carry larger aromatic rings into the oil fraction. The value of X-best indicates the average number of hydrogens that are adjacent (alpha) to aromatic rings. In our example of diethyl benzene X = 2, while toluene would have X = 3. A value of X less than 2 would indicate more substitution on the α carbon.

Table 6c gives a summary of the nmr structural parameters from the distillate subfractions. The key features are the increase in aromaticity (fa) going from the light ends (.5) to the heavy ends (.63), the H_{ar}/C_{ar} ratio changes dramatically going from the light to middle cuts which confirms the presence of saturated hydrocarbon and/or long chains on small rings in the light ends. The nmr data indicates that the degree of substitution is not changing very much, which in turn confirms that neither hydrogenation nor splitting are over shadowing the distillate fraction.

- Simulated Distillation

An important comparison of solvent extracted material and a distillate is how well their simulated distillation profiles agree. Figure 11a compares the simulated distillation profiles of each oil/distillate as a function of temperature and weight percent distilled. The trend is very clear at each weight fraction, the distillate contains the least amount of material while Method W oils contain the most. The largest difference is at the 97% distilled where both solvent extracted oils had higher boiling materials. The efficiency of

Table 6c

Structural parameters derived and calculated from proton magnetic resonance for three distillate subfractions L, K and D obtained at IBP-420°F (L), 420-550°F (K) and 550-850°F (D)

	L IBP-420°F	K 420-550°F	D 550-850°F
H_{ar}	27.9	31.6	32.9
H_{α}	23.1	29.0	29.5
H_{aL}	46.0	38.0	36.8
H_{OH}	2.2	1.4	0.7
fa ('H)	.51	.59	.63
σ	35.3	34.7	32.9
H_{ar}/C_{ar}	1.21	1.02	.89
X_{best}	2.0	1.9	2.0

Figure 11a

Shows the comparison of GC-simulated distillation of the oils/distillate derived from each of the three different separation mehtods.

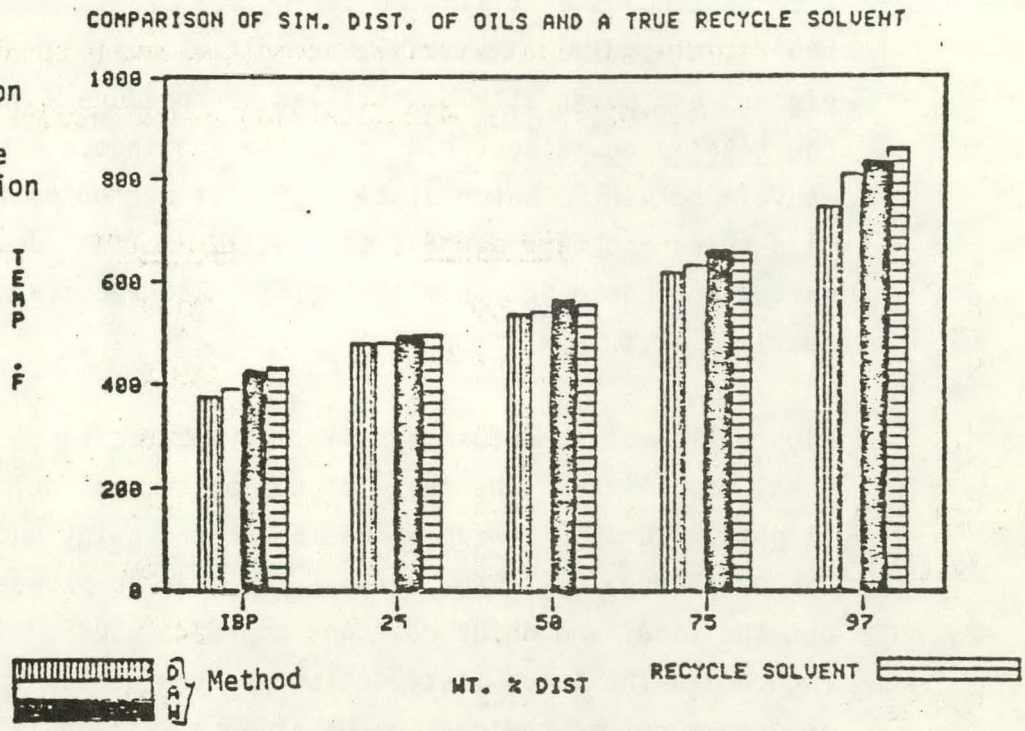
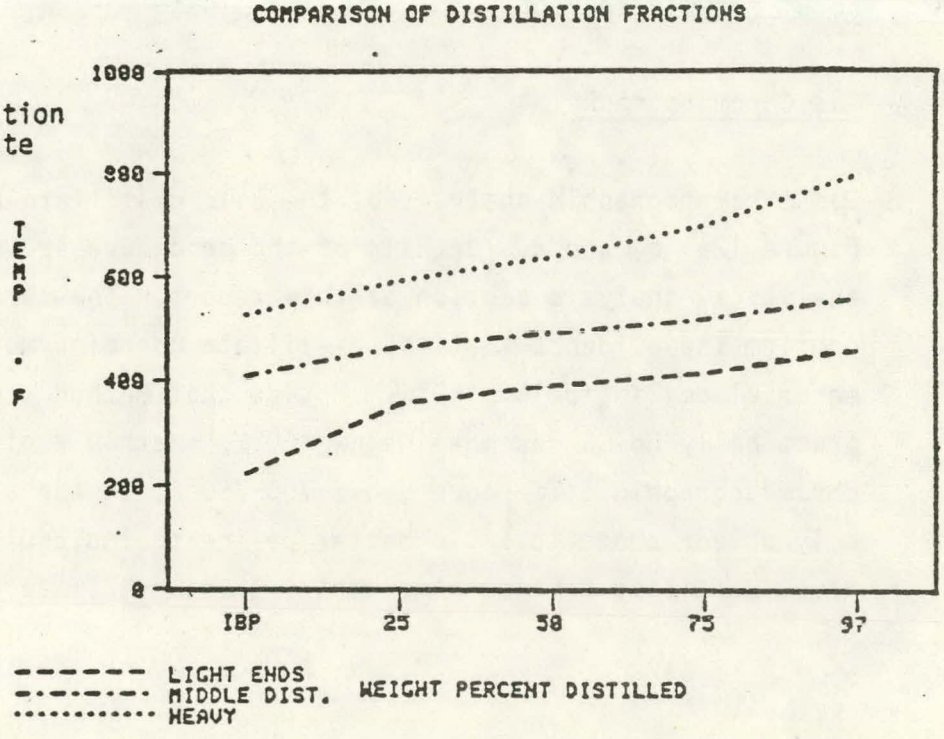


Figure 11b

Shows comparison of GC-simulated distillation of the total distillate and its distillate subfractions.



Light ends: IBP-420°F
Middle dist.: 420-550°F
Heavy ends: 550-780°F

the distillation unit and its mode of operation -- batch vs. continuous -- must be taken into consideration. The bar identified as recycle solvent in Figure 11a is a Wilsonville pilot plant solvent derived from continuous distillation during the SRC-I process. Note that the recycle solvent has a higher initial boiling point and the highest end point at 97% distilled. Procedure W when applied to the total product best simulates the continuous distillation of a recycle solvent. Batch distillation as performed in this investigation tried not to superheat the bottoms so that destructive repolymerization could be minimized. This also reduced the yield by nearly 6 wt.%.

Figure 11b compares the distillation subfractions obtained from the total distillate. The range of cut points was held to IBP-420°F (light), 420-550°F (middle) and 550°F-end point under 0.5mm Hg vacuum (heavy). As can be seen, the overlap between cuts is small but the final end point does not approach 850°F. As discussed for Figure 11a the batch distillation procedure does not seem to provide as deep a cut as the continuous still at Wilsonville does for the total recycle solvent.

- Gas Chromatography

Gas chromatographic analysis of the oils/distillate are shown in Figure 12a, b, and c. Details of the procedure are given in the analytical analysis section of this report. The chromatograms confirm the evidence that the distillate contains more light ends, material boiling below 450°F. Notice that Method W oils show practically no GC response below 400°F. Method W oils show slight chromatographic difference above 700-750°F, in the area of 3-4 ring polynuclear aromatics. To better define the molecular compounds we have identified 9 major components, these are listed in Table 7.

Shows the gas chromatogram of the oils/distillate obtained by the three different separation methods. The GC retention time was converted to the respective boiling points of the individual components identified in the fraction.

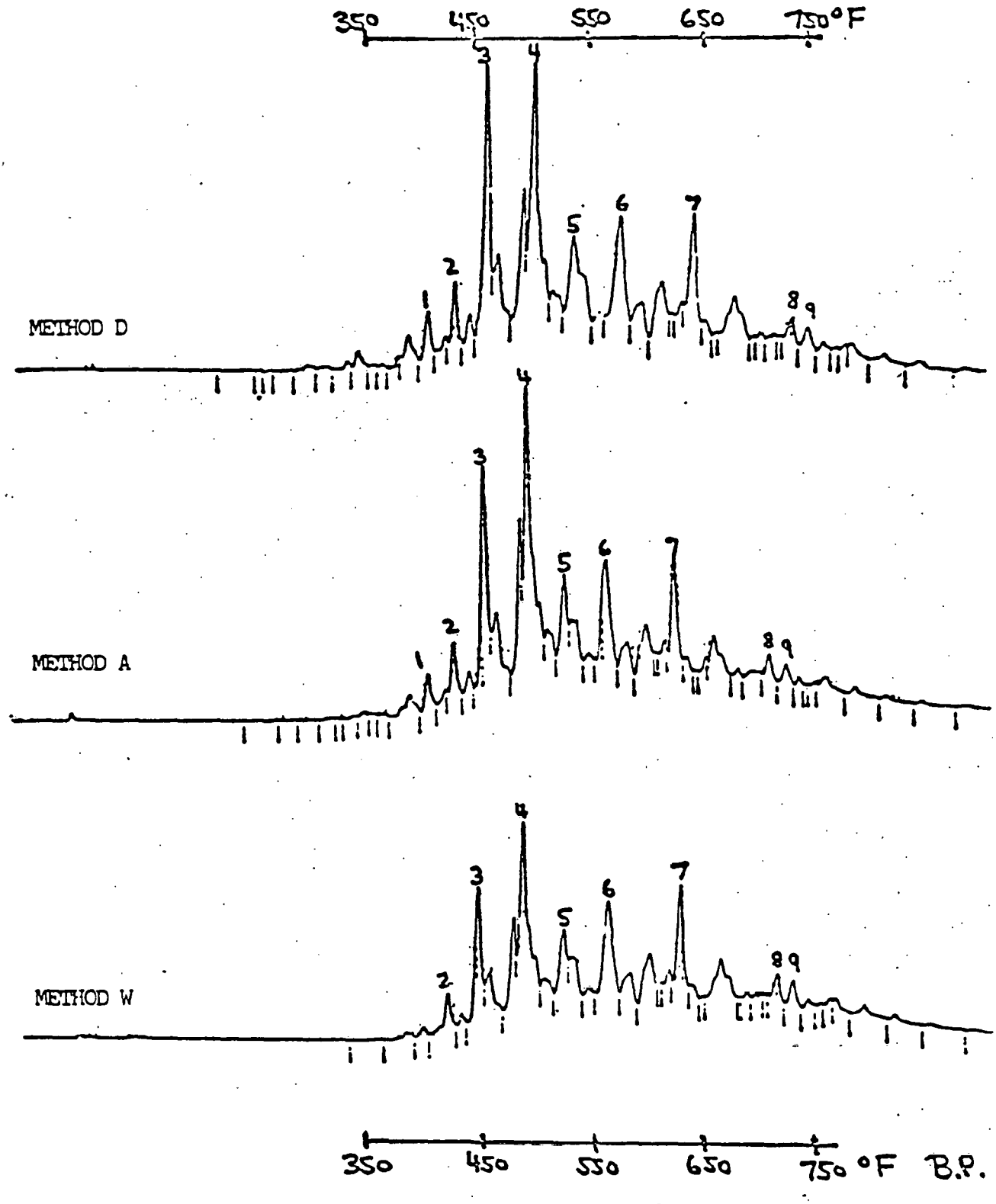


Table 7

Compound Identification

#	Compound
1	diethyl benzene
2	naphthalene
3	2-methyl naphthalene
4	di-methyl naphthalene
5	acenaphthene
6	fluorene
7	phenanthrene
8	fluoranthene
9	pyrene

The numbered compounds refer to Figures 12, 13 and 14.

The major compound types are the 2-ring di-alkylnapthalenes. If one compares the data from the simulated distillation by gas chromatography to this data the complexity of the samples becomes apparent.

If we now compare the distillate subfractions by using the same chromatographic conditions as used for Figure 12 we observe the distribution of compound types as a function of temperature, Figure 13. The high chromatographic resolution reveals that each subfraction is very complex. Identification of nine major components was made to reference the sharpness of the distillation cut-point and to define compound-types found in each subfraction. The light ends, IBP-420°F, contains mostly one and two ring alkylaromatics and phenols, middle distillate, 420-550°F, has more 2 ring and polynuclear aromatics with bridgeheads (PNA) e.g. acenapthene, which do not donate their hydroaromatic hydrogen. The highest boiling fraction is mostly three-and four-ring PNA systems.

Figure 14 provides a clue as to the identity of the material that is left behind as oils in the SRC when isolated by distillation. Figure 14a is the total distillate and Figure 14b the oils isolated from the SRC by solvent extraction. To enhance the signal-to-noise ratio the amplitude in 14b is 10 times greater. All of the higher boiling material may not elute under these conditions. Note that the major components are phenanthrene, pyrene, fluoranthene and fluorene. This region of the chromatogram is similar to the heavy ends of Figure 13c. As discussed earlier this SRC-oil represents 3-4% of the total product and 10-15% of an SRC that is derived from batch distillation bottoms.

Refractive Index

A common analytical reference tool for characterizing distillates is the refractive index. To provide an example, we have chosen to use the fractions from distillation. Figures 15a and 15b give the refractive index measured as the transmittance of light at 30°C. The refractive index can be used as a measure of composition, its

Shows the GC chromatogram of the three distillate subfractions and the total distillate.

FIGURE 13

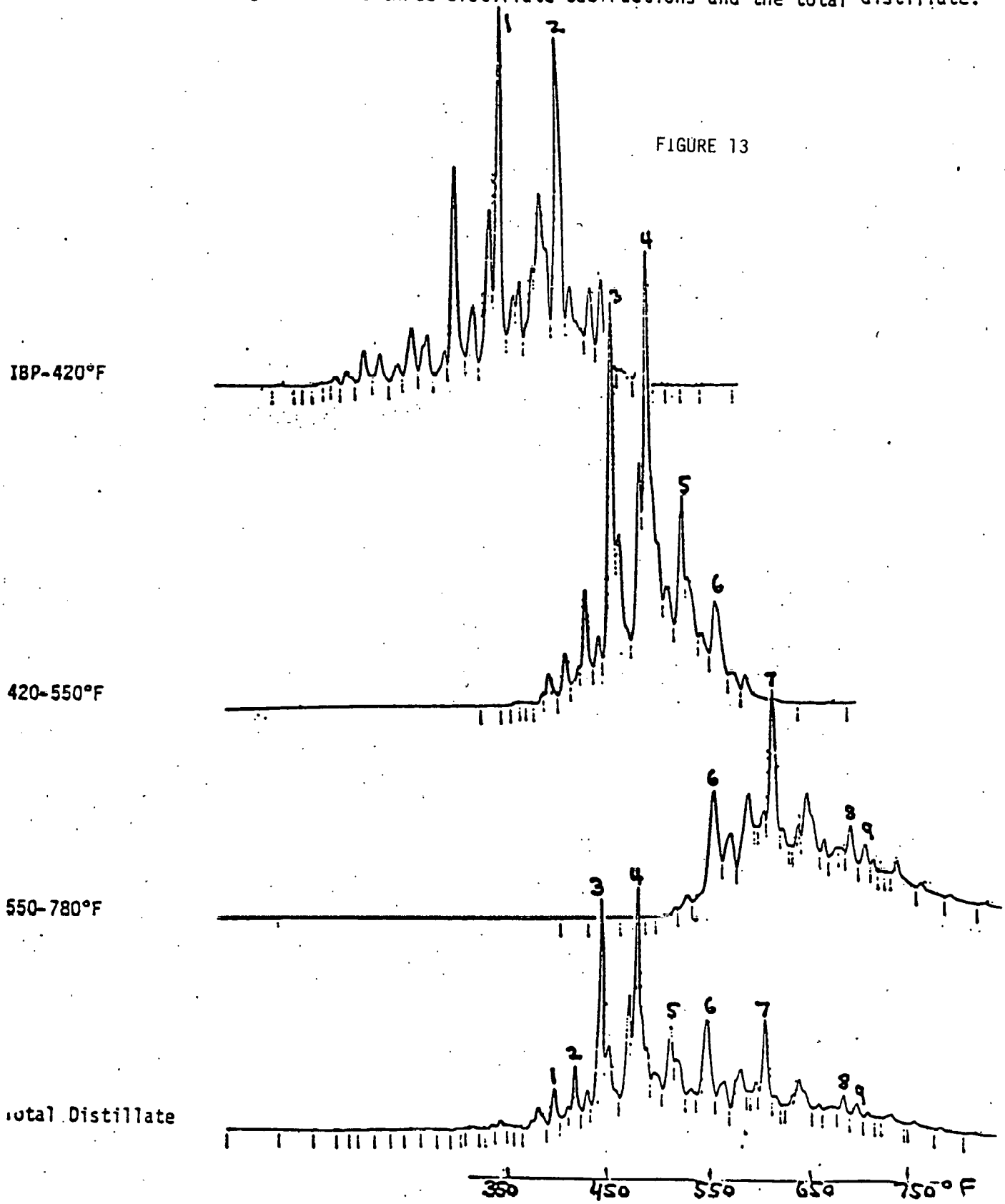


Figure 14

Shows the GC chromatogram of the total distillate (a) and the SRC derived oil (b).

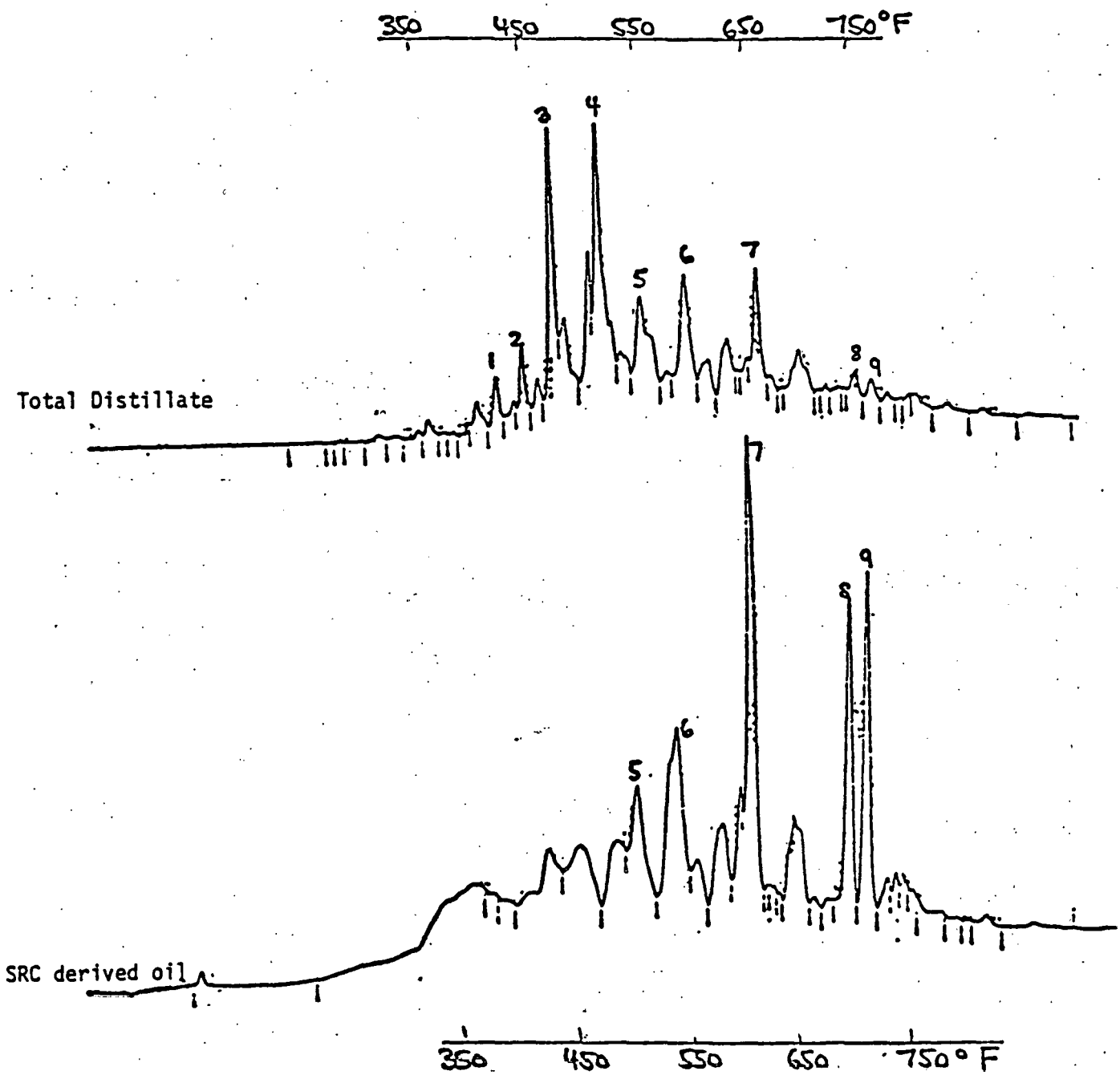


Figure 15a

Refractive index of the oils/distillate obtained by the three different separation methods.

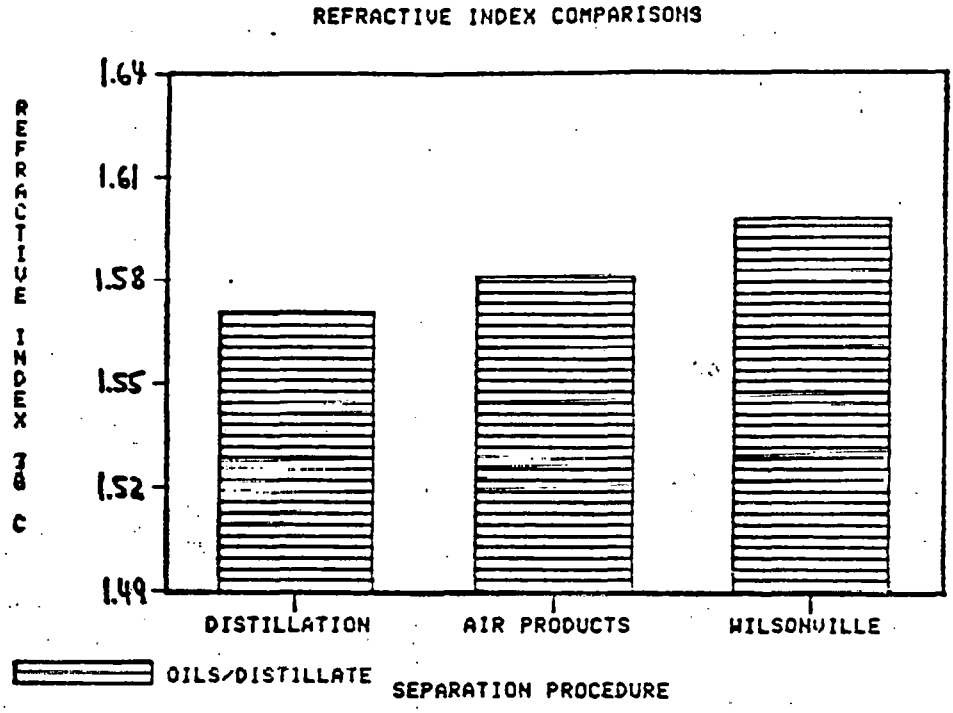
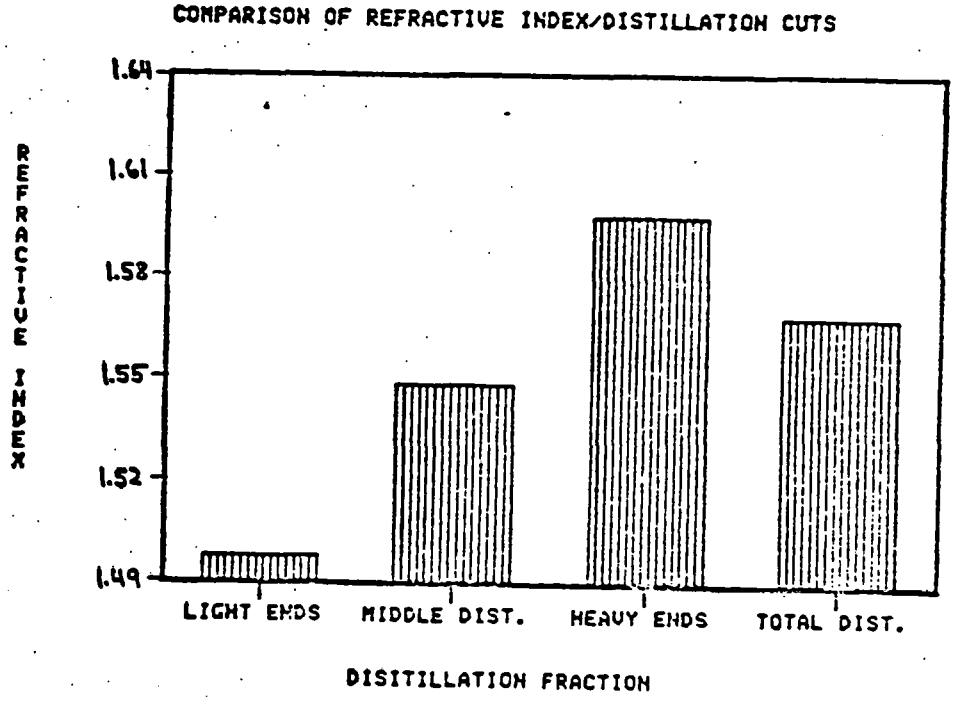


Figure 15b

Refractive index of the three distillate cuts and the total distillate.



value increasing with aromatic content. From our analysis of the distillate fraction we know that the distillate subfractions increased in molecular weight, increased in aromaticity (fa), increased in ring size and decreased in phenol content as the boiling range increased. We observe a substantial change in the refractive index that correlates with its physical-chemical properties.

Figure 15a gives the refractive index of each oil/distillate measured as the reflectance of the sample at 30°C. An increase in the refractive index represents an increase in c=c conjugation and/or heteroatom content. We found the distillate to give the lowest value (1.568) and the oils from procedure W the highest value (1.600). This confirms our observation that the total distillate had less polynuclear aromatic material that contains smaller rings with the least conjugation. The refractive index provides a first measure of relative composition and molecular structure for the oils and distillate subfractions.

Figure 15b shows the refractive index of the distillate subfractions and the total distillate. The refractive index of the light ends (IBP-420°F) is the lowest and the heavy ends (550-FBP) gave the highest value, 1.500 and 1.600, respectively. Therefore the molecular make-up of the distillate clearly indicates that the oils left behind by distillation must be large ring systems - as shown by Figure 14 b.

Conclusions

The third quarter was devoted to evaluation of three analytical procedures for laboratory reproducibility and comparison of the resulting fractions for differences in molecular composition.

In comparing similar fractions from each procedure we found many more differences than similarities. Similarities were found in the elemental composition of the fractions and may be attributed to the precision of the elemental analysis (CHONS) methods employed.

Difficulties in working with coal-derived liquids stems from the complexity in molecular composition. There appears to be a continuum of molecular species in coal liquids that include aliphatic, aromatic, hydroaromatic, phenols and nitrogen bases that range from 1 to 6 rings with mono to tri alkyl substitution. At our present level of understanding there is no definite chemical or physical separation procedure that can provide absolute classification of the entire product stream.

The results of our study show that differences in chemical composition and physical properties are apparent both on the molecular level and the primary fraction level among the three methods tested. We observe that the number average molecular weight for Procedure D distillate is less than that of the solvent separated oils. Procedure A oils, using only n-pentane as extractant, gave a smaller molecular weight than Procedure W oils, where n-pentane: benzene (10:1) was used. This can be attributed to larger molecular species being co-solubilized with the addition of benzene. The preasphaltene molecular weight is greatest for the distillation bottoms. We attribute this to possible repolymerization of oils, asphaltenes, and preasphaltenes during the prolonged (3-6 hours) heating of the total sample.

Gas chromatography used for both simulated distillation and molecular profiles showed that the distillate contained more light (IBP-420°F) material than solvent separated oils but did not achieve an end point of 850°F. In comparing the solvent separated oils, procedures A and W produced materials that gave higher boiling points but could not duplicate an authentic continuously distilled

recycle solvent from the Wilsonville pilot plant. A forced high temperature distillation was conducted giving an end point only 40°F less than the authentic recycle solvent, and a distillate yield increase from 66 to 72%.

Gas chromatography showed that the oil material left behind by distillation becomes the oil associated with the SRC. This SRC-oil contains mostly 3 and 4 ring polynuclear aromatics and is less polar than either the distillate or the asphaltenes.

The distillation procedure produced a bottom (>850°F) that may have undergone repolymerization as evident from our analytical characterization. The preasphaltene content increased 40% (10 vs. 14) over the solvent separated fraction, and the molecular weight gained nearly 1000 mass units to 2800.

The solvent separated preasphaltenes and residue were chemically similar, giving the same yield and ash content, respectively. The oils and asphaltenes exhibited different chemical and physical properties. The differences, molecular weight, yield and refractive index are attributed to solvent composition and the operation sequence used to isolate them.

The elapsed laboratory time required to conduct each procedure does become important. Solvent separation Procedures A and W require nearly 11 hours to prepare equipment, conduct the separation, clean-up and write a report. Procedure D takes nearly 12 hours for the distillation and 10 additional hours for the solvent separation. For quality control of a small process development unit such times and costs could be tolerated on the justification of receiving high precision data. A 6,000 TPD demonstration plant would require a turn-around of 4-5 hours and quantitative data that reflects process changes in product quality.

The best time efficient approach to date has been a compound class separation into saturate/aromatic/polars by liquid chromatography developed at Mobil (1978). This procedure suffers from poor material recovery (70-95%) and fractions that cannot be analyzed because only a few milligrams are received as product. Therefore, the classical oil/asphaltene/preasphaltene/residue solvent separation must be made more precise and far less time consuming until we can develop new procedures.

In summary, we have shown that separation of coal-derived liquids into oils-asphaltenes-preasphaltenes-residue can be achieved with a precision of ±2%. The fractions are dependent upon the separation sequence or operation (distillation *vs.* solubility) for yield and molecular composition. As routine procedures all three methods can be performed well with a few weeks of laboratory training. Elapsed time of analysis varies from 10/12 to nearly 22 hours. This factor and our characterization data lead us to conclude that a standard solvent separation method, such as a combination of Procedure A and W should be automated to reduce subjectivity and man-hours. We propose to design, construct, and test such a device as a quality control tool for coal liquefaction during FY 81.

Acknowledgements

We wish to acknowledge the participation of the research technical staff, C. Kayhart, S. Dukett, S. Staub and S. Heppe of CRDD who carried out the solvent separation procedures, and to M. Oakes of CRSD-Linwood who conducted the distillations.

Special graditude is extended to A. Z. Kamzelski, CRSD, who conducted the gas chromatographic profiles of all the oils and distillate subfractions, and D. Yoder and M. Chaykovsky who prepared and ran the NMR analyses.

This entire work was a joint venture between CRDD and CRSD.

APPENDIX

Appendix I

Total Product

Distillation Separation

Procedure D

A) Oils - Material distillable from IBP to <850°F.

B) SRC - Pyridine soluble portion of distillation bottoms.

C) Residue - Pyridine insoluble portion of distillation bottom.

D) SRC - Oils/asphaltenes/preasphaltenes are determined by Procedure W. A five (5) gram sample of the SRC is recovered from the pyridine solubles and replaces the total product as the starting material.

Distillation: A 300 gram total product liquid sample is removed from the holding can after heating to 60°C and thorough mixing. Great care must be taken to obtain a well-mixed sample.

The sample is then distilled in a 1" x 6" vacuum jacketed distillation unit packed with podbielniak heli-pak high efficiency packing. The total plates as determined by Pod's data book indicate 15 at total full reflux. A reflux ratio of 10:1 at 550°F. Fractions were collected at IBP to 420°F, and 420 to 550°F under 100 mm Hg, and 550-end point (850°F) under 0.5 mm Hg. The pot temperature was 650°F at final end point.

The distillation bottoms were pyridine extracted to yield the SRC and residue.

The SRC was then solvent separated by Procedure W to give SRC-oils, asphaltenes, and preasphaltenes.

Appendix II

Total Product

Solvent Separation Procedure

A

A) Oils - Pentane Solubles/Benzene Soluble/Pyridine Soluble

B) Asphaltenes - Pentane Insoluble/Benzene Soluble/Pyridine Soluble

C) Preasphaltenes - Pentane Insoluble/Benzene Insoluble/Pyridine Soluble

D) Residue - Pentane Insoluble/Benzene Insoluble/Pyridine Insoluble

This procedure is carried out at room temperature under nitrogen using high quality solvents. The sample may be liquid, solid or a mixture thereof, with less than 1% material boiling below (300°F). Under laboratory conditions one (1) individual with technical training can perform the analysis in one (1) day. With experience one (1) technician can handle two (2) units and complete the operation in less than eight (8) hours. A reproducibility study of the solvent separation procedure was made on a total product liquid (sample XCL-23-132PL) The results of this study are given in Table 1.

Table 1

Reproducibility of the Solvent Separation Procedure

	Mean	Standard* Deviation
oils	63.3%	1.06%
asphaltenes	8.7%	0.94%
preasphaltenes	9.7%	1.23%
residue	18.2%	0.31%

*The result of five trials.

Equipment Required:

1. Branson Model 350 Sonicator with 1/2" horn
2. Millipore 142 mm pressure filter with 1500 mL capacity #XX42-142-35 and YY-30-142-35 with 142 mm filter, 5 micron, LSWP 142-50
3. Glassware for solvent transfer lines
4. Round bottom distilling flasks - 500 mL, 250 mL, 2 each
5. Rotovapor Re 120, VWR #27582-406
6. Vacuum pump and trap
7. Nitrogen-Gas (0-20 psi adjustable), pressure filter feed

   Nitrogen-Gas (0-20 psi adjustable), rotovapor feed

   Nitrogen-liquid (1-2L), freeze sample (Dewar)
8. a) n-Pentane -

   b) Benzene -

   c) Pyridine -

   d) Methanol -

   Grade of solvent depends upon ultimate use of sample subfractions Pesticide, Distilled in Glass, or HPCL grade are acceptable.
9. Fume hood 150-200 cfm air rate exchange
10. Cooling water or heat exchanger for rotovapor condenser
11. Balance to read weights ± 0.005 grams or better with maximum load 200 grams.

Safety Features:

Solvents must be used only under the fume hood and transferred from bottle to flask by hand pump. Workers must wear protective gloves and overalls for laboratory work. Hands can be cleaned with Go-Jo waterless hand-cleaner, mild scrubbing followed by a warm water wash. All normal safety precautions must be observed during the full operation.

Sample Handling:

The sample chosen for this procedure must be representative of the process unit output. Great care must be given to the isolation of approximately 50 grams of gross product.

The sample once chosen must be kept free of air (oxygen), heat and light. Samples not ready for separation should be stored at 4°C under a blanket of nitrogen. Hot samples may be taken in 316 stainless steel bottles (DuPont #03226, 235 mL 61 x 140 mm with screw cap). Samples may be warmed to 65°C in the cans and sonicated for 15 minutes with 1/2 inch tip to induce good mixing just prior to taking a 5 gram actual work-up sample.

Procedure

The laboratory equipment is prepared in the following order:

a) Adjust and clean ultrasonic unit equipped with 1/2" horn with methylene chloride.

b) Put in place Millipore filter after taking weight of dry filter element. Ensure that all O-rings fit well with no leaks (test with n-pentane under 10 psi). Use Teflon tape (3/4") to wrap screw fittings and seals.

c) Prepare rotovapor-bath temperature at 55-60°C for n-pentane; nitrogen flow rate should just cause 1/4-1/2" dimple in liquid of 250 ml flask.

d) Cooling liquid for rotovapor condenser should be less than 10°C.

Step 1 Tare a 150 mL heavy wall Pyrex beaker, add 8 grams read to ± 0.005 grams of the desired coal-derived sample. Add approximately 100 mL of liquid nitrogen slowly to the beaker to maintain a quiet solution. Total volume of liquid nitrogen used may exceed 500 ml.

Step 2 With a Pyrex glass stirring rod (3/8"D), grind the frozen sample to a fine powder. This step requires 5-8 minutes. Fill with more liquid nitrogen to maintain at least 30 ml volume while grinding.

Step 3 Allow the liquid nitrogen to evaporate to just above the solid mixture. Add with moderate (micro-probe 1/3", power level 3) sonication 100 mL of n-pentane. Some stirring may be required - keep tools out of beaker while sonic power is on. Sonciate for 5 minutes at power level 5.

Step 4 Allow mixture to settle (1-2 minutes) decant supernatant into filter unit, refill beaker with n-pentane and sonicate again for 3-5 minutes. Allow decant liquid to filter into a 250 mL flask - do not allow filter to dry from this time onwards.

Step 5 Repeat Step 4 twice for a total of approximately 300 mL n-pentane. If catch flask fills transfer to rotovapor and begin to remove n-pentane under nitrogen at approximately 60°C. Transfer the solids with small portions (25-50 mL) of pentane.

Do not discard beaker, hold for additional transfer of solvents to filter. This assures removal of maximum amount of material and reduces loss.

Step 6 Filter the solids, adding nitrogen pressure (5-10 psi) if needed. Add new pentane via original beaker as needed for a total of approximately 2 L. This amount can be recollected from rotovapor unit during the continuous solvent removal steps.

Step 7 Continue solvent filtering (up to 2 L) until the filtrate is a very light yellow/green. At the end of the pentane extraction, with approximately 25 mL pentane in the filter, add 100 mL benzene and continue as in Step 6 for 2.5 L. The new filtrate is collected in a new 500 mL flask (tare). Continue to transfer filtrate to rotovapor - waterbath temperature 75°C. Nitrogen flow rate 1/2" dimple.

Step 8 The pentane solubles from steps 6 and 7 should be held on rotovapor for 2 minutes after the last drop of pentane has condensed in the catch flask. Remove, clean and dry outside of the flask containing the oils (reddish) and weigh. From difference on tare:

Yield of oils:----------grams

Step 9 The benzene extraction is carried out in a similar fashion as in Steps 6-8. The benzene solubles are removed from rotovapor when 10-20 mL of solution remain. The flask is swirled in liquid nitrogen to evenly coat 2/3 inner flask and freeze the solution in place. Quickly transfer flask to vacuum line (1 mm Hg) with trap and allow flask to stand unheated to freeze dry the benzene (sublime) in about 1 hour.

Yield of asphaltenes----------grams

Step 10 After the last benzene extraction begin to add pyridine and continue extraction as in steps 6-8. Remove the solvent at 90°C under 1/4-1/2" nitrogen dimple. Two liters of pyridine are required. The last wash should be pure methanol (100 mL), followed by nitrogen gas at 5 psi for 10 minutes. As the pyridine is just nearly removed (approx. 5-10 mL) stop and add 10-15 mL benzene. Swirl flask to mix contents and freeze-dry as in Step #9 for one hour. If pyridine odor remains, add 50 mL methanol and sonicate with microptip for 3 min., decant into tared Millipore filter and wash with n-pentane, allow to dry 15 minute under dry nitrogen.

Yield of preasphaltenes----------grams

Step 11 The residue will dry in-place after washing with 50 mL methanol and 50 mL methylene chloride. Stop nitrogen, gently remove filter and weigh.

Yield of residue----------grams

Step 12		
	Oils	A
	Asphaltenes	B
	Preasphaltenes	C
	Residue	D

A + B + C + D = Total recovered

Original mass of sample = MS.

MS - total recovered = net loss or gain.

If gain of weigh is observed solvent may be left in oils or asphaltenes.

If loss of weigh is observed oils have volatile matter.

Add net loss to mass of oils (A + net loss) and calculate over material recovery.

		Recovered	Corrected	%
Report:	Oils	A	A + net loss	
	Asphaltenes	B	B	
	Preasphaltenes	C	C	
	Residue	D	D	
		Total Recovered	MS	100%

It is now possible to compare samples derived during the coal conversion process with a high degree (± 1%) of reliability, and in a short amount of time. Once the classical separation has been made, the subfractions can now undergo a first level chemical characterization.

Appendix III

Total Product

Solvent Separation

Modified Wilsonville Procedure

W

A) Oils - Soluble material in pentane-benzene (10:1) during the precipitation of the benzene soluble asphaltene.

B) Asphaltenes - Soluble material in benzene and insoluble by precipitation in pentane-benzene (10:1).

C) Preasphaltenes - Benzene insoluble-pyridine soluble material by solvent extraction/filtration.

D) Residue - Pyridine insolubles.

Equipment Required: Same as that listed for Procedure A.

Safety Features: As described for Procedure A.

Sample Handling: As described for Procedure A.

Procedure

The laboratory equipment is prepared in the following manner:

a) Adjust and clean ultrasonic unit equipped with 1/2" horn with methylene chloride.

b) Put in place Millipore filter after taking weight of dry filter element. Ensure that all O-rings fit well with no leaks (test with n-pentane under 10 psi). Use Teflon tape (3/4") to wrap screw fittings and seals.

c) Prepare rotovapor-bath temperature at 55-60°C for n-pentane; nitrogen flow rate should just cause 1/4-1/2" dimple in liquid of 250 ml flask.

d) Cooling liquid for rotovapor condenser should be less than 10°C.

Step 1 Tare a 150 mL pyrex beaker, add 5 grams read to ± 0.005 grams of the desired total coal-derived product. Add approximately 100 mL benzene and sonicate 10 minutes with the 1/2" horn at power level 7.

Step 2 Tare filter element and prepare filter unit. Pour supernatant benzene soluble into filter and catch in tared 1 L receiving flask.

Step 3 Add 100 mL portions of benzene and sonicate 2-4 minutes to rapidly extract benzene solubles. Repeat this step 4 times. Each supernatant is passed through filter and recovered.

Step 4 At the 5th wash pour all beaker contents into filter and rinse beaker with 100-200 ml benzene in 50 mL portion.

Step 5 Continue benzene extraction via filter apparatus for 2.5 L, or until slight color remains - 3.5 L.

Step 6 The benzene insolubles are extracted with 3 L of dry pyridine that has been warmed to 60°C. Catch in a tared flask.

Step 7 The pyridine insolubles are washed with 200 mL methanol, and 100 mL methylene chloride followed by a nitrogen flush for 15-20 minutes to remove excess solvent. The filter is removed, weighed and residue recovered.

Step 8 The pyridine solubles are recovered for pyridine on a rotovapor RE under nitrogen gas, 1/2" dimple, at 90-100°C waterbath temperature. Preasphaltenes are recovered after being washed with 200 mL methanol and dried.

Step 9 The benzene solubles are reduced in volume of benzene tc approximately 50 mL. A 1 L beaker is filled with 500 mL n-pentane and placed ready to be sonicated, 1/2" horn.

Step 10 The concentrated benzene solubles are decanted into the n-pentane while the sonic power is at 3. The original flask may be washed with 10 mL benzene to remove any material and washed with n-pentane, 50 mL.

Step 11 The oils are recovered by filtering the mixture created in Step 10 through a 5μ millipore filter. The insolubles are washed with 500-1000 mL pentane. Oils are finally recovered by rotovap under nitrogen at 60°C. To ensure benzene removal flask must be rotating 5-10 minutes past the last drop of material condensing. Check by GC for NMR for benzene removal.

Step 12 Asphaltenes may be recovered from the filter, or better washed out with 250 mL benzene. Benzene is removed by rotovap and nitrogen flow at 75°C to just 10-20 mL. The tared flask is then frozen in liquid nitrogen and the benzene sublimed under vacuum (1 mm Hg) for 1-2 hours.

Losses are due to removal of light ends from oils or transfer error. If transfer error can be reduced by experience the loss may be assigned to the oils to complete the material recovery.

Appendix IV

Solvent Fractionation of Solvent Refined Coal For Characterization

Procedure #34550-3*

1. Scope

This method is designed to characterize high molecular weight bituminous materials by separating into three group classifications, using solvents as the media. Since results will vary according to the conditions of solvent treatment, the procedure is quite detailed and must be closely followed. The method has been developed primarily to characterize coal extracts.

2. Principle

Coal extracts are separated by solvent fractionation into the following three high molecular weight fractions:

A. Benzene Insolubles -- that fraction of the solvent refined coal (SRC) that is insoluble in benzene at its atmospheric boiling point

B. Asphaltenes -- the fraction of the benzene-soluble SRC insoluble at room temperature in a mixture of 100 parts of pentane and 9 parts of benzene when the ratio of the liquid mixture to the weight of benzene solubles is 109.

C. Oil -- the benzene-soluble, pentane-soluble fraction of the SRC.

3. Apparatus Required

(1) Alundum thimbles, 45 mm x 127 mm size, round bottom RA 98 type
(2) Soxhlet extractor
(3) Beaker A, a 600 mL Griffin beaker
(4) Beaker B, a 100 mL Berzelius beaker
(5) Beaker C, a 800 mL Griffin beaker
(6) Buchner funnel, with fritted disc, medium porosity, 150 mL capacity
(7) Wide mouth, 4 oz. sample bottle

4. Reagents

(1) Benzene, reagent grade
(2) Pentane, practical grade
(3) Celite 545, Anal. filter aid

5. Procedure

A. Separation of the Benzene Insoluble Fraction

*Consolidation Coal Company, Procedure #44

(1) Grind approximately 10 grams of solvent refined coal sample (SRC) to minus 100 mesh and place in 1 oz. bottle.

(2) Dry the SRC sample in oven at 105°C for 1 hour. At the same time dry an alundum thimble (1) containing 1-2 grams of celite at 105° for 1 hour.

(3) Remove both to desiccator and allow to cool to room temperature.

(4) Weigh thimble containing celite and record on calculation sheet at (2) and (5).

(5) Place 1-3 grams of SRC in thimble and weigh. Record at (1) on calculation sheet (Note A). Subtract (2) from (1) on calculation sheet and record at (3). This is the weight of sample.

(6) Mix celite and SRC as well as possible by rolling and tapping carefully.

(7) Place thimble in extraction apparatus.

(8) Put 3 boiling stones and approximately 250 mL benzene in 500 mL flask. Assemble apparatus as shown in Figure 1.

(9) Set powerstat at approximately 80.1°C, 80 volts and turn on heat. Check carefully for overflow of thimble and plugging in capillary at bottom of extractor as soon as reflux starts.

(10) At end of four hours stop extraction, remove thimble, allow to drain in beaker. Check for precipitate on outside of thimble. If present, remove by washing with benzene and transfer washings back into thimble.

(11) Stir material in thimble with small spatula. Replace thimble in extractor and continue extraction.

(12) Repeat steps (10) and (11) at 8 hours, 12 hours, 16 hours, and 20 hours. Benzene should now be coming through clear; if still cloudy, continue 4-hour runs.

(13) Allow extractor to cool and drain.

(14) Remove thimble and let stand in air until visibly dry.

(15) Place thimble in vacuum oven and dry with at least 29 inches of mercury, vacuum, and 100°C for 4 hours.

(16) Remove, place in desiccator to cool. Weigh and record at (4) on calculation sheet. Subtract (5) and (4) and record at (6). This is the weight of Benzene Insoluble Fraction.

COAL PRODUCT CHARACTERIZATION

June 1980

I. S. Kingsley

F. K. Schweighardt

Compound identification in three distillate cuts of a product liquid.

Compound identification by high performance liquid chromatography and by gas chromatography (HPLC and GC) was performed on a product liquid sample obtained during a CPDU run.

Sample XCL-23-169PL was generated from the conditions below:

XCL-23-169 Process Condition

Hydrogen Pressure	170 atm (2500 psi)
Temperature	454°C (850°F)
LHSV	2.0 hr^{-1}
Hydrogen	2.2 wt % slurry
Feed	30% Pyro KY#9 coal
Solvent	70% Wilsonville Process Solvent

Three distillate cuts were obtained in a 300 g sample batch type distillation by CRSO Linwood:

Cut 1: IBP-215°C (IBP-420°F) at 4 weight %
Cut 2: 215-288°C (420-550°F) at 51 weight %
Cut 3: 288-415°C (550-780°F = FBP) at 45 weight %

The weight percent distribution of the distillate fraction is shown in Figure 1.

HPLC conditions for the chromatographic separation, as shown in Figures 2a-c, were:

Stationary Phase - 5 micron silica
Mobile Phase - 100% isooctane
Liquid Flow Rate - 0.5 ml/min

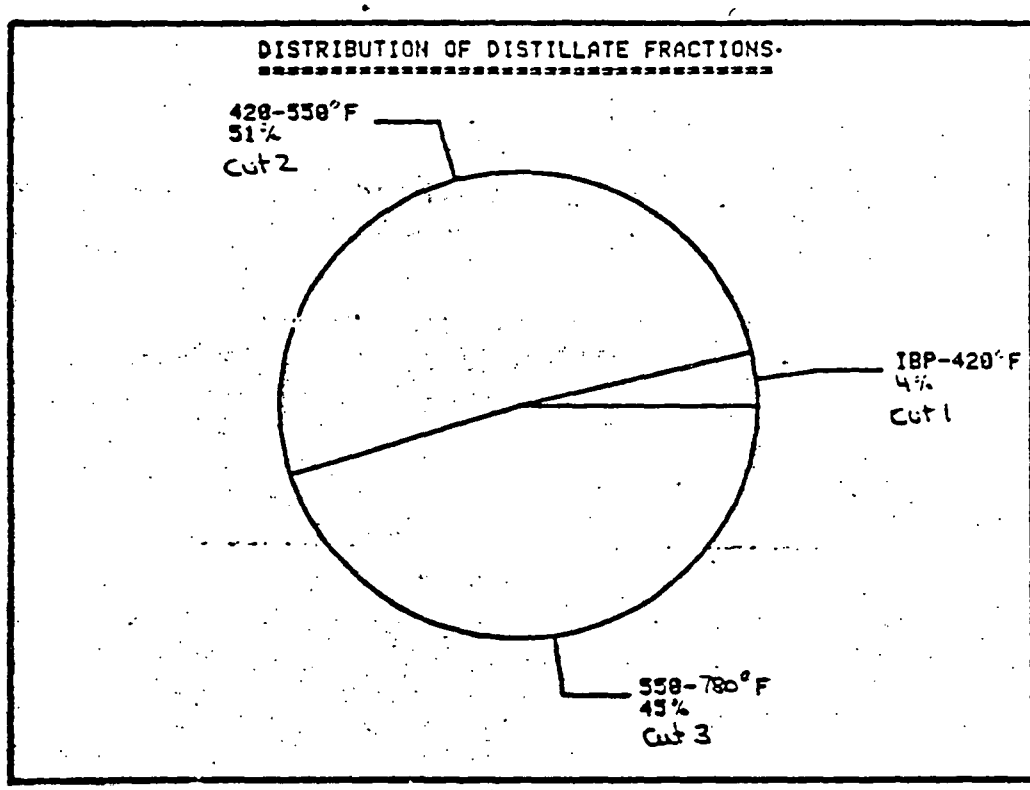


figure 1. Weight percent distribution of distillate cuts 1, 2 and 3.

The x-axis of the chromatograms shows the retention time from right to left and the y-axis is a function of intensity of absorption at 290 nm of the components. The retention time of a component using the above HPLC conditions is a function of solubility in the mobile phase and the component's interaction with the stationary phase. Therefore, nonpolar, smaller molecular components will elute before polar or larger molecular components.

Cut 1 (Figure 2a) shows three major peaks over a total retention time of 16.4 to 34 minutes before achieving baseline.

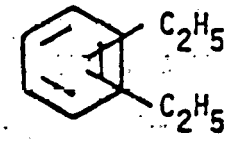
Cut 2 (Figure 2b) shows five major peaks over a total retention time of 16.6 to 38.3 minutes before achieving baseline.

Cut 3 (Figure 2c) shows three major peaks over a total retention time of 25 to 64 minutes before achieving baseline.

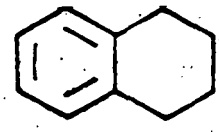
The increase in retention time shown with increasing boiling range of the distillate cuts is indicative of more polar and/or larger molecules in the higher boiling range distillate cut. Identification of the HPLC peaks has not been carried out at this time.

Gas chromatographic separation of the three distillate cuts was performed for compound identification as shown in Figure 3a-c. Using the chromatogram of a known compound mixture, Figure 3a shows:

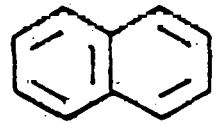
diethylbenzenes (1)



tetralin (2)



naphthalene (3)



as the major compounds in distillate cut 1 (IBP-215^{o}C).

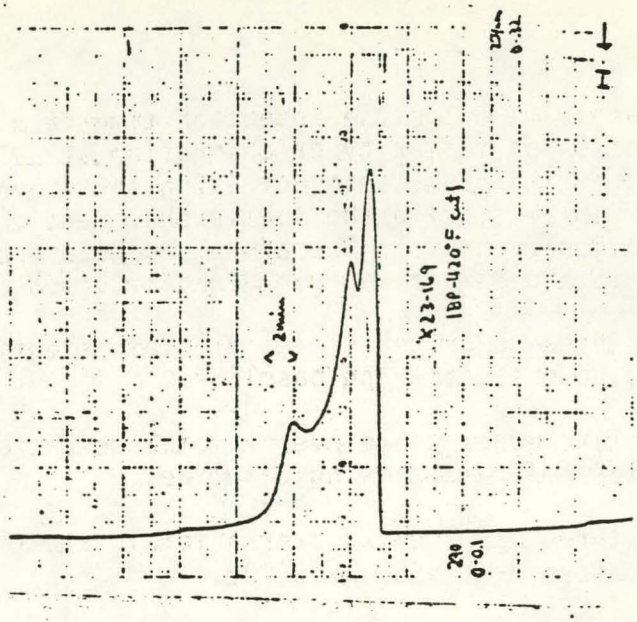


figure 2a.
HPLC chromatogram of distillate cut 1.

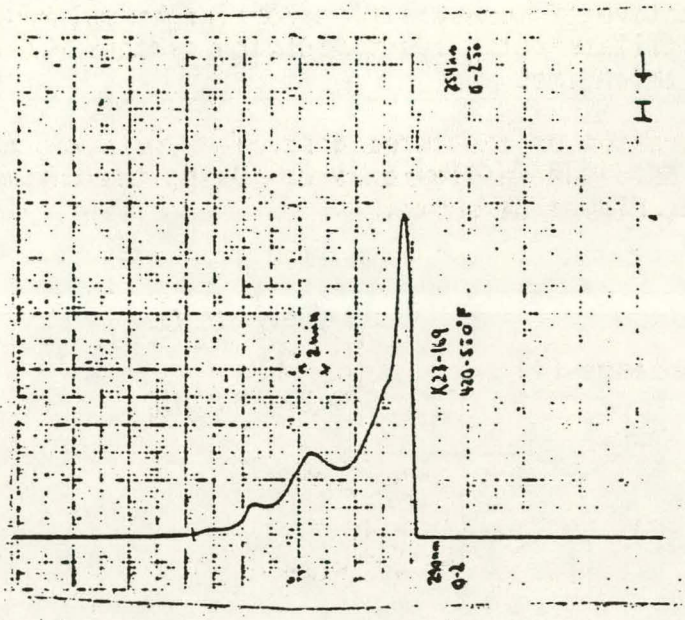


figure 2b.
HPLC chromatogram of distillate cut 2.

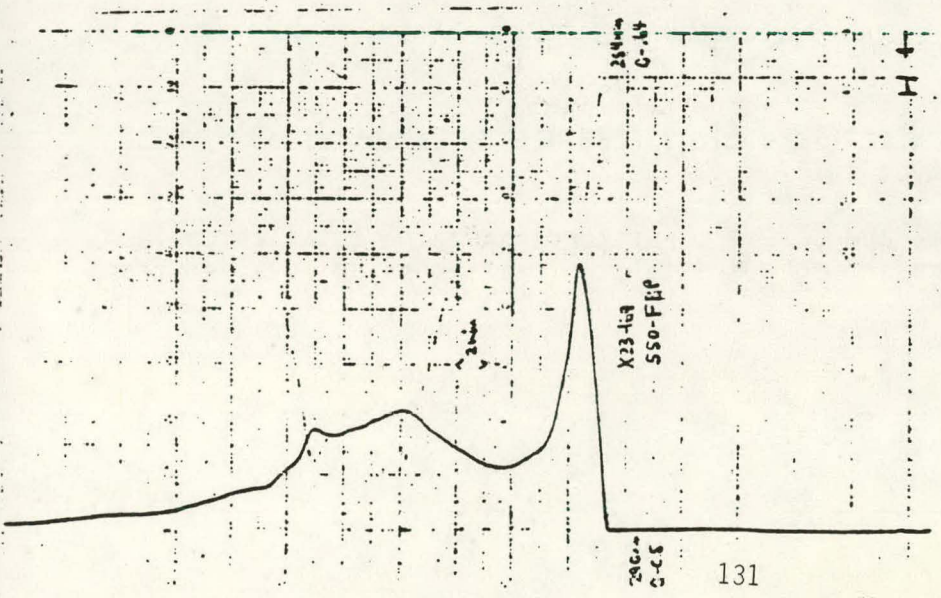
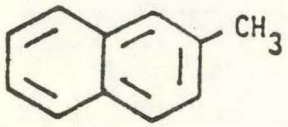


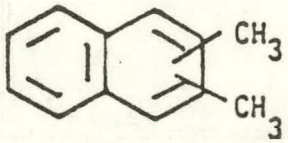
figure 2c.
HPLC chromatogram of distillate cut 3

Figure 3b shows:

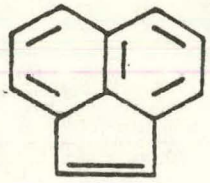
2-methylnaphthalene (4)



dimethylnaphthalene (5)



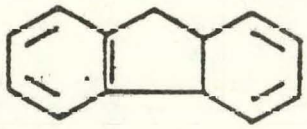
acenaphthene (6)



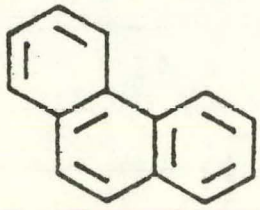
as the major compounds in distillate cut 2 (215-288°C).

and Figure 3c shows:

fluorene



phenanthrene



as the major compounds in distillate cut 3 (288-415°C), as obtained by CRSD Linwood on a 300 g batch type still.

Figure 4 shows the HPLC (a) and GC (b) chromatograms of the total recombined distillate fractions, representing a distillate fraction as is obtained from IBP-780°F.

figure 3a.
GC chromatogram
of dist. cut 1

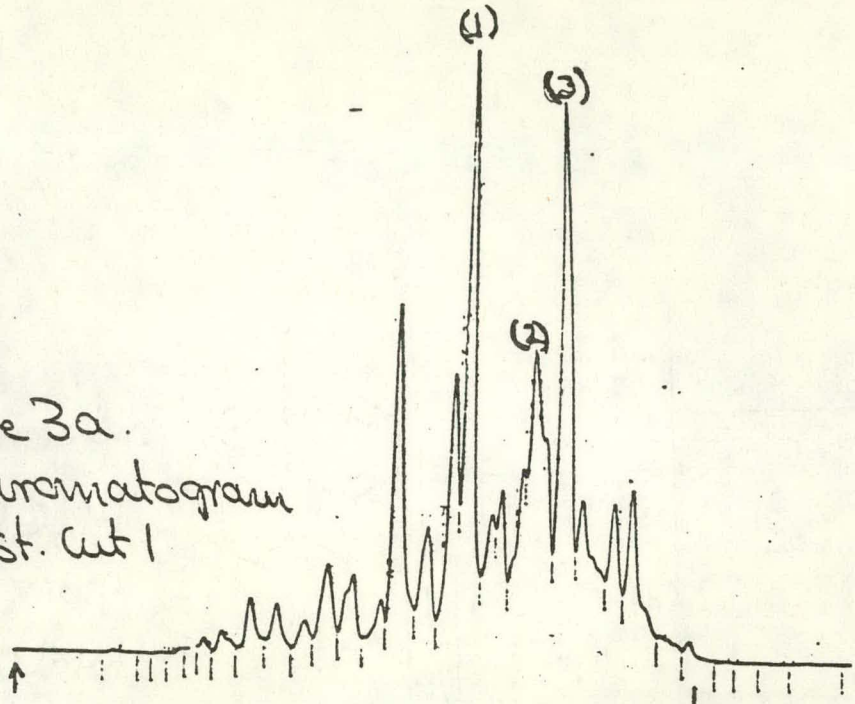


figure 3b
GC chromatogram
of dist. cut 2

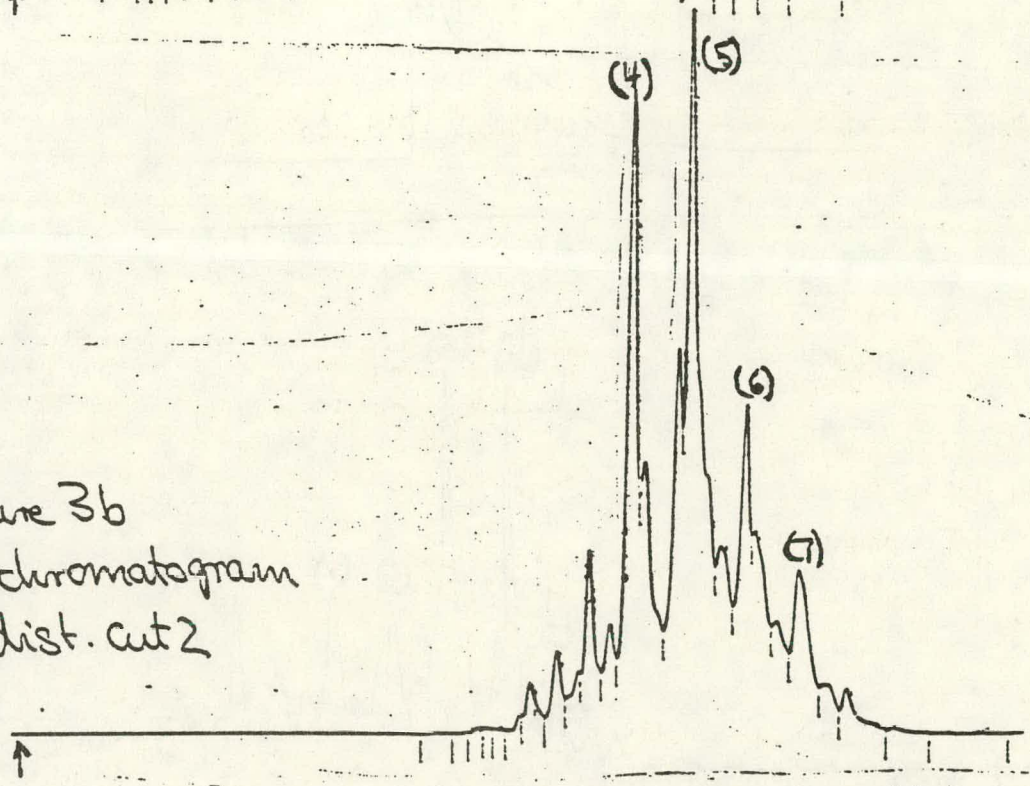
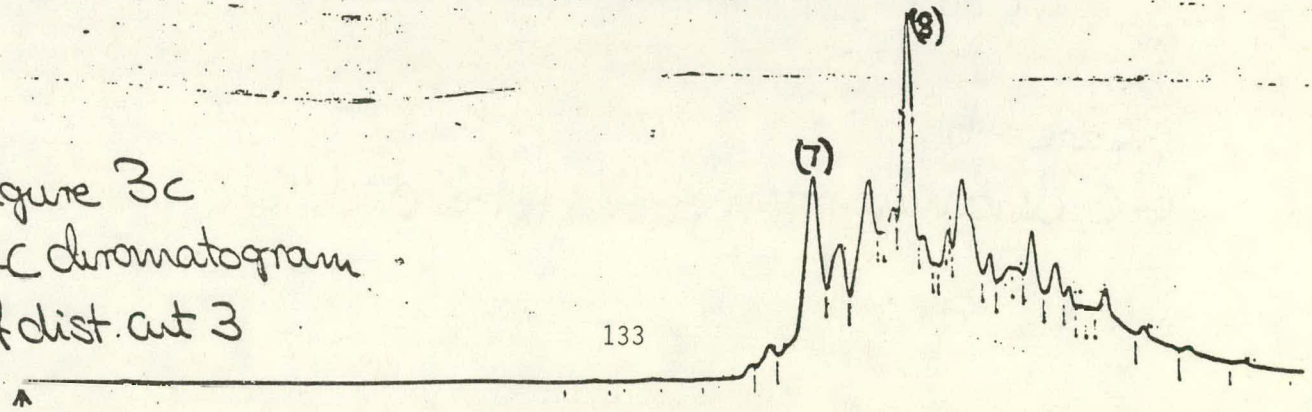


figure 3c
GC chromatogram
of dist. cut 3



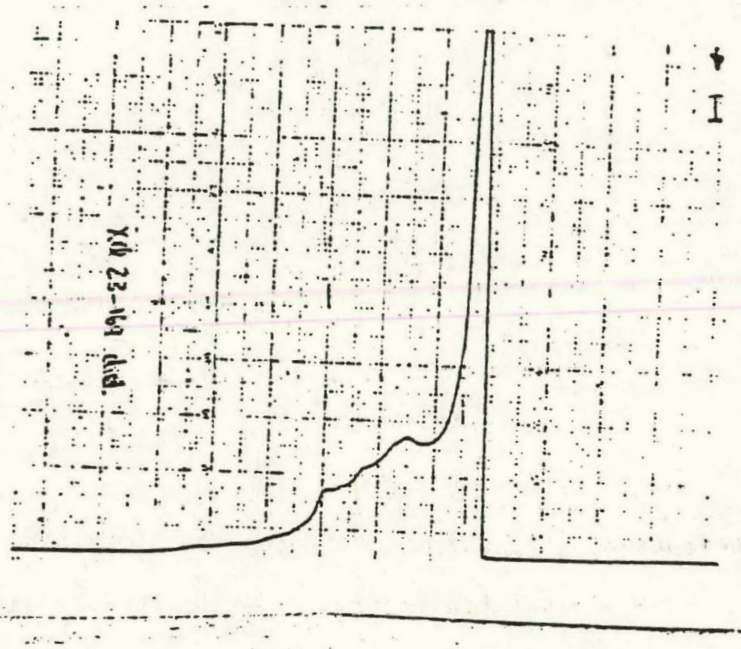


figure 4a
HPLC chromatogram of the total distillate

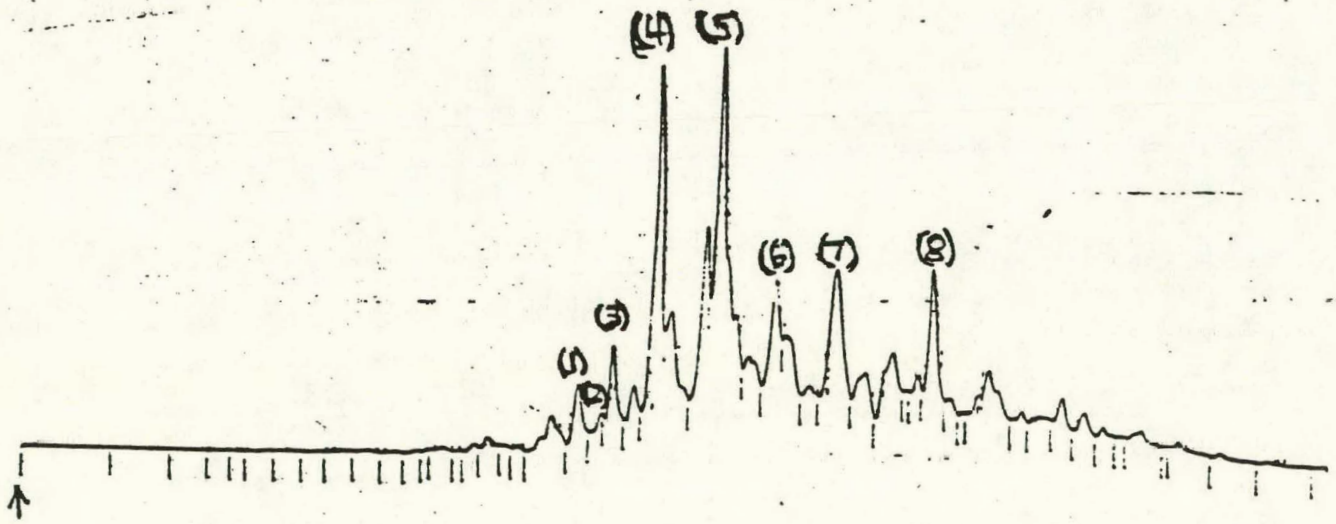


figure 4b.
GC chromatogram of the total distillate.

Attachment 6

Methods Development: (1) Column Chromatographic Separation

(2) Application of GC to the Characterization of a Hydrogen Donor Solvent

Coal Liquids Analysis

I. S. Kingsley

F. K. Schweighardt

ABSTRACT:

A. In order to demonstrate the precision (reproducibility) of the APCI Solvent Separation Procedure it was necessary to repeat the procedure five times with a CPDU coal derived product liquid.

B. ° It was observed that the molecular composition of the phenolic fraction derived from a Wilsonville recycle solvent, V131B/190AMB changed over a period of one to seven weeks. The sample was stored at room temperature with indirect sunlight exposure during the test period.

1. ° Multiple column chromatographic separations of a hydrogen donor solvent were performed and the reproducibility of weight fractions was determined.

° Column adsorption material in the chromatographic procedure was varied to find an optimal combination of silica and alumina for column separation of a hydrogen donor solvent into specific functional groups, saturate, aromatic, phenolic and N-bases.

2. ° A hydrogen donor solvent (HDS) was separated into its functional group fractions and then characterized by gas chromatography (GC) and GC-simulated distillation. Several key components present in the HDS were identified.

I. INTRODUCTION

During this reporting period considerable attention has been given to two basic questions faced in developing a coal-derived product data base.

A. Development of a reproducible and sound APCI coal liquids solvent separation procedure.

B. Characterization of recycle solvents.

In the past an outline of the new method used in the CRDD coal work-up lab was presented. We now present our study of the reproducibility of this method.

Most of the activities during this period were devoted to developing solvent characterization methods. Four different aspects of this subject were investigated.

1. Storage stability of recycle solvent
2. Reproducibility of column chromotography
3. Selection of optimum adsorbants for column chromatography
4. Application of gas chromatography in the characterization of a hydrogen donor solvent.

II. OBJECTIVE

The objective of this project is to establish standard procedures to efficiently analyze and characterize coal-derived materials from process studies at Trexlertown and to support the ICRC SRC-I demonstration plant program.

III. WORK AND RESULTS

A. Reproducibility of solvent separation procedure for product liquid samples.

A product liquid sample (XCL-132PL) was separated by the APCI solvent separation procedure as shown in Figure 1, to establish a range of variation to be expected from this method. Five samples were taken from the original product liquid sample and the solvent separation procedure, outlined in the previous report, was performed on each sample. The results and error analysis are given in Table I, and show reproducibility, as determined by the standard deviation, to be approximately 1%.

B. Selective Characterization of Recycle Solvent

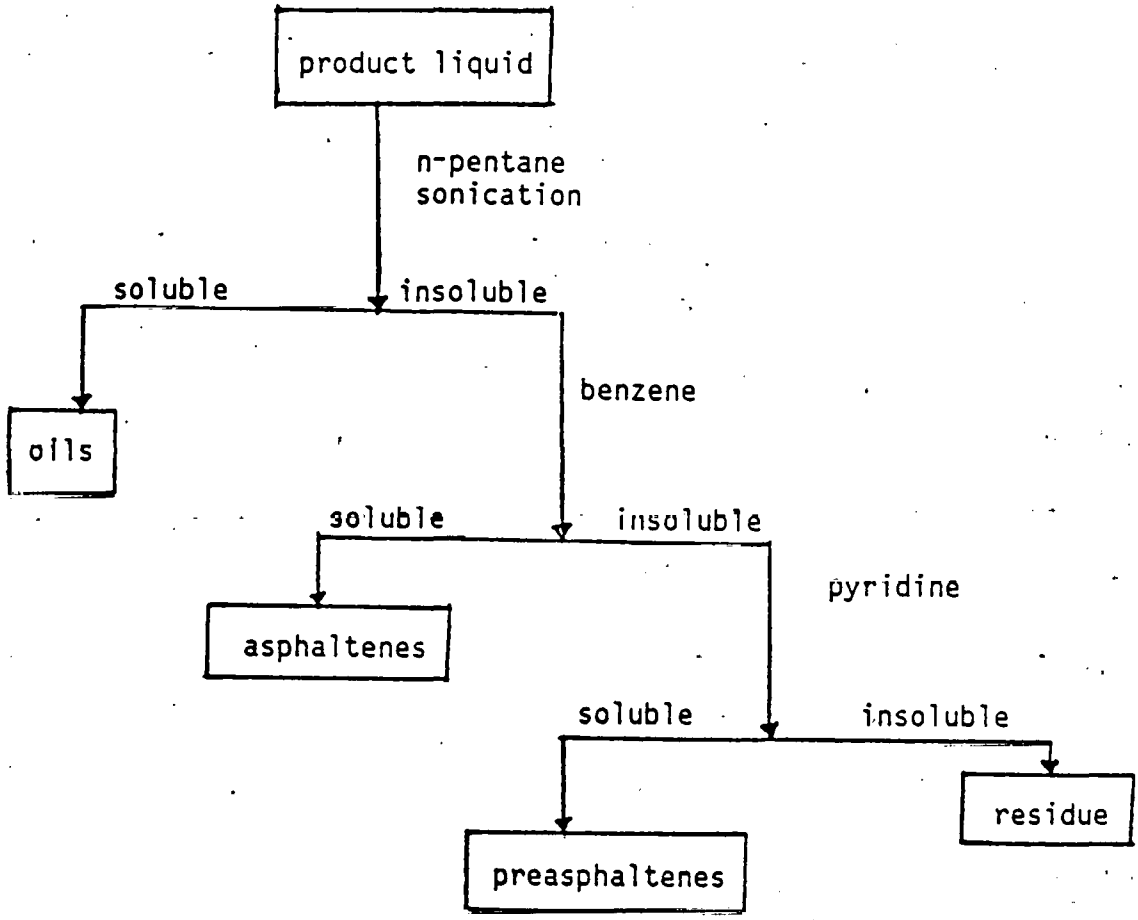
1. Storage stability of the phenolic fraction of a Wilsonville recycle solvent, V131B/190AMB.

The recycle solvent was subjected to a functional group separation as outlined in Figure 2. Nitrogen base components were removed first, because they are known to irreversibly bind to silica gel used later in the procedure. As described, the saturate hydrocarbons elute first and do not respond to UV light at 320 nm. Aromatic hydrocarbons elute as a combined fraction that give a large fluorescent response. The polar fraction is last to elute and contains hydroxyl species such as phenols and alcohols.

The phenolic fraction was intentionally stored at room temperature, 25°C, in a fume hood with indirect sunlight exposure. Over the course of seven weeks the infrared (IR) spectrum of this phenolic fraction was taken as a smear on NaCl plates. After less than two weeks a small absorption peak at 1730 cm^{-1} was noted, Figure 3. This vibration absorption is indicative of carbonyl, C=O, groups of the aldehyde RHC=O and ketone $R_2C=O$ kind.

Air Products

Figure 1



APCI Solvent Separation Scheme

Table I

Results of Solvent Separation Reproducibility Study

Sample # wt. in grams	1	2	3	4	5
initial sample	5.00	4.96	5.71	4.95	4.92
oils	3.13	3.12	3.60	3.03	2.97
asphaltenes	.40	.44	.48	.51	.40
preasphaltenes	.56	.41	.54	.44	.53
residue	.91	.89	1.04	.89	.92
recovered	5.00	4.86	5.66	4.87	4.82
% recovered	100	98	99	98	98
oils	62.6	64.9	63.9	62.8	62.4
asphaltenes	8.0	8.9	8.4	10.3	8.1
preasphaltenes	11.2	8.3	9.5	8.9	10.8
residue	18.2	17.9	18.2	18.0	18.7

Reproducibility of the Solvent Separation Procedure

	Mean	Standard Deviation
oils	63.3%	1.06%
asphaltenes	8.7%	0.94%
preasphaltenes	9.7%	1.23%
residue	18.2%	0.31%

Figure 2

Column Separation of a Process Solvent

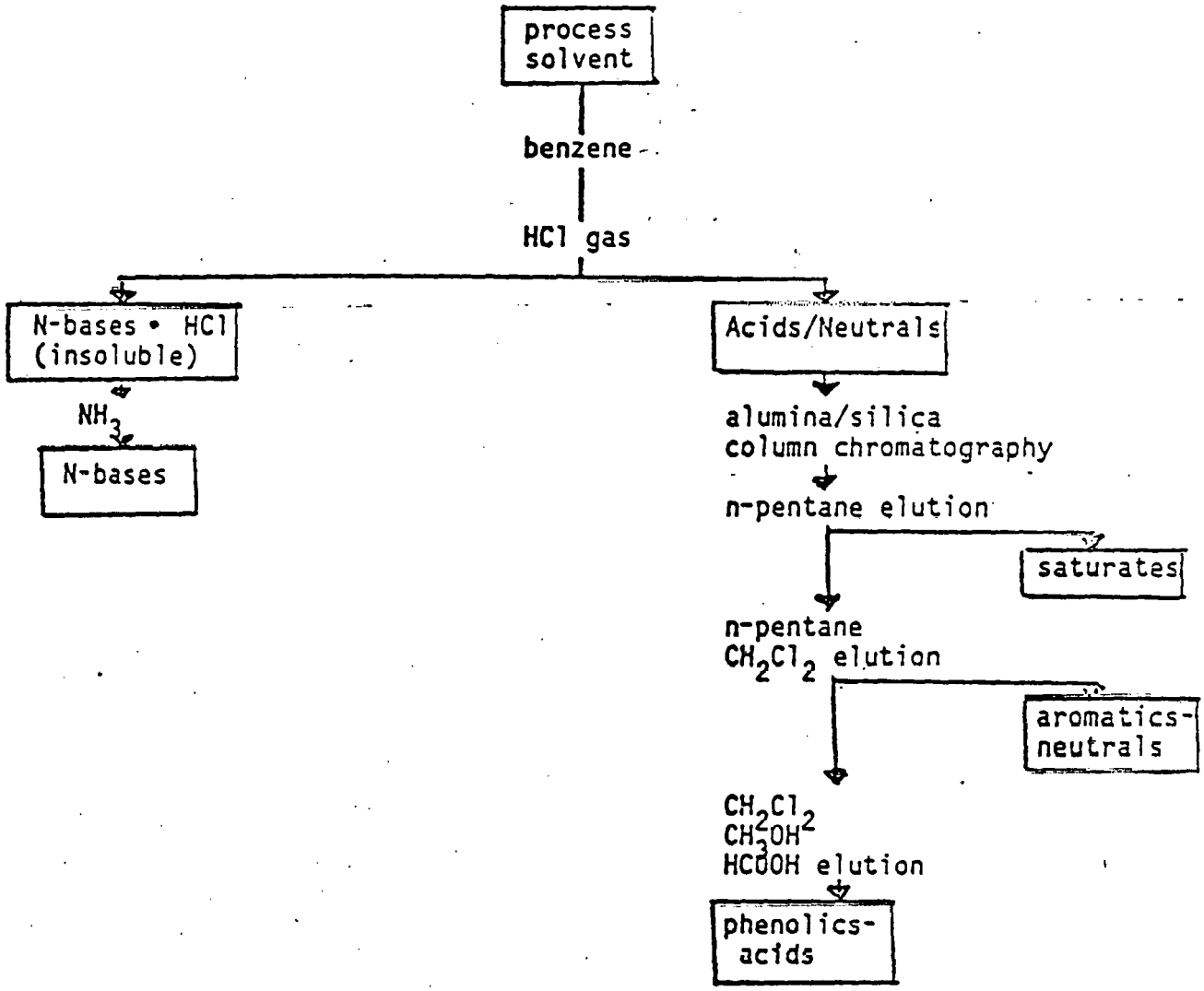
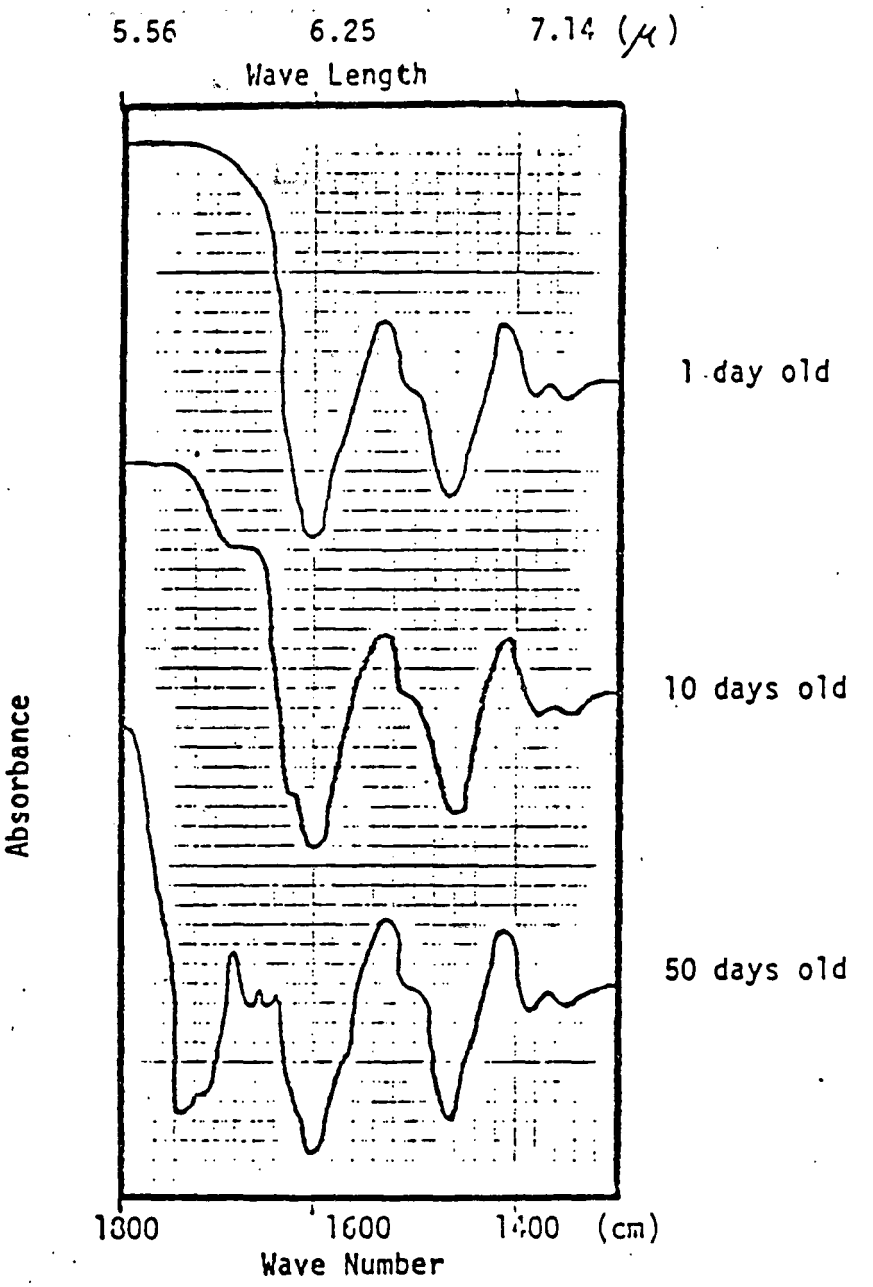


Figure 3



IR SPECTRA of phenolic fraction
(190 AMB) fresh and aged

This observation is very clear evidence that oxidation occurs with coal-derived materials and that the phenolic/hydroxyl components are very active. To confirm this observation, samples of the aged material were analyzed by ultra-high resolution mass spectrometry (HRMS) at the University of Nebraska (Michael Gross), and by combined gas chromatography-mass spectrometry (GC-MS) at Brigham Young University (Milton Lee). Both laboratories confirmed that carbonyl-containing species were present, and that dimethyl benzaldehyde (I) was a major component.

2. Reproducibility study of the column chromatographic procedure for the characterization of hydrogen donor solvents.

   A Wilsonville recycle solvent (V131B/190AMB) was separated by a mixed silica/alumina 1:1 (v/v) column into saturates, aromatics, phenolics and nitrogen bases as outlined in Figure 2. The fractions were weighed after solvent removal. Results of four different separations are given in Table II as well as the error analysis of this experiment.

3. Optimization of the column material in the column chromatographic procedure for a recycle solvent.

   Column chromatography of hydrogen donor or recycle solvent (drum #F219 WRS) was performed as outlined in Figure 2. The loading configuration of the alumina and silica absorbents in the column was varied to determine the optimal separation of the solvent into the saturate, aromatic and phenolic fractions after removal of the nitrogen bases.

   The elution scheme for each column was the same, using the same amounts of solvents to elute each fraction. The various column configurations which were used are shown in Figure 4. The intimate mixture of silica and alumina in Column V has been used in previous column separations. The results are given in Table III.

   Columns II and V gave poor total recovery probably due to excessive amounts of phenolics irreversable bound to the silica in the absorption column. Column IV showed very poor initial flowrates but gave a larger fraction of saturated compounds than the other columns. Column III would be a good column if the saturates and aromatics are not needed as two separated fractions but could be grouped as hydrocarbons. If the fraction of saturate in the recycle solvent is the most important item, column configuration IV is to be used.

Table II

Weight % Recovered by Column Separation

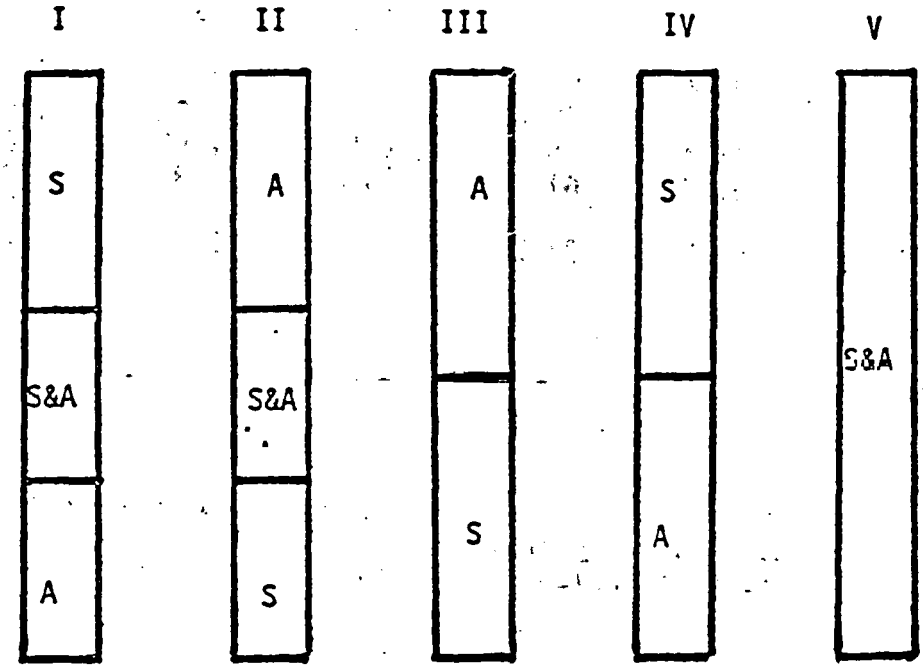
Sample #	1	2	3	4
saturates	6	8	8	7
aromatics	57	61	65	64
phenolics[1]	35	28	25	29
N-bases	2	3	3	1

results were normalized in favor of the phenolic fraction.

Reproducibility of the Column Separation

	Mean	Standard Deviation
saturates	7	0.9
aromatics	62	3.6
phenolics	29	4.2
N-bases	2	1.0

FIGURE 4



Column configuration for separation optimization using silica(S), alumina(A) and a homogeneous mixture of silica and alumina (S&A).

Table III

Results from Column Separation Optimization Study

Column #	I	II	III	IV	V[3]
% recovery	91.8	86.8	91.3	91.7	86.6
phenolics [1]	31.4	28.2	28.7	30.6	34.4
saturates	17.4	4.3	6.0	27.6[2]	12.2
aromatics	51.3	67.6	65.2	41.8	53.3
sat. & arom.*	68.7	71.9	71.2	69.4	65.5

* total hydrocarbon
1 Normalized to account for phenolics irreversible bound to silica.
2 Fraction showed contamination by aromatic fraction.
3 Column is identical to silica/alumina columns used in previous work.

4. Application of GC to Characterization of a Hydrogen Donor Solvent

A Wilsonville hydrogen donor solvent (HDS), V131B/190AMB was solvent separated into oils, asphaltenes and preasphaltenes, Figure 1, and gave 97%, 2.5% and 0.5% respectively. Column chromatography on silica/alumina, Figure 2, of the same solvent resulted in a functional group distribution that gave 7% saturates, 62% aromatics/ hydroaromatics, 29% phenolics/hydroxyl compounds and 2% nitrogen bases. The chromatographic fractions were then characterized further by gas chromatography (GC), and GC-simulated distillation.

a. Gas Chromatographic Characterization

The advantages of gas chromatographic separation over a GC-simulated distillation characterization is the enhanced resolution of individual compound peaks, so a more precise molecular profile can be assertained. The GC conditions were:

Detector	Hydrogen Flame Ionization
Liquid Phase	8% SP-2100
Solid Phase	Gas-chrom Q
Column Temperature	Programmed at +50°C for 10 min. then 5°C/min to 300°C
Sampler Induction Temp.	150°C
Carrier Gas	He
Flow Rate	30 cc/min
Column Length/Diameter	10 ft by 3/16 in. OD
Sample Size	0.9 l
Detector Temperature	310°C
Calculated Theor. Plates	2668 per meter

The chromagrams are shown in Figures 5-9. A model compound mixture was run for peak identification and relative retention time (r_t) measurements.

Figure 5a shows the chromagram for the initial HDS, Figure 5b the nitrogen bases and Figure 5c the N-base free material (precolumn). No significant peak pattern change occurred after removal of the N-bases. The N-base free material shows virtually the same chromatographic pattern as the initial HDS. This eliminates the possibility of determining the amount of N-bases in the total sample by peak quantification in the chromagram of the total HDS.

Figure 6a shows the N-base free sample (precolumn), which contains saturates, aromatics/hydroaromatics and phenolic/ hydroxyl compounds. Figure 6B shows the hydrocarbon fraction (saturate and aromatic), and Figure 6c shows a model compound mixture containing aromatic and saturate. The peak identified by arrow in Figure 6a disappears after removal of the phenolic compound, arrow in Figure 6b. Therefore, this peak is indicative of the phenolic compounds. Comparing chromagrams Figure 6a with Figure 6c, compounds #7, 9, 14, 18 and 20 of the mixed model compounds are present in the precolumn material and can be identified as naphthalene, 2-methyl naphthalene, n-tridecane, dimethyl naphthalenes, phenantrene, anthracene, n-octadecane, fluoranthene and n-heneicosane and pyrene. The structures of these compounds are shown in Figure 10.

Figure 7a shows the precolumn material containing saturates, aromatics and phenolics, Figure 7b shows the isolated saturate fraction and Figure 7c shows a saturate compound model mixture. Compounds 3 and 4, n-tridecane and n-tetradecane are identified to be the two major compounds in the saturate fraction. The chromagrams also show that C_{10}-C_{29} (nonacosane), all normal paraffins, are present in decreasing amounts in the HDS.

Figure 8a shows the chromagrams of the N-base free sample, Figure 8b the aromatic fraction thereof, and Figure 8c an aromatic model compound mixture. The four major peaks in the unseparated sample are also the major peaks in the aromatic fraction and are identified from the model compound mixture chromagram as 2-methyl naphthalene, dimethyl naphthalenes, fluorene, phenanthrene and anthracene.

Figure 9a shows the chromagram of the N-base free HDS, 9b the phenolic fraction and 9c the precolumn material after removal of the phenolic fraction. Figure 9b shows a very large peak, which is missing in the phenolic free fraction, as seen on Figure 6b. This peak therefor is specific for the phenolic fraction in the HDS.

Quantitative evaluation of characteristic peaks of each fraction was attempted. The peak area in the mixed chromatogram (precolumn) plus the remainder of peak areas present in the fractionated chromatogram represent the peak areas of the individual fraction in the mixed chromatogram.

Table IV shows the peaks chosen, retention times, percent peak intensities of the chromagrams and the last column is a calculation of the fraction present in the precolumn HDS material as follows:

$$C = A + A\left(1 - \frac{B}{100}\right),$$

where, A = % intensity in precolumn chromagram for a peak at r_t
B = % intensity in fraction chromagram for a peak at r_t
C = calculated % fraction present in the precolumn HDS

Figure 5

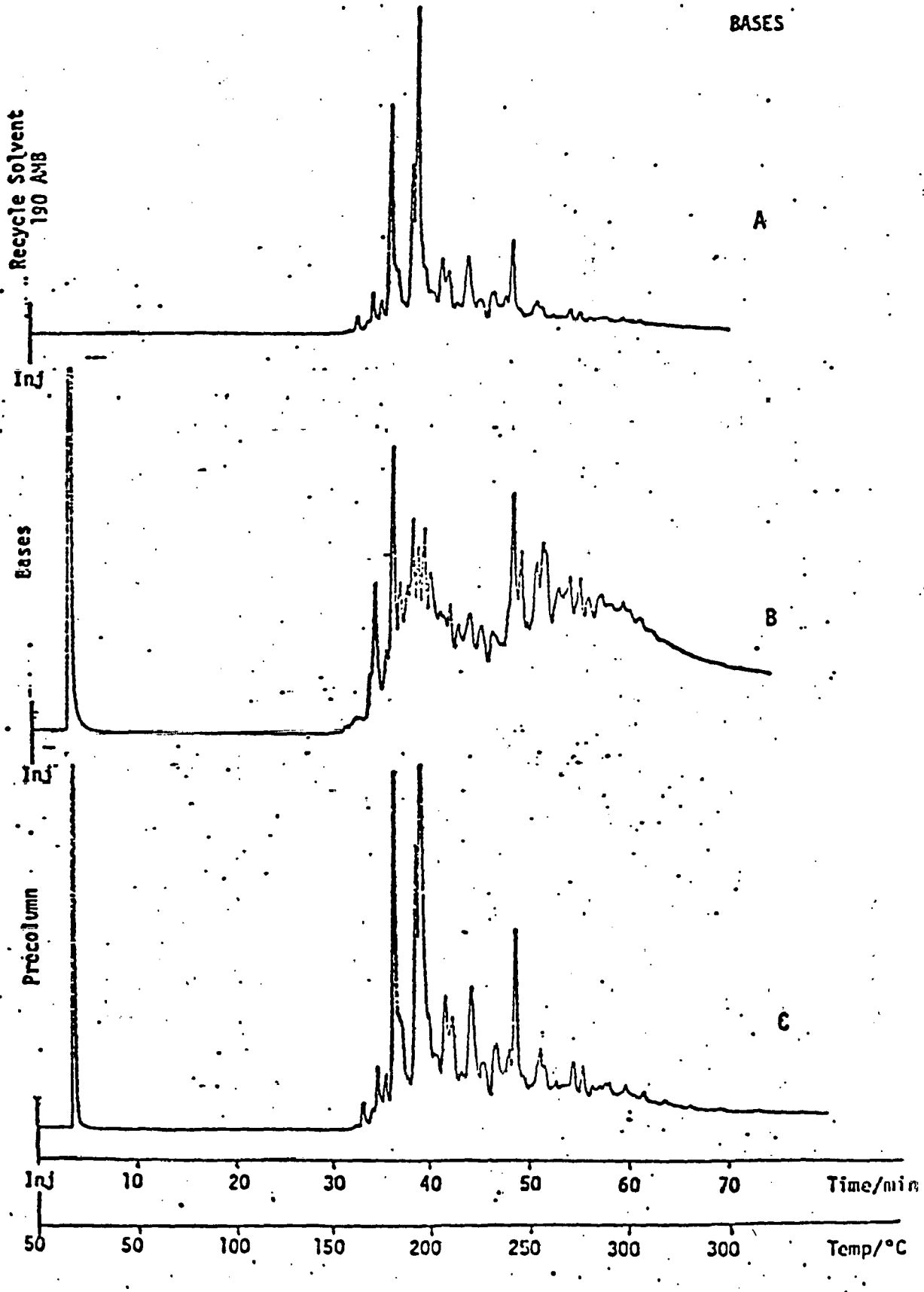

BASES
Recycle Solvent
190 AMB
A
Inj
Bases
B
Inj
Precolumn
C
Inj
10
20
30
40
50
60
70
Time/min
50
50
100
150
200
250
300
300
Temp/°C

Figure 6

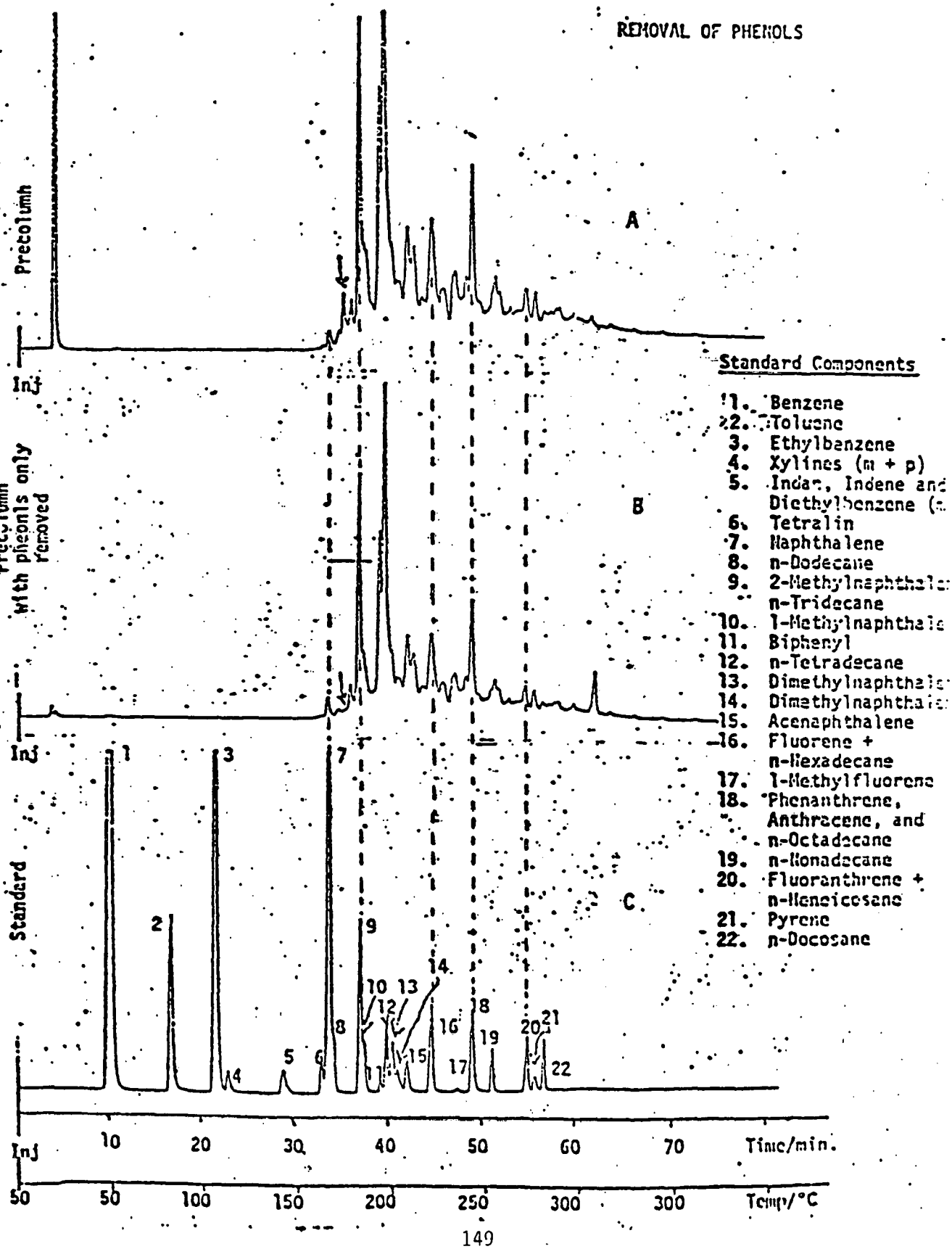

REMOVAL OF PHENOLS
Precolumn
A
Inj
Pri column with phenols only removed
B
Inj
Standard
C
Inj
Time/min.
Temp/°C
Standard Components
1. Benzene
2. Toluene
3. Ethylbenzene
4. Xylines (m + p)
5. Indan, Indene and Diethylbenzene (
6. Tetralin
7. Naphthalene
8. n-Dodecane
9. 2-Methylnaphthale
n-Tridecane
10. 1-Methylnaphthale
11. Biphenyl
12. n-Tetradecane
13. Dimethylnaphthale
14. Dimethylnaphthale
15. Acenaphthalene
16. Fluorene + n-Hexadecane
17. 1-Methylfluorene
18. Phenanthrene, Anthracene, and n-Octadecane
19. n-Nonadecane
20. Fluoranthrene + n-Heneicosane
21. Pyrene
22. n-Docosane

Figure 1

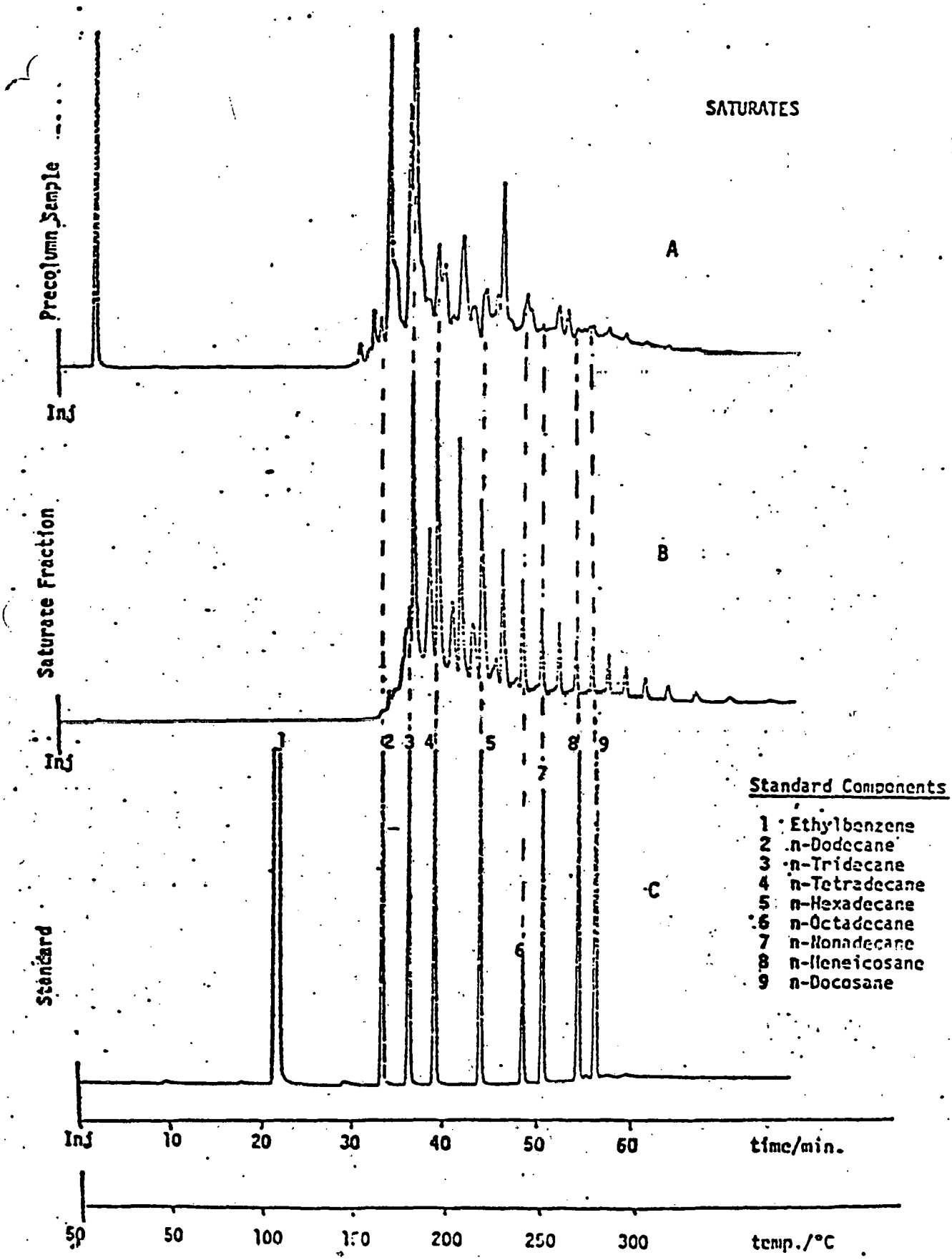

SATURATES
Precolumn Sample
Inj
A
Saturate Fraction
Inj
B
1
2
3
4
5
6
7
8
9
Standard
C
Standard Components
1 Ethylbenzene
2 n-Dodecane
3 n-Tridecane
4 n-Tetradecane
5 n-Hexadecane
6 n-Octadecane
7 n-Nonadecane
8 n-Heneicosane
9 n-Docosane
Inj
10
20
30
40
50
60
time/min.
50
50
100
150
200
250
300
temp./°C

Figure 8

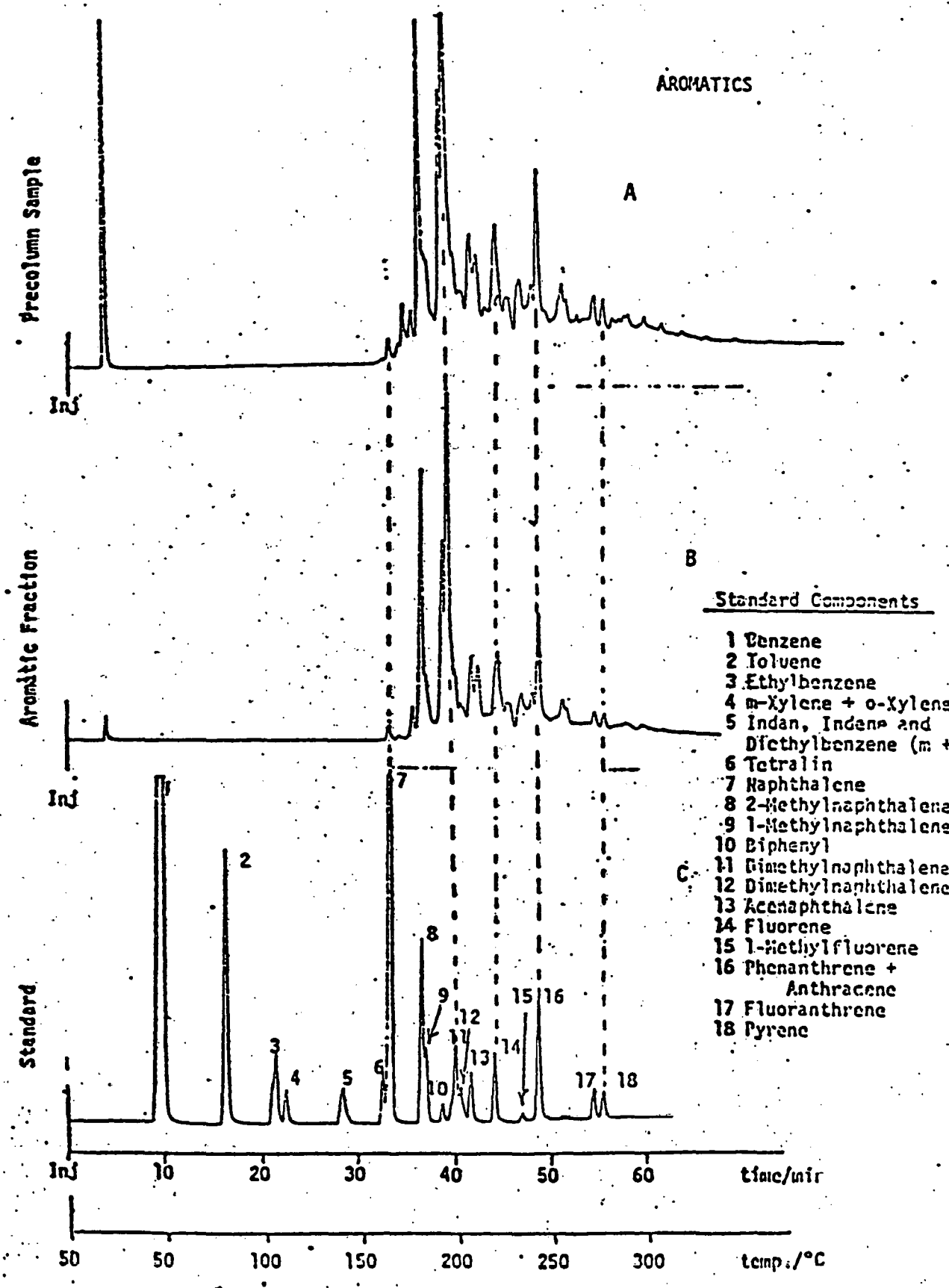

AROMATICS
Precolumn Sample
A
Inj
Aromatic Fraction
B
Inj
Standard
C
Inj
10
20
30
40
50
60
time/min
50
50
100
150
200
250
300
temp./°C
Standard Components
1 Benzene
2 Toluene
3 Ethylbenzene
4 m-Xylene + o-Xylene
5 Indan, Indene and Diethylbenzene (m +
6 Tetralin
7 Naphthalene
8 2-Methylnaphthalene
9 1-Methylnaphthalene
10 Biphenyl
11 Dimethylnaphthalenes
12 Dimethylnaphthalenes
13 Acenaphthalene
14 Fluorene
15 1-Methylfluorene
16 Phenanthrene + Anthracene
17 Fluoranthrene
18 Pyrene

Figure 9

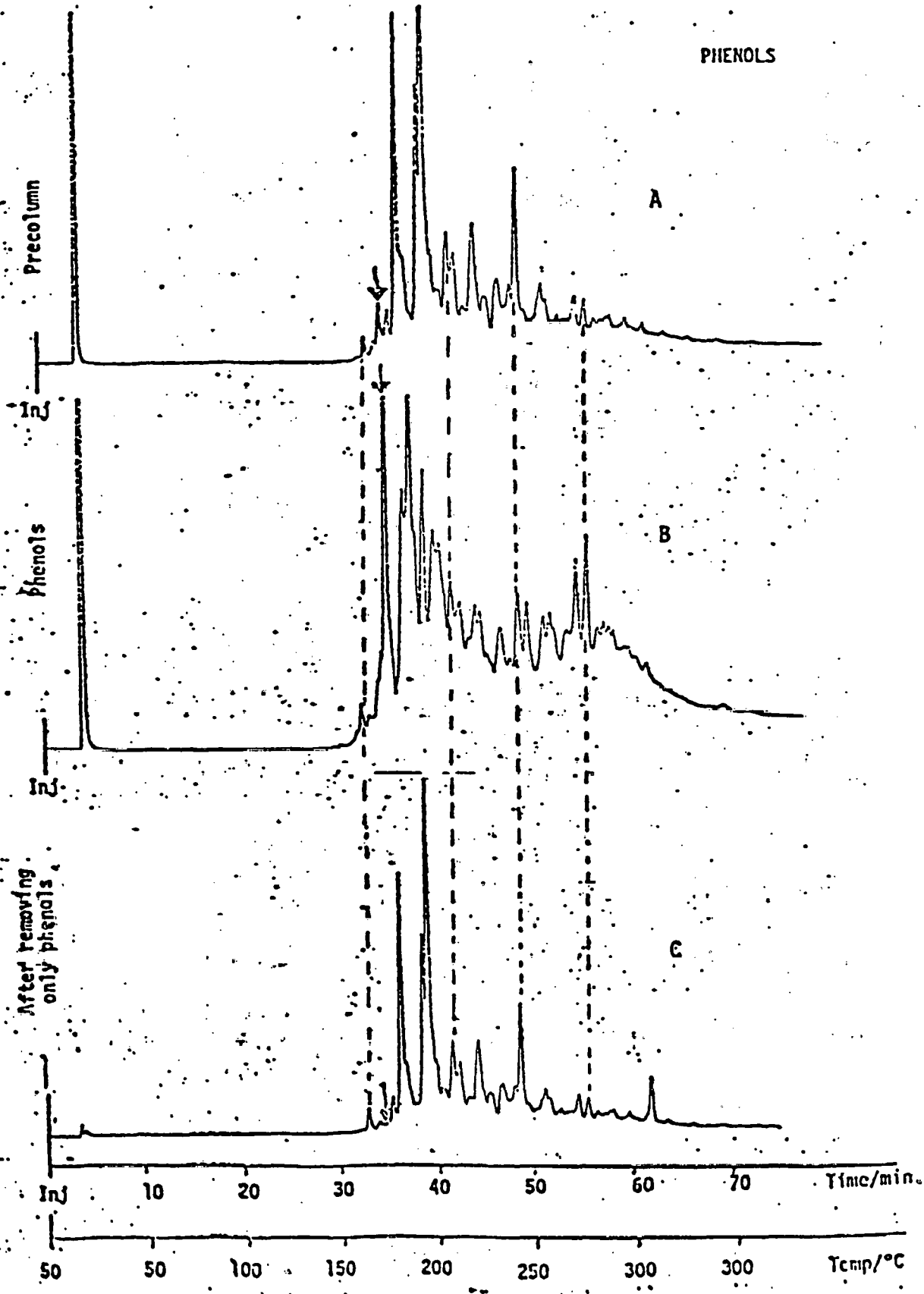
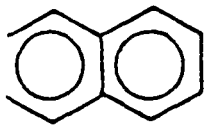
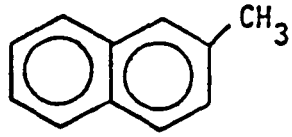

PHENOLS
Precolumn
A
Inj
Phenols
B
Inj
After removing only phenols
C
Inj
10
20
30
40
50
60
70
Time/min.
50
50
100
150
200
250
300
300
Temp/°C

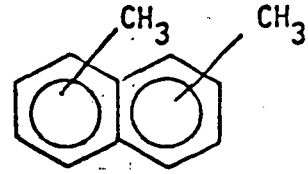
Figure 10



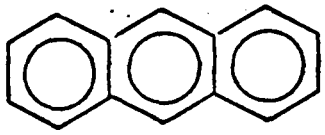
naphthalene



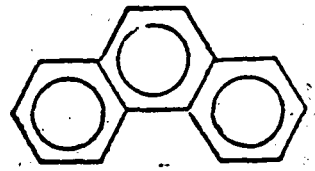
2-methyl-naphthalene



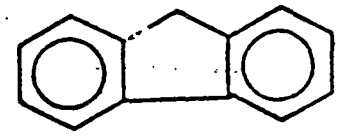
dimethyl-naphthalenes



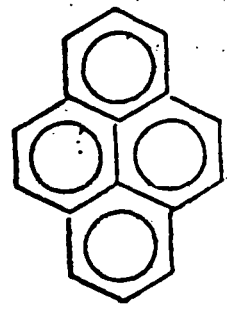
anthracene



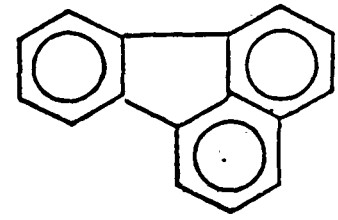
phenanthrene



fluorene



pyrene



fluoroanthene

$CH_3(CH_2)_{11}CH_3$ tridecane

$CH_3(CH_2)_{12}CH_3$ tetradecane

$CH_3(CH_2)_{16}CH_3$ octadecane

$CH_3(CH_2)_{19}CH_3$ heneicosane

$CH_3(CH_2)_{27}CH_3$ nonacosane

Table IV

r_t	characteristic for	% in precol. chromagram	% in fraction chromagram	calculated % fraction in precolumn
45.4	saturates	1.29	6.93	21
43.7	aromatics	3.26	3.86	22
35.8	phenolics	1.18	5.80	57

Comparing the GC calculated results with the actual weight fractions obtained by column separation it appears there is very little agreement in all three fractions.

b. Characterization by GC-simulated Distillation

The GC-simulated distillation was performed on the total HDS and its subfractions. The hydrocarbon chromagrams, Figure 11, show profiles very similar to those obtained by GC. The boiling ranges and % material distilled for the total HDS and its subfractions are given in Table V.

The boiling point profile are similar over the entire temperature range for the total HDS and its subfractions. It is unlikely that a temperature cut can be used to segregate one fraction from another.

IV. CONCLUSIONS

A. Reproducibility of total recoveries by the APCI solvent separation method of product liquid samples shows a standard deviation of 1%.

- Coal-derived liquids must be carefully stored under nitrogen or argon at 4°C to maintain or prolong molecular integrity. If we are to analyze the compounds from Wilsonville, Tacoma or even the Allentown Laboratories, the samples must be preserved to reduce sample oxidation.

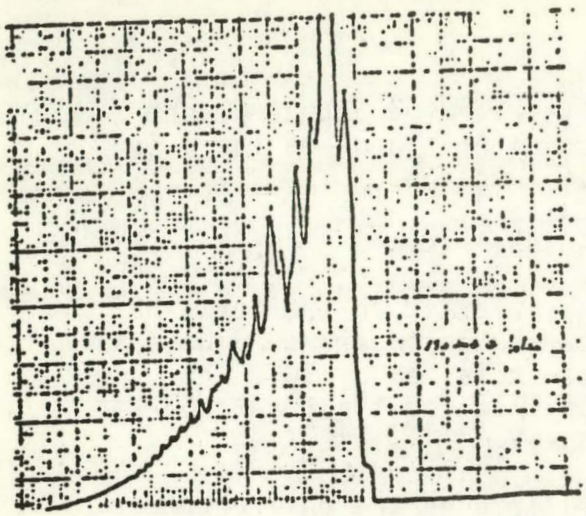
- A relatively large variation in the weight percent of recovered material from the column chromatographic separated saturates/aromatics/phenolics/N-bases indicates a need to improve the technique prior to establishing the procedure in the work-up laboratory.

- Optimization of column packings for the column separation procedure showed that a column Type III (see Figure 4) is to be used for a rapid and reliable separation of a hydrogen donor solvent into a mixed fraction of aromatics/saturates and a phenolic fraction. When the saturated fraction is required as a separate fraction of the hydrogen donor solvent, a column of Type IV (see Figure 4) is to be used.

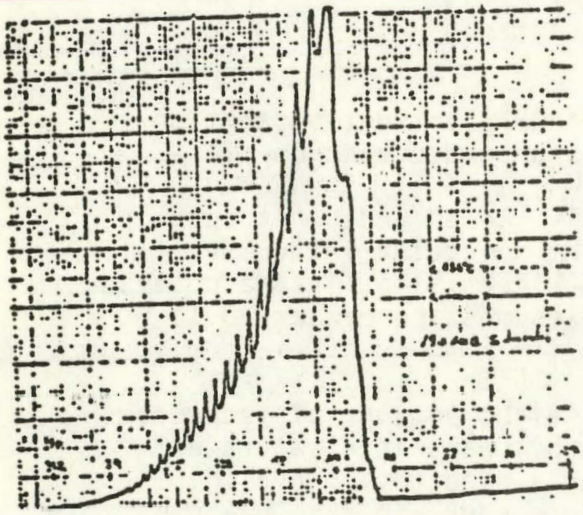
- A hydrogen donor solvent (HDS) and its functional group fractions were characterized by gas chromatography (GC) and GC-simulated distillation. Key compounds present in the HDS were identified as:

  2 methyl naphthalene
  dimethyl naphthalenes
  fluorene
  phenanthrene
  anthracene
  fluoranthene

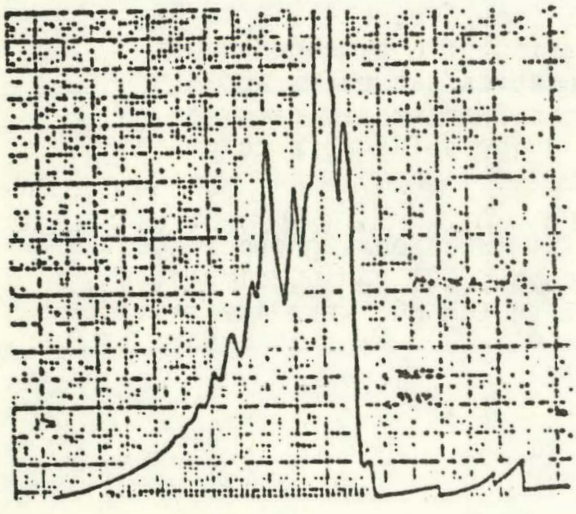
GC-Simulated Distillation
Figure 11



Recycle Solvent



Saturates



Aromatics

← Temperature

Table V

GC-Simulated Distillation [°F]

	total HDS	satur.	arom.
IBP	422	426	423
25%	486	495	486
50%	536	543	532
75%	637	625	625
95%	802	770	776
FBP	921	864	900

pyrene
n-tridecane and n-tetradecane

An attempt was made to quantify the functional group fractions directly from the chromagrams, but this failed.

Separation of the HDS into functional group fractions via temperature cuts from the GC-simulated distillation was shown futile at this point.

V. ACKNOWLEDGEMENTS

The GC experiments were designed and carried out by Ann Kamzelski, CRSD, who should be credited for her excellent work.

Coal Products Characterization

F. K. Schweighardt, I. Kingsley

N-Base Separation from Process Solvent

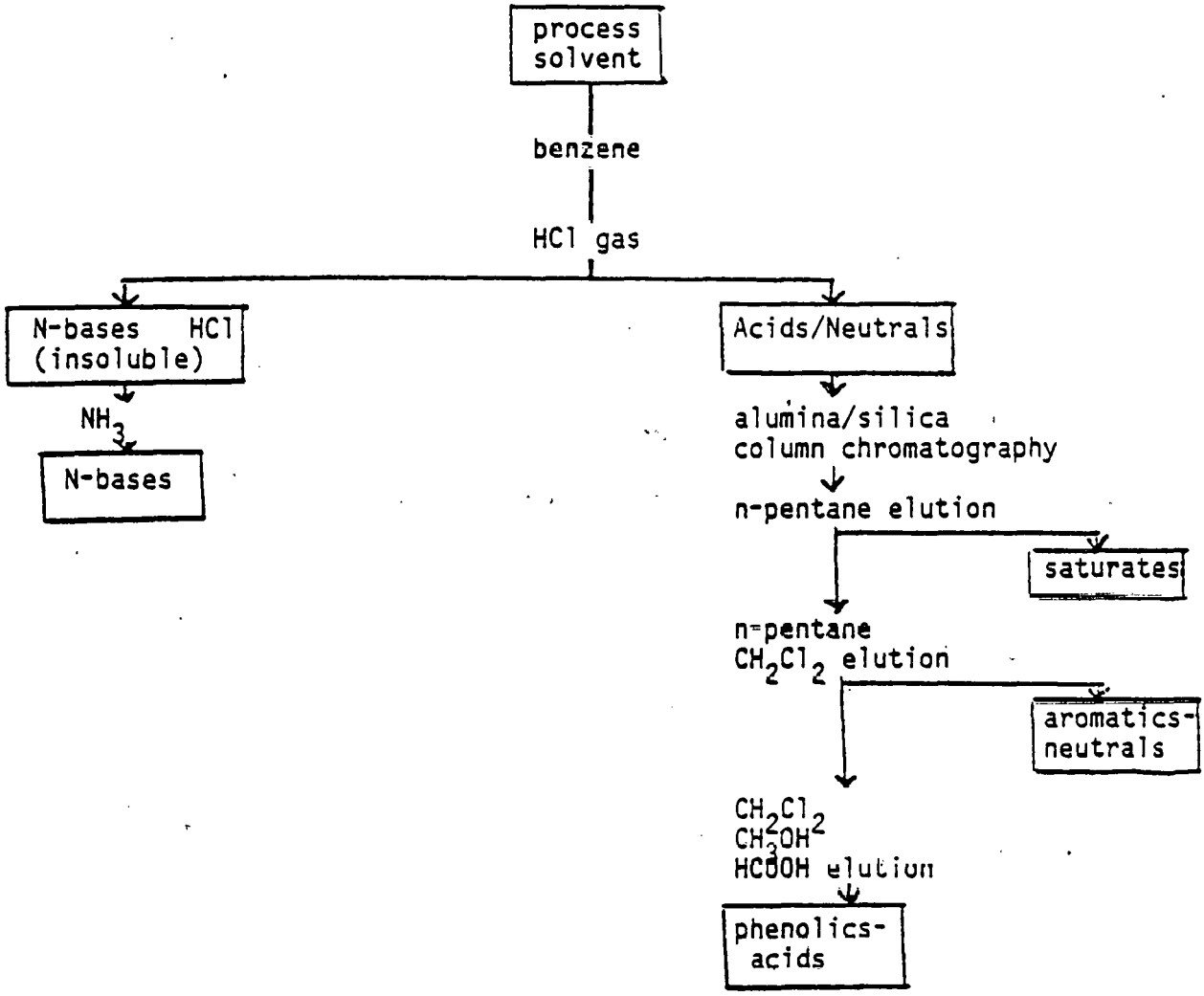
A new technique has been applied to the characterization of hydrogen donor process solvents. A Wilsonville recycle solvent (V131B) 190 AMB was treated with HCl(g) while in benzene solution to remove N-base components as HCl-adducts. The benzene soluble remaining (acid/neutrals) were column chromatographed to give three subractions: 1. saturates, 2. aromatic/hydroaromatics, and 3. phenolic acids. The base components were reclaimed by passing NH_3 through a mixture of the HCl-adducts in benzene. An outline of this procedure is given in Figure 1 and the results from separation of the V131B Wilsonville recycle solvent from Rum 190 AMB are as follows:

Subfraction	Wt. Percent
Saturates	18
Aromatic	51
Acids/Phenolics	26
Bases	5

Each subfraction will be subjected to further characterization to determine hydrogen distribution (H_{NMR}), CH/NH percent (NIR), boiling point distribution (Sim Dist-GC) and elemental analysis.

Figure 1

Column Separation of a Process Solvent



Attachment 7

High Performance Liquid

Chromatographic Procedure

PROCESS SYSTEMS GROUP

RESEARCH AND DEVELOPMENT DEPARTMENT PROGRAM AREA REPORT

FOR
JULY/AUGUST/SEPTEMBER
1980

Air Products

PROCESS SYSTEMS GROUP

R&D PROJECT SUMMARY REPORT

JULY/AUGUST/SEPTEMBER 1980

TITLE: Energy Systems

PROGRAM AREA: X

PROGRAM MANAGER: J. C. Tao

87-1-X023 - Two-Stage Liquefaction & Coal Liquids Analysis

A novel high performance liquid chromatographic procedure was developed and optimized to quantitatively profile the hydrocarbon neutral fraction of a coal liquefaction recycle solvent.

87-1-X024 - Solid-Liquid Separation

Work progressed on the installation of the Boll and Kirch candle filter at Emmaus.

87-1-X705 - Application of SRC as Anode Coke

Laboratory equipment has begun to arrive and installation has begun.

87-1-X716 - Cryo-Recycle Development - PECO Demo Plant

Support of the Marcus Hook project continued. Progress was made on the mini-computer/CYCSYN interface, the Technical Manual, process hazards analysis, operator training, and the revised development plan.

PROCESS SYSTEMS GROUP
DEVELOPMENT PROJECT REPORT
JULY/AUGUST/SEPTEMBER 1980

Title: Coal Liquids Analysis
Project No.: 87-1-X023-02
Project Leader: Frank K. Schweighardt
Principal Investigator: Ilse S. Kingsley

ABSTRACT

A High Performance Liquid Chromatographic Procedure (HPLC) was developed to quantitatively profile the hydrocarbon neutral fraction of a coal liquefaction recycle solvent. The HPLC procedure was optimized for mobile phase (HPLC solvent), maximum detector response, chromatographic resolution, and reproducibility. The HPLC system was interfaced with a Tektronix 4052 graphics display unit for data reduction and storage.

I. INTRODUCTION

Development of a novel HPLC procedure to profile polynuclear aromatics (PNA's) from recycle solvents was initiated during this reporting period. Instrumentation was assembled and interfaced with a microprocessor to allow for unattended methods development. This maximized the efficient overnight use of this equipment. Recycle solvents of varying hydrogen donor efficiency (Procedure #43080-60) were obtained from the Wilsonville pilot plant. Chromatographic conditions were incrementally changed to optimize peak to peak separation, and detector response for both ultraviolet (UV) and refractive index (RI). This procedure will be used to routinely screen recycle solvents from Wilsonville, Tacoma SRC-II, and the Coal Process Development Unit (CPDU) at Trexlertown during FY 81.

II. OBJECTIVE

The overall objective of the coal liquids analysis project is to develop and demonstrate the applicability of new analytical techniques to coal derived liquids. In particular, methods are developed that will provide correlation between coal processing variables and the product streams of a SRC-I conversion process.

This quarter was devoted to the analysis of the hydrogen donor recycle solvent (HDRS), defined as the 450-850°F distillate.

III. WORK AND RESULTS

Two Wilsonville recycle solvents, WRS #49679 (drum #F-217) called "F", and WRS #49675, called "B", were separated into polar and nonpolar fractions by column chromatography using silica/alumina. The nonpolar fraction defined as FA and BA consisted of saturates, aromatics and hydroaromatics, was the subject sample of this report. It is assumed that these components, less the saturates, contribute most to the transfer of gaseous hydrogen to coal and its thermolysis products. This report covers:

- Fingerprinting optimization of the chromatogram, i.e., conditions leading to the maximum number of peaks with baseline resolution.
- Selection of UV-detector wavelengths for maximum response.
- Reproducibility of retention times.
- Relationship of UV response and differential refractive index for quantifying components.

Summary of findings:

- Optimum chromatographic conditions were found using a reversed phase column C-18(ODS) and acetonitrile as the mobile phase.

- Maximum UV-response was found at 295 nm on the variable wavelength UV-detector.

- Four standard components, naphthalene (1), phenanthrene (2), 2,3-dimethylnaphthylene (3), and pyrene (4) were used to assess reproducibility (retention time). Reproducibility was found to be ±0.1 minutes of a 15 minute chromatogram.

- The response of the differential refractometer provided a relative measure of component concentration while the UV-detector at 295 nm, due to the variability of molar absorptivity, was selected to enhance the absorption of 2-3 ring aromatic components.

Analysis of Recycle Solvents

The two recycle solvents were chosen to represent different degrees of hydrogen donor capability as determined by the microautoclave test (Method No. 43080-60, Catalytic, Inc.) performed at Wilsonville. The results of this solvent quality test, the elemental composition, and the molecular weight of the solvents are given in Table I.

Table II gives the weight percent boiling point distribution of the recycle solvents as determined by simulated distillation, ASTM D-2887.

Fractionation of the solvents into polar and nonpolar groups, resulted in 59 and 77 weight percent nonpolars for Wilsonville recycle solvents "F" and "B", respectively.

Table III gives the optimized chromatographic conditions, and where applicable, the range of conditions tested.

Chromatographic Results

All chromatograms were obtained at a sample concentration of 3 mg/ml in CH_2Cl_2 using a 20 ul sample loop. Figure 1 shows a series of four chromatograms at different UV-wavelengths obtained for the nonpolars of

Table I

Solvent Quality Index by Microautoclave Test, Elemental Composition and Molecular Weight of Wilsonville Recycle Solvents B and F

	B	F
Carbon	91.71	87.57
Hydrogen	7.41	8.30
Oxygen	0.40	2.88
Nitrogen	0.44	0.76
Sulfur	0.04	0.48
$\bar{n}$ Molecular Weight	210	177
Solvent Qual. Index	89.4	69.8

Table II

Weight Percent Distribution by Boiling Point (°F)
of Wilsonville Recycle Solvent "B" and "F"

	Boiling Points	
Weight Percent	"B"	"F"
1	436	400
10	620	442
20	656	469
30	674	485
40	691	510
50*	711	537
60	730	572
70	747	604
80	773	651
90	804	712
95	823	767
FBP	873	868

*Note the temperature at which each solvent is 50% distilled.

Figure 1

Reversed Phase HPLC of the Nonpolar Fraction FA of Wilsonville Recycle Solvent "F" at Different Detector Wavelengths

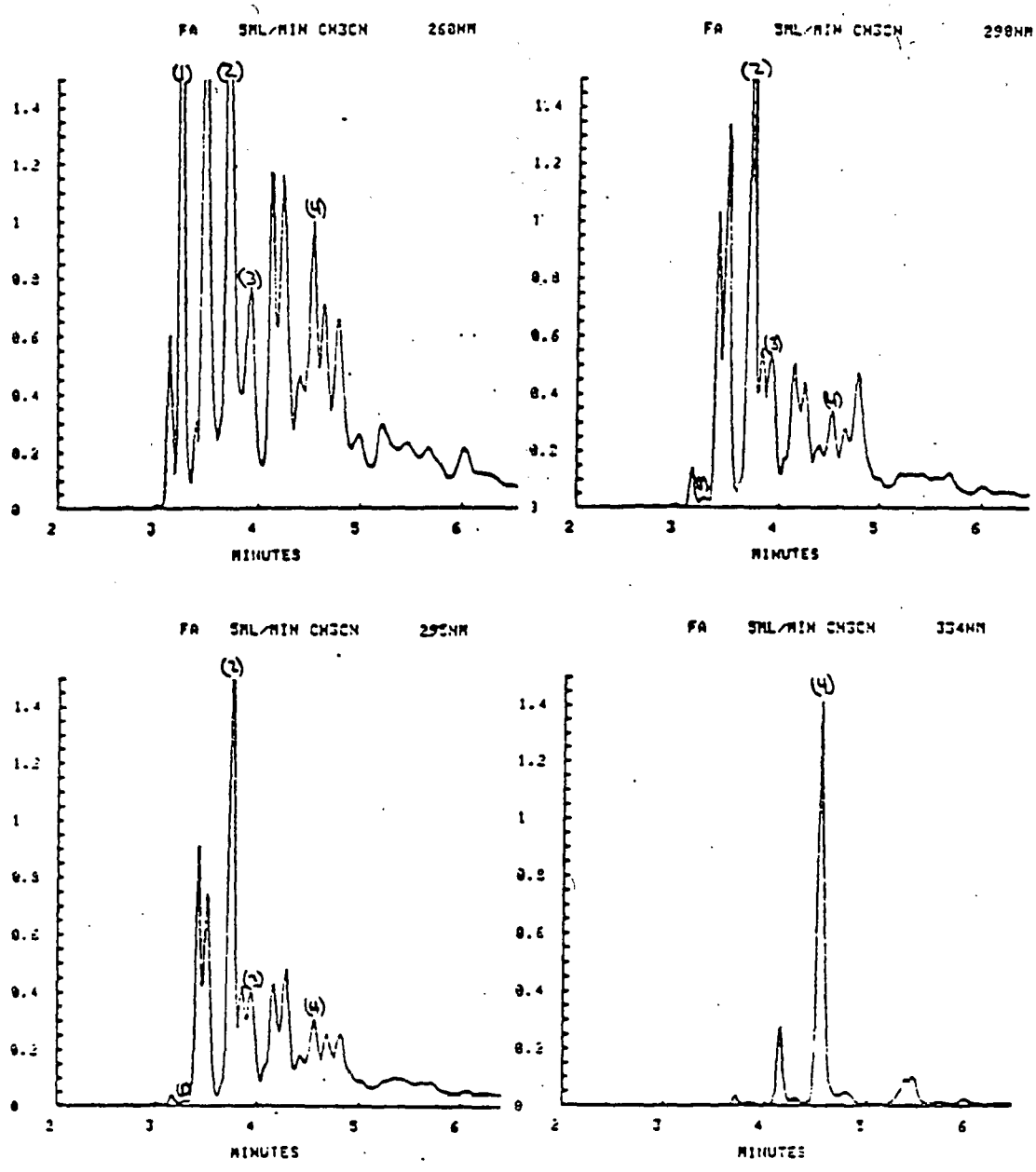


Table III

Optimized Chromatographic Conditions for Reversed

Phase RPLC of the Nonpolar Fraction of Wilsonville Recycle Solvent

	Range of Conditions				
	Mobile Phase	Detectors	Flowrate mL/min	Column	Sample Loop Size
	0-100% CH_3CN in	UV 260, 290	1.5, 3,	ODS C-18	100 ul
	100-0% MeOH	295, 334 nm	5		20 ul
		RI			
Optimized Condition	100% CH_3CN	UV 295 nm	5 mL/min	ODS C-18	20 ul

Sample "F". Detector response at 295 nm was chosen as the standard wavelength because all absorbances could be displayed with nearly equivalent response including the major component phenanthrene (2). The absorbance at 334 nm, although not representative of the total distribution of components, does provide selectivity for four ring PNA's, e.g., pyrene (4). Model components identified are peak (2) naphthalene and peak (3) 2,3-dimethylnaphthalene.

Figure 2 compares the nonpolar fractions of the recycle solvents at 295 nm and 334 nm. The major differences at 295 nm is the greater distribution of 2-3 ring PNA's in FA and alkylated (C_1-C_4) 3 and 4 ring PNA's in BA.

These findings are confirmed with the chromatograms obtained at 334 nm. Concentration of pyrene (4) was found to be approximately 3 times greater in Sample BA than in FA. The 334 nm chromatograms also show a series of components with retention times from 5-8 minutes in BA, that are of larger ring size than pyrene. These components were not detectable in Sample FA.

Figure 3 provides a comparison of the RI and the UV-detector at 290 nm for the nonpolar fraction of Wilsonville recycle solvent F. This sample was run at a 10 mg/ml concentration using a 20 ul sample loop.

Peak (1) naphthalene, although barely detected at 290 nm shows a significant response using the refractive index detector. The response of peak (3) and the peak between components (2) and (3) at 290 nm is very similar, but the refractive index shows that peak (2) is present at a much higher concentration. Reproducibility of retention times was established at .1 min over 15 minutes. The refractive index detector provides a relative quantitative measure of the components in the nonpolar fractions of recycle solvents. An exact comparison of component concentration can be made if equal sample weights are chromatographed.

Figure 2

Reversed Phase HPLC of the Nonpolar Fraction FA and BA of Two Wilsonville Recycle Solvents at 295 and 334 nm Detector Wavelengths

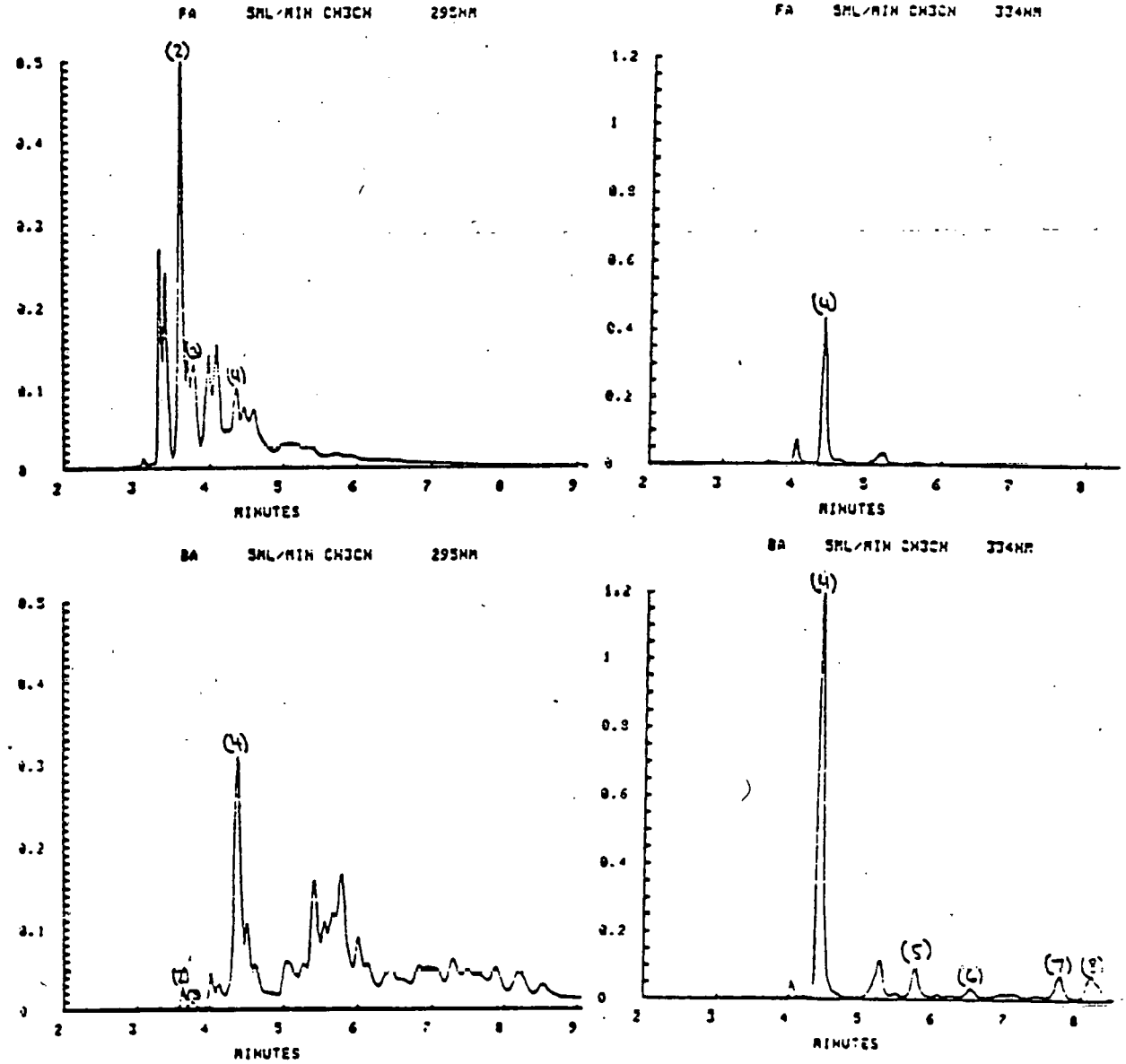
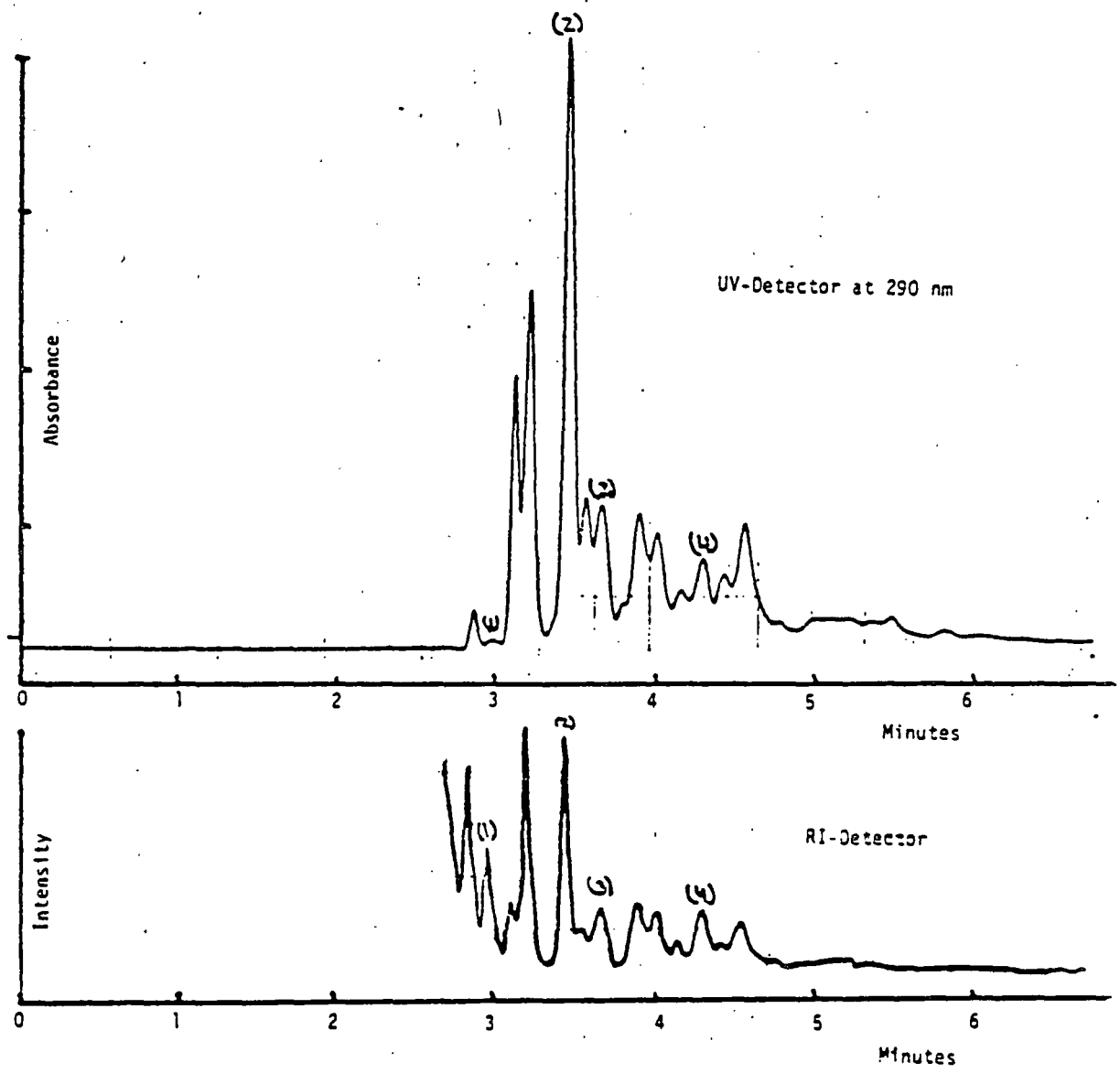


Figure 3

Reversed Phase HPLC of Nonpolar Fraction F3 From Wilsonville Recycle Solvent "F" Using a UV-Detector at 290 nm and a Refractive Index Detector



CONCLUSION

- A novel liquid chromatographic procedure has been developed to profile the nonpolar of HDRS.

- Chromatographic conditions were optimized for mobile phase, maximum detector response in the UV, chromatographic resolution on an ODS-C_{18} reversed phase column.

- The chromatographic procedure was used to demonstrate the differences in the neutral fractions between two Wilsonville recycle solvents characterized by the microautoclave test to be different in quality.

- This procedure will be used during FY 81 to profile recycle solvents from Wilsonville, Tacoma SRC-I/II, and CPDU-CRDD.

Evaluation for the Nonpolar Fraction of a Wilsonville Recycle Solvent by Reversed Phase High Performance Liquid Chromatography

September 1980

Ilse S. Kingsley

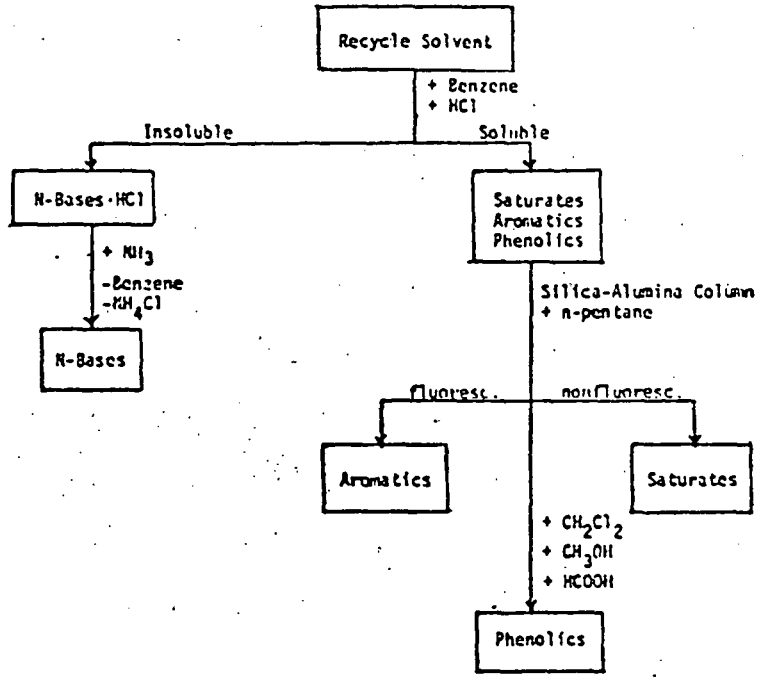
A Wilsonville recycle solvent (WRS #49679) drum #F-217 was separated into its functional group fractions as shown in Scheme I. The nonpolar fraction, consisting of the aromatics and the saturates, was then used at a 10 mg/ml concentration for the study of reversed phase chromatography. This report covers:

I. fingerprinting optimisation of the chromatogram, i.e.. condition leading to the most peaks with best resolution in the chromatogram
II. evaluation of different mobile phases
III. evaluation of different detector wavelengths
IV. peak identification of four peaks in the chromatogram
V. effect of flowrate on resolution and analysis time
VI. sample loop size variation effect on the chromatogram
VII. relationship of UV response with differenital refractive index as mean of chromatograph detection

A summary of findings is listed below.

I. Fingerprinting chromatography using acetonitrile and methanol at 260 and 290 nm showed a more detailed chromatogram with acetonitrile at 290 nm than with methanol and at 260 nm.
II. Gradient elution between 100% acetonitrile and 100% methanol showed best resolution of peaks in 100% acetonitrile at 290 nm.
III. HPLC at 260, 290, 295 and 334 nm showed one peak of a pyrene type structure as determined by absorbance ratios, and three peaks of another long condensed aromatic ring structured components.
IV. Standard components identified naphthalene, phenanthnene, 2,3 dimethylnaphthalene and pyrene as components in the sample tested.

Scheme I



Column chromatographic separation scheme for separation into nitrogen bases, saturates, aromatics and phenolics.

V. The flow rate can be increased from 1.5 ml/min to 3 ml/min and even 5 ml/min without change in retention volume or resolution of the highly complex chromatogram. This reduces the analysis time from 25 to about 10 minutes per sample.

VI. A change in sample loop size from 20 ul to 100 ul does not effect the chromatogram with respect to resolution of peaks or retention time.

VII. Differential refractive index detection aids the determination of relative concentration of components detected, whereas UV detection can be used for monitoring specific components and simplification of chromatograms.

I. Preliminary Peak Assignment by 260/290 nm Wavelength Fingerprinting

The chromatographic conditions were:

Flowrate	1.5 ml/min
Column	ODS 5μ 250 mm x 10 mm
Sample loop	20 μl
UV Detector	at 260 nm and at 290 nm
Mobile phase	100% CH_3OH and 100% CH_3CN

Four chromatograms were obtained, which are shown in Figure 1 through 4.

Based on the significantly different chromatographic "fingerprint" obtained by changing the detector wavelength from 260 to 290 nm and by changing the mobile phase an attempt was made to locate peaks obtained by CH_3CN elution in the CH_3OH chromatograms.

Peak #1 in Figure 1 at 260 m, has a higher absorbance than at 290 nm (Figure 2). Switching mobile phase from CH_3CN to CH_3OH peak #1 seems to split into two peaks as seen at 260 nm (Figure 3) one of which doesn't visualize at 290 nm. Adding the approximate peak areas of the two first peaks in Figure 3 one arrives at the approximate ratio of 260/290 for peak #2 in CH_3OH as seen for CH_3CN as a mobile phase.

Peak #2 shows a very high 260/290 ratio in CH_3CN as well as CH_3OH. Therfore one can assume the same types of compounds to elute at this relative retention time using both mobile phases.

Peak #3 in CH_3OH (Figure 2) shows a low 260/290 ratio and therefore one could find a peak of the similar ratio seen in Figure 3 which shows up as a shoulder in Figure 4 as peak #3 eluting after peak #4, using CH_3OH as a mobile phase.

Peak #4 in CH_3CN (Figure 1 and 2) shows a high 260/290 ratio, where as peak label #4 in CH_3OH (Figures 3 and 4) give a low 260/290 ratio. This indicates the presence of a different group of components in peak #4 eluting with CH_3CN, versus the elution with CH_3OH.

Peak #5 shows an absorbance above 2.0 in each of the four chromatograms which can indicate the elution of the same group of components in each mobile phase at that retention time.

Figure 1 ODS-HPLC at 260 nm in CH_3 CN

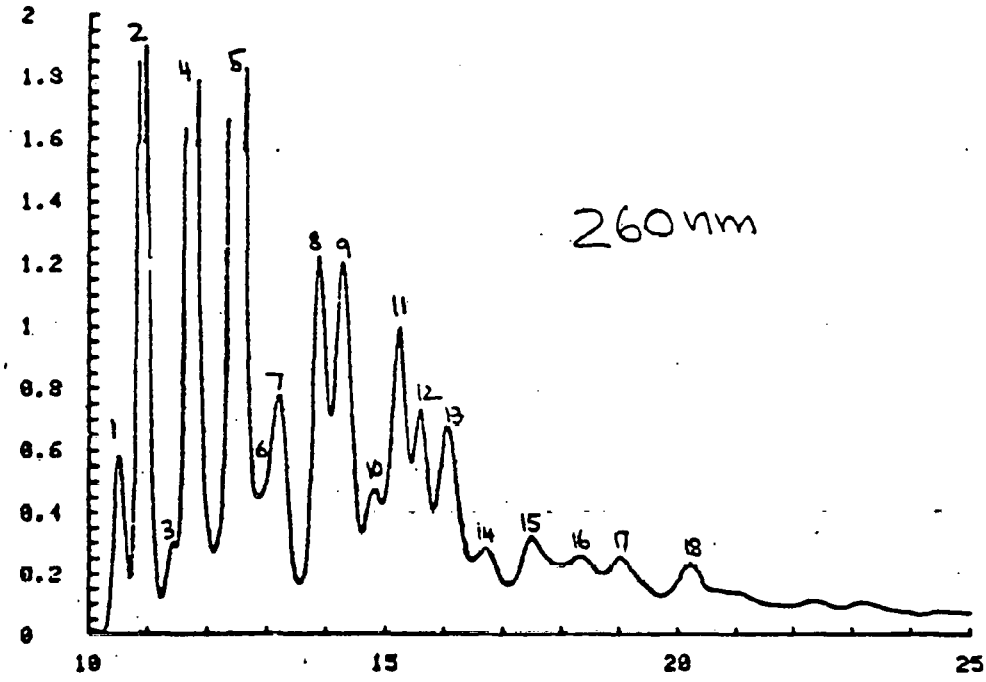


Figure 2 ODS-HPLC at 290 nm in CH_3CN

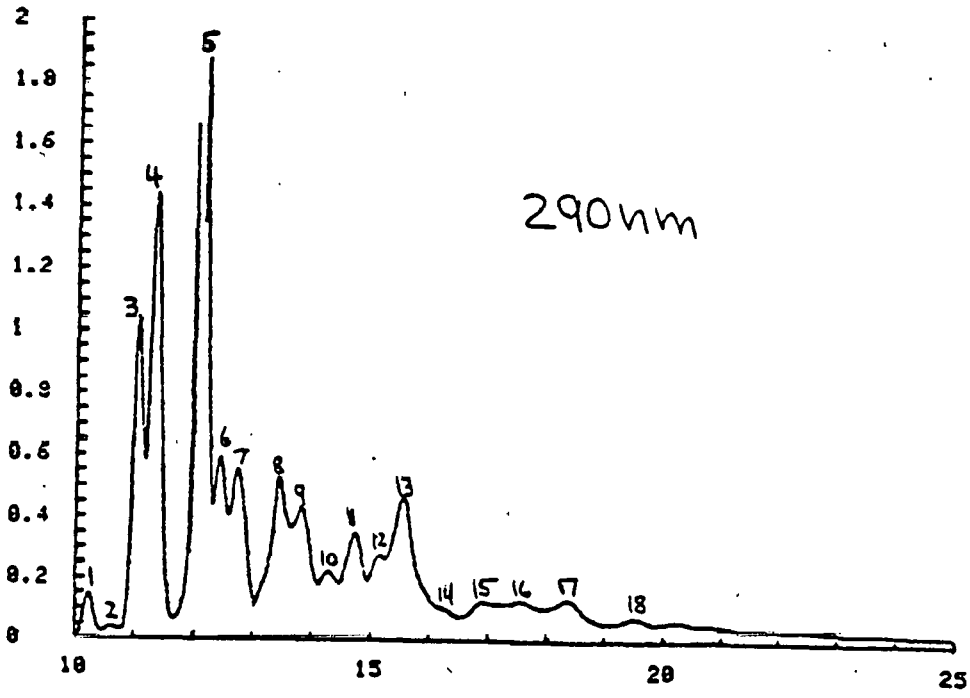


Figure 3 ODS-HPLC at 260 nm in CH_3OH

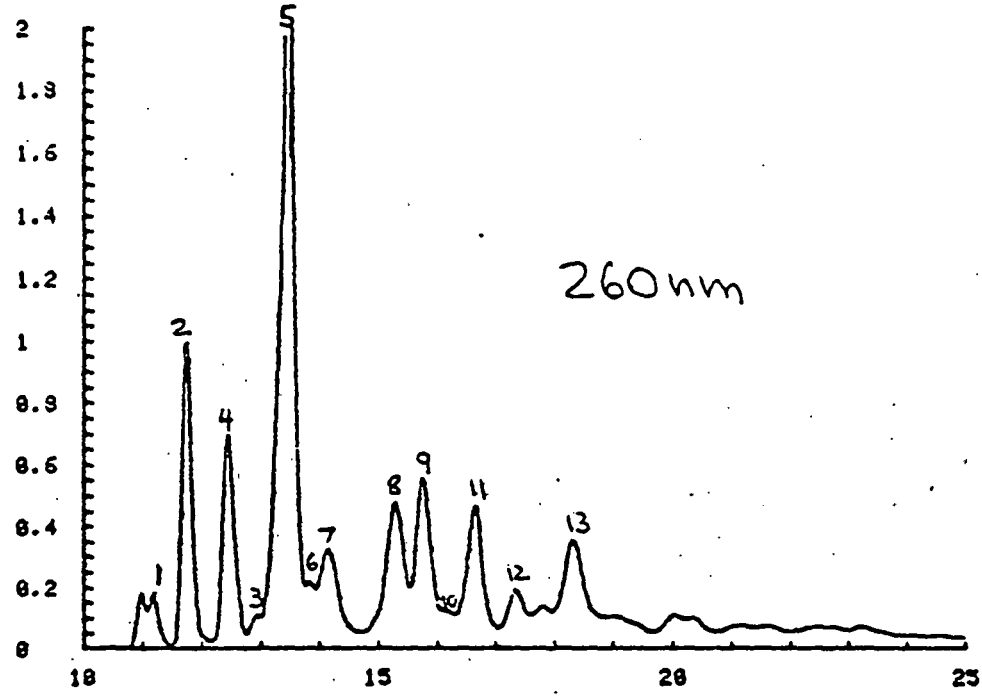
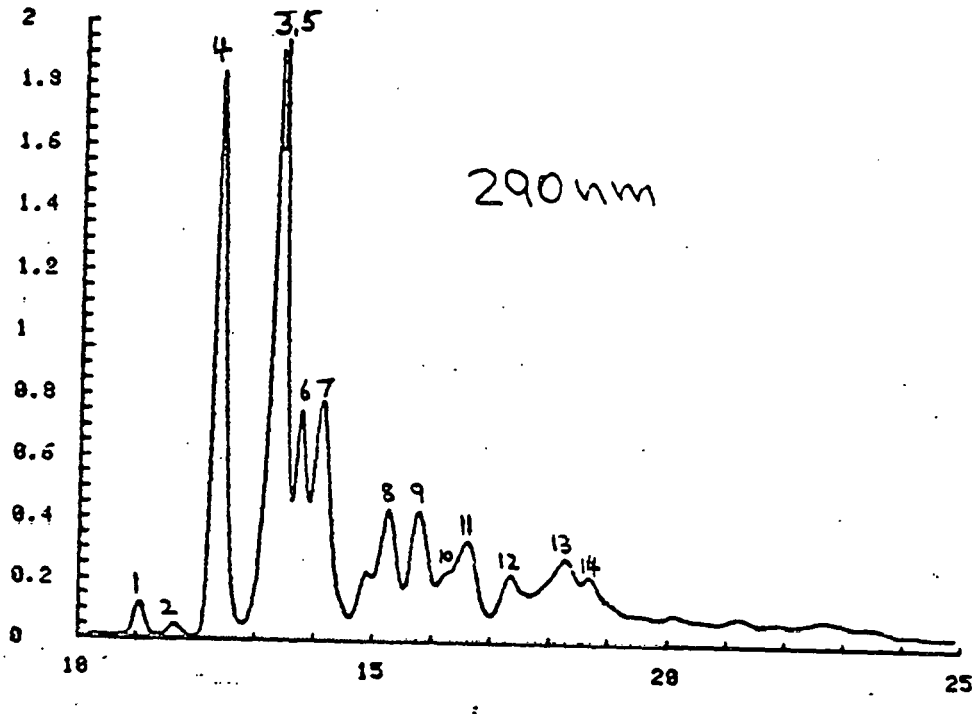


Figure 4 ODS-HPLC at 290 nm in CH_3OH



Peak #6 shows a low 260/290 ratio and can therefore be identified at the same relative elution order in both mobile phases. Peak #7 shows a different absorbance ratio, in CH_3CN versus CH_3OH, which again indicates different component composition at that elution time in the different solvents; this is also the case for peaks #8 and 9. Figure 4 shows also a peak at 290 nm which is not visible at 260 nm, but does not separate into a discrete peak using CH_3CN. Peak #10 can be noticed as a small peak between peaks #9 and 11 in each chromatogram.

The assignments and alignments of the following peaks becomes less certain due to the peak spreading at the longer retention times. A tentative assignment is shown in the four figures.

The best fingerprint chromatogram chosen was 100% CH_3CN at 290 nm.

II. Mobile Phase Optimization

The chromatographic conditions were chosen as

flow rate	1.5 ml/min
column	ODS 5μ 250 mm x 10 mm
detector	UV 290 NM
sample loop	20 μl
mobile phase	CH_3OH, CH_3CN at different ratios.

The mobile phase was varied as shown below:

run	CH_3OH	% CH_3CN
1	0	100
2	25	75
3	50	50
4	75	25
5	90	10
6	100	0

The resulting chromatograms are shown in Figure 5 through 10 corresponding to runs #1 through 6 above. The y-axis shows the absorbance at 290 nm, the x-axis shows the minutes, which can be related to the volume eluted by the flow rate of 1.5 ml/min.

It was observed that

- a shift in order of elution occurred with peak #3, #6, #7, and #12.
- resolution of peaks #15 through 18 obtained by a CH_3CN mobile phase diminished with increasing concentration of CH_3OH in the mobile phase.
- retention time of initial peaks increased with increasing concentration of CH_3OH
- at 100% CH_3OH a peak was observed between peaks #6 and 8 (see Figure 10) which could not be identified in any of the other mobile phase combinations.

Figure 5 ODS-HPLC in 100% CH_3CN

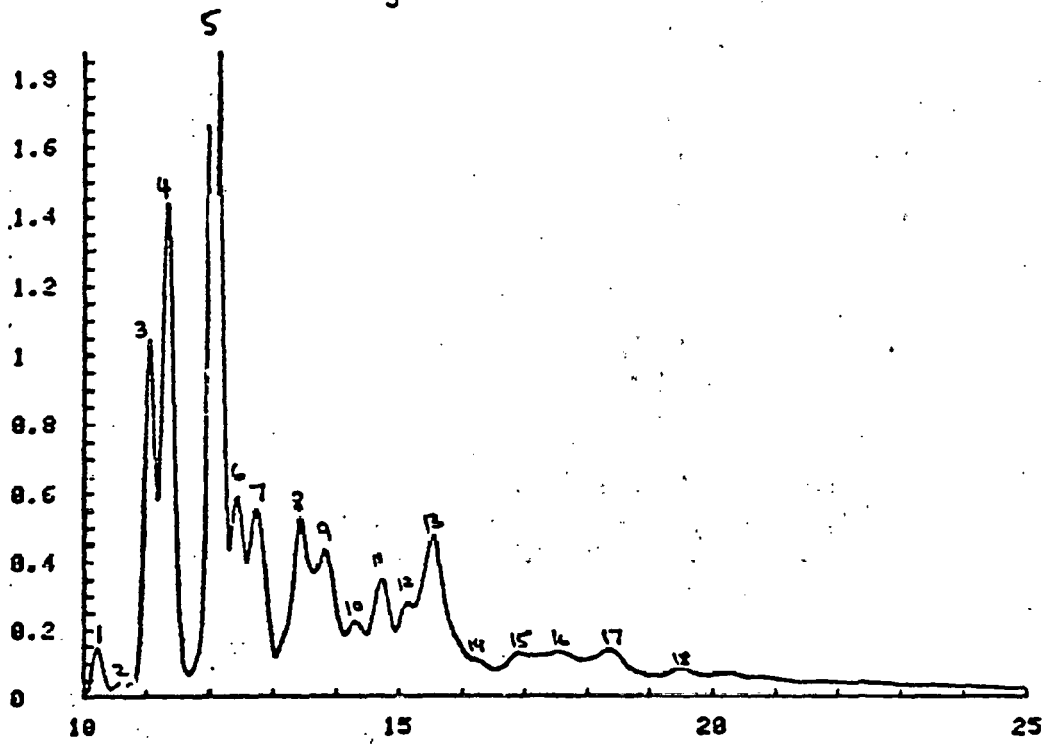


Figure 6 ODS-HPLC in 75% CH_3CN 25% CH_3OH

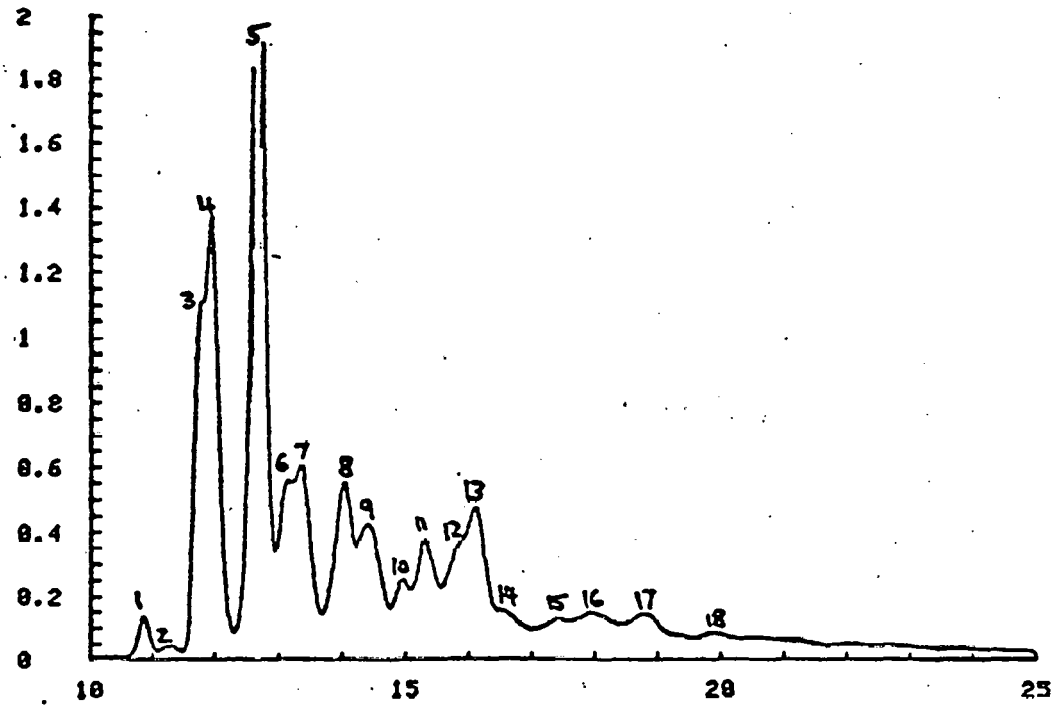


Figure 7

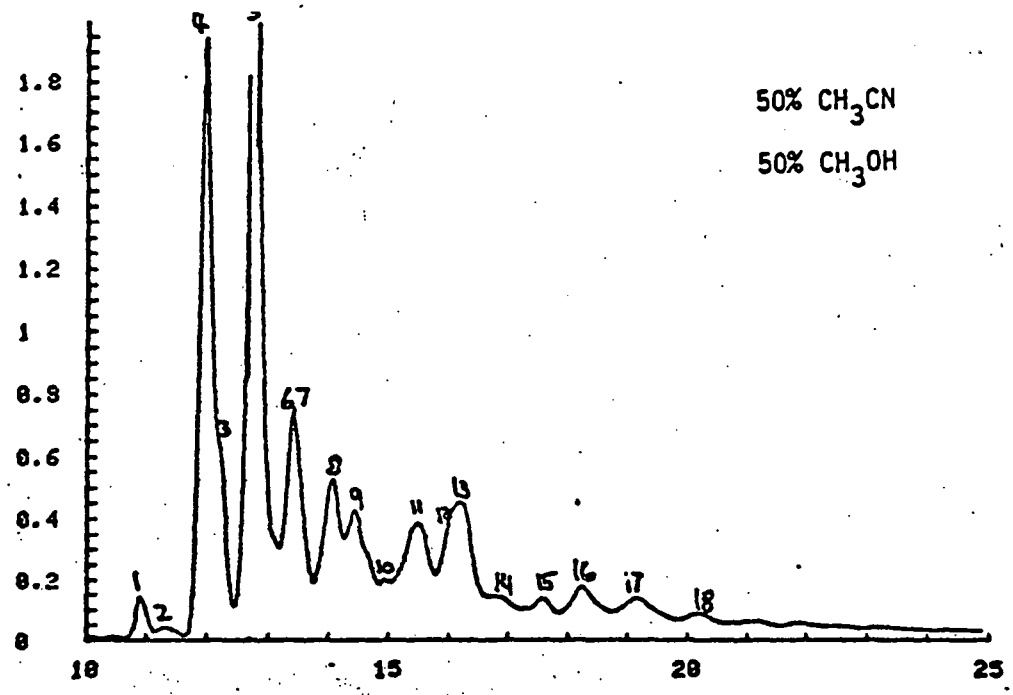


Figure 8

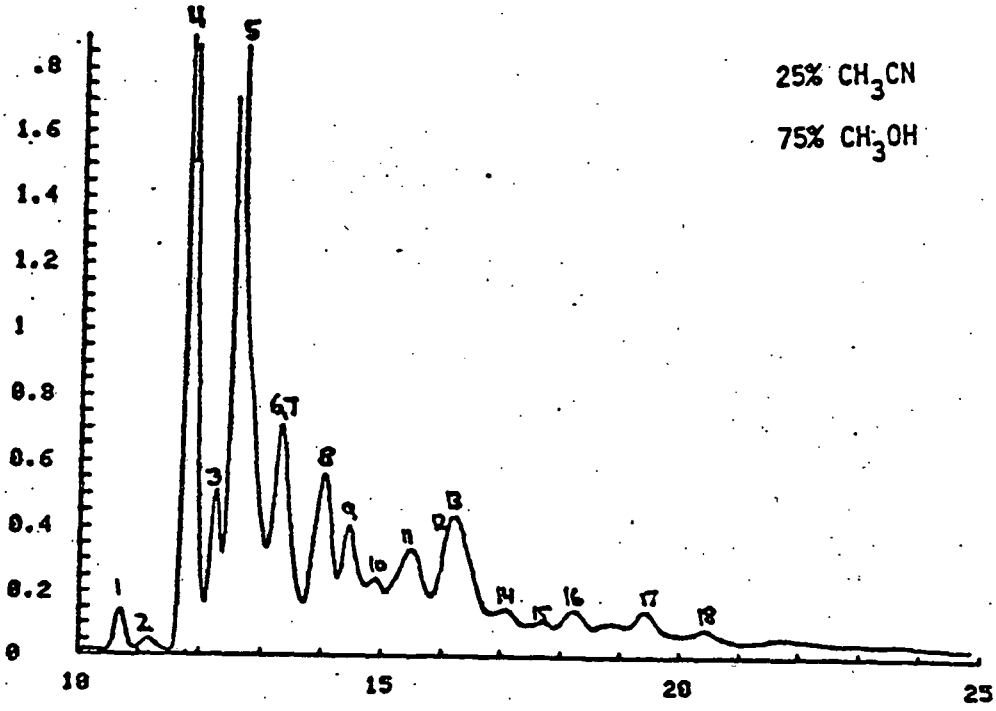


Figure 9

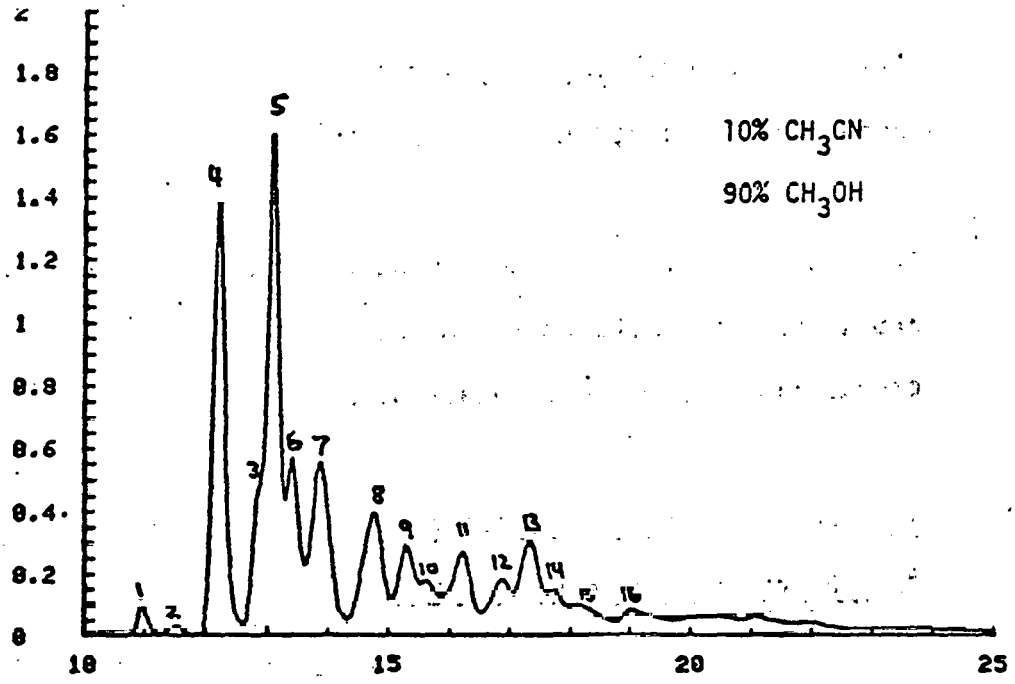
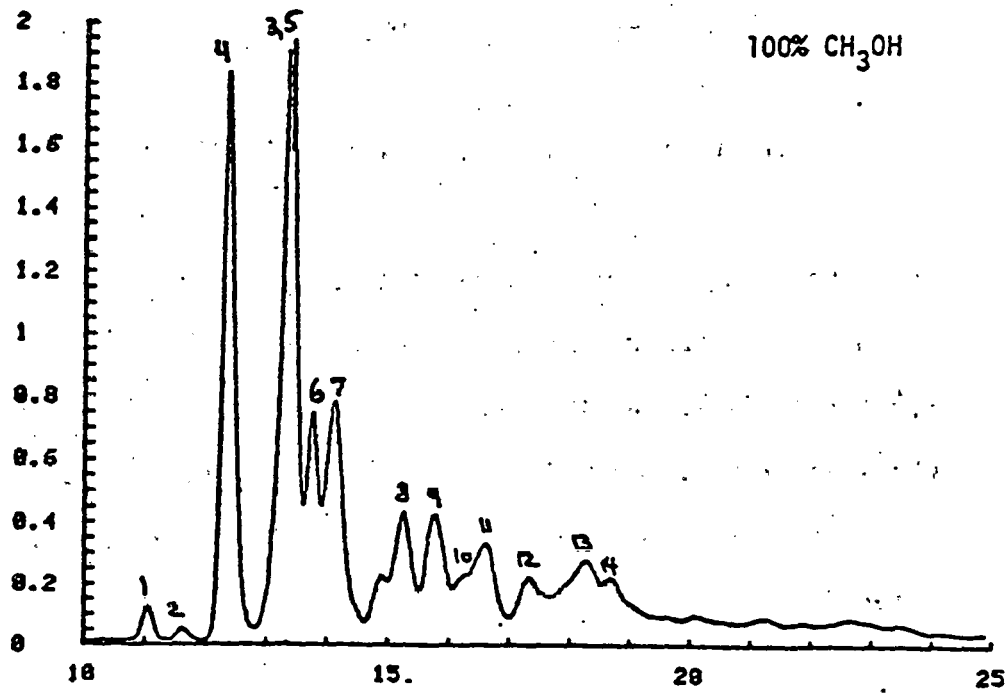


Figure 10



The shift in peak height by variation of the mobile phase indicates unresolved, overlapping peaks shifting peak numbers.

The most resolved peak pattern was observed with 100% CH_3CN and this mobile phase was chosen to be used for future chromatographic separation of nonpolars on reversed phase HPLC.

III. HPLC Reversed Phase Chromatography of Nonpolar Fraction of a Recycle Solvent at Different Wavelengths

The chromatographic conditions wre chosen as:

flow rate	5 ml/min
column	ODS 5μ 250 mm x 10 mm
sample loop	20 μl
mobile phase	CH_3CN
detector	UV at 260, 290 and 334 nm

The wavelength 334 nm was chosen as a specific detector for pyrene which has a λmax at 334 as shown in Figure 11, i.e., the molar absorptivity (E) has a maximum at the wavelength of 334 nm. The chromatograms obtained are shown in Figure 12. It was noted that the chromatogram obtained at 260 nm seemed to be shifted to the right by 0.5 minutes retention time.

F[illegible] spectrum of pyrene and chrysene

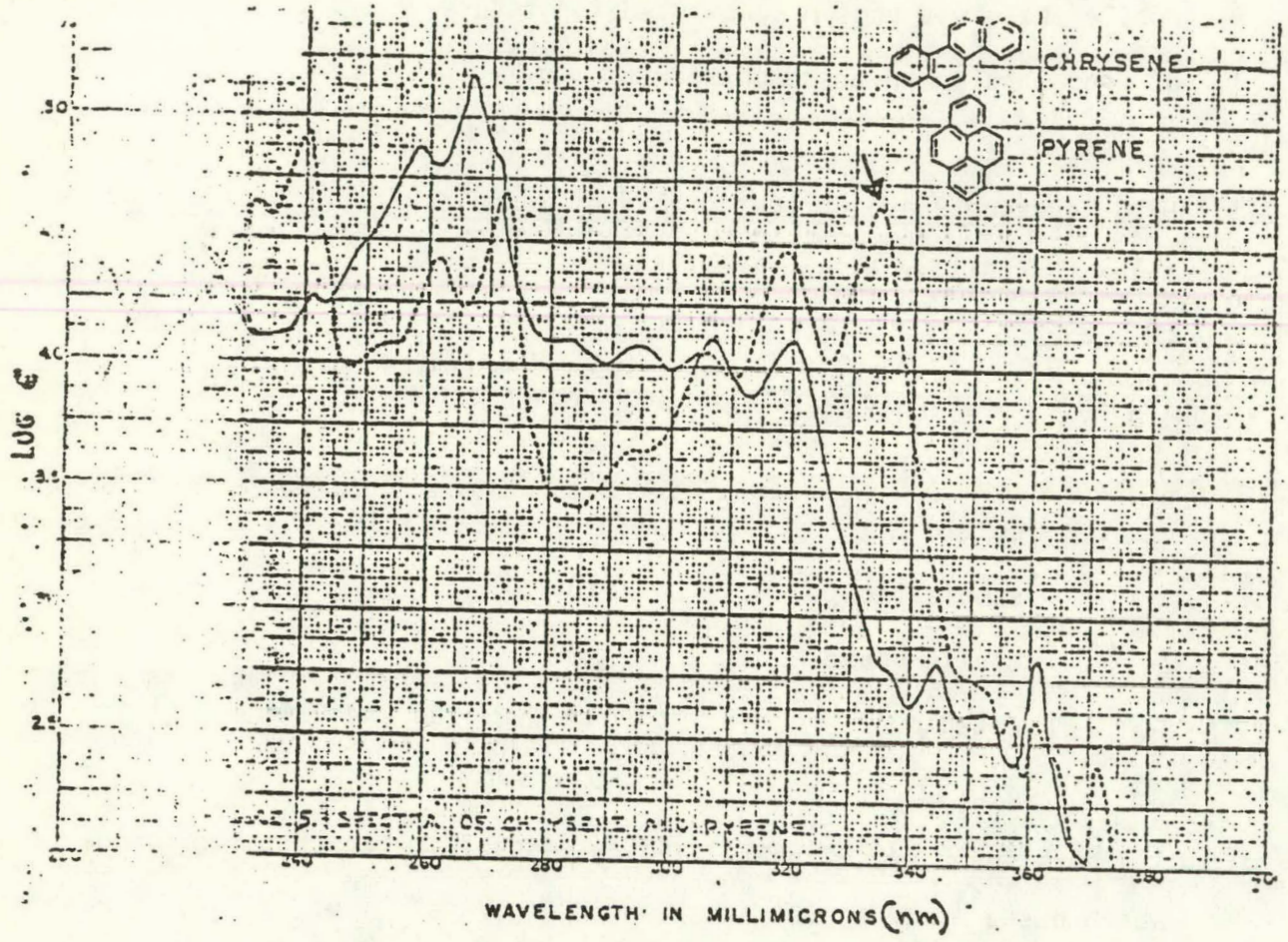
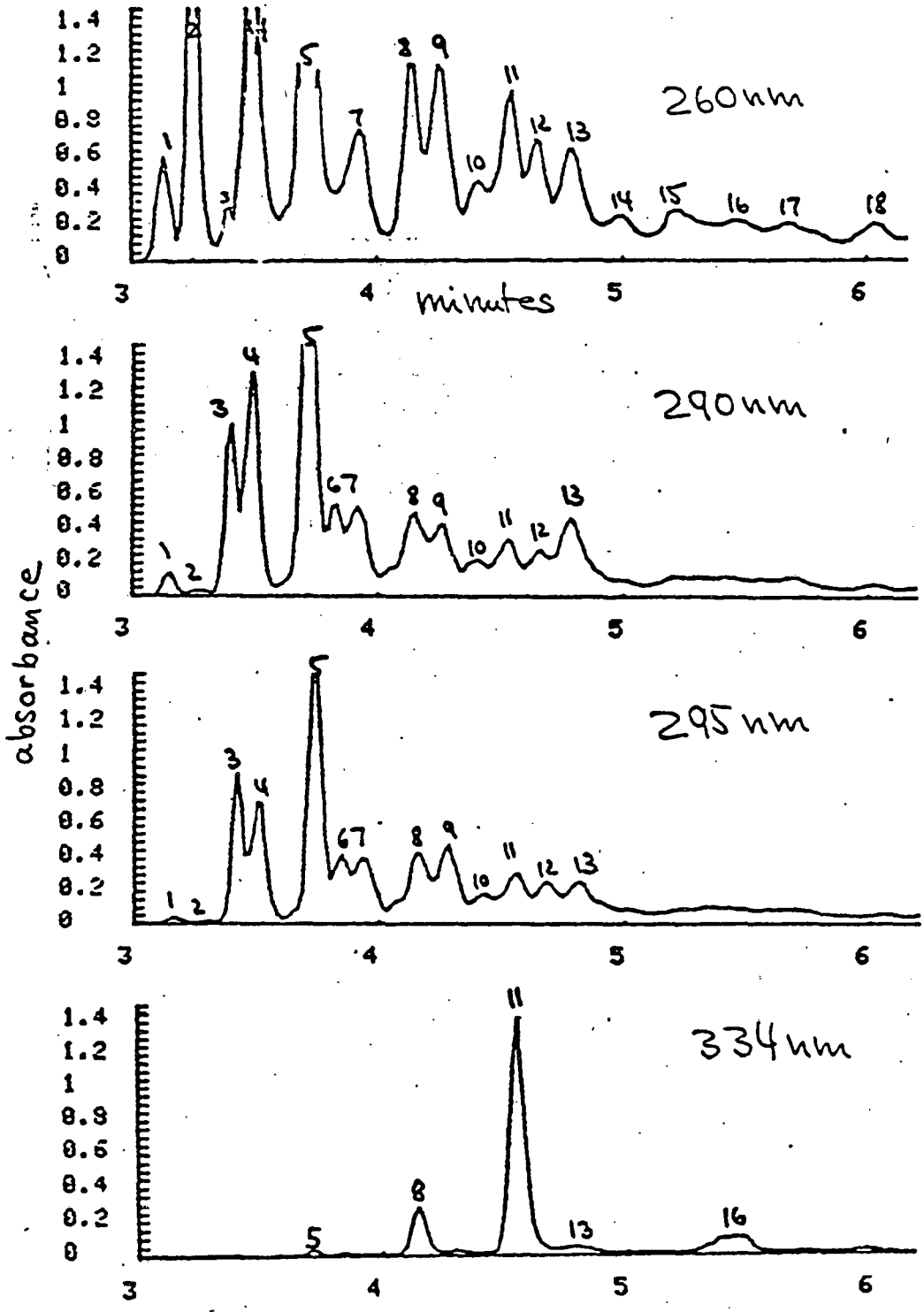


FIG. 5. SPECTRA OF CHRYSENE AND PYRENE

Figure 12 ODS-HPLC using different detector wavelengths



The log "E" for pyrene at the three chosen wavelengths is:

260 nm	4.425
290 nm	3.575
334 nm	4.650

and the absorbances obtained for peak #13 in Figure 12 at these wavelengths show:

260 nm	0.68
290 nm	0.47
334 nm	0.67

The relative absorbances for the pure pyrene spectrum and for peak #13 are very similar. One can therefore say that peak #13, based on the absorbance ratios may be pyrene or alkylated pyrene compound -- which has a very similar absorbance spectrum.

Peaks #9, #14, and #17, which are the other peaks visual at 334 nm might be components of larger condensed aromatic ring structure than the other peaks observed only at 290 and 260 nm.

The higher wavelength should only be used if there is specific interest in the larger condensed aromatic ring structures. It does not warrant as detailed a fingerprint as the 290 and 260 nm detector delivers.

IV. Compound Identification

The retention times of the nonpolar chromatogram compared with the retention times obtained by HPLC of four pure components known to be present in the nonpolar fraction of coal liquids.

The chromatographic conditions were:

flowrate	1.5 mL/min
column	ODS 5μ 250 mm x 10 mm
sample loop	20 μl
mobile phases	100% CH_3CN and 100% CH_3OH
detector	UV at 290 nm

The standard components chosen were

naphthalene

2,3 dimethylnaphthalene

phenanthene

pyrene

9,10 dihydrophenanthene

Retention times obtained for the pure components are listed below:

	CH_3CN	CH_3OH
naphthalene (A)	10.6	11.0
phenanthene (B)	12.6	13.3
2,3 dimethylnaphthalene (C)	13.0	13.8
9,10 dihydrophenanthene (E)	12.6	14.0
pyrene (D)	15.4	16.7

Figure 13

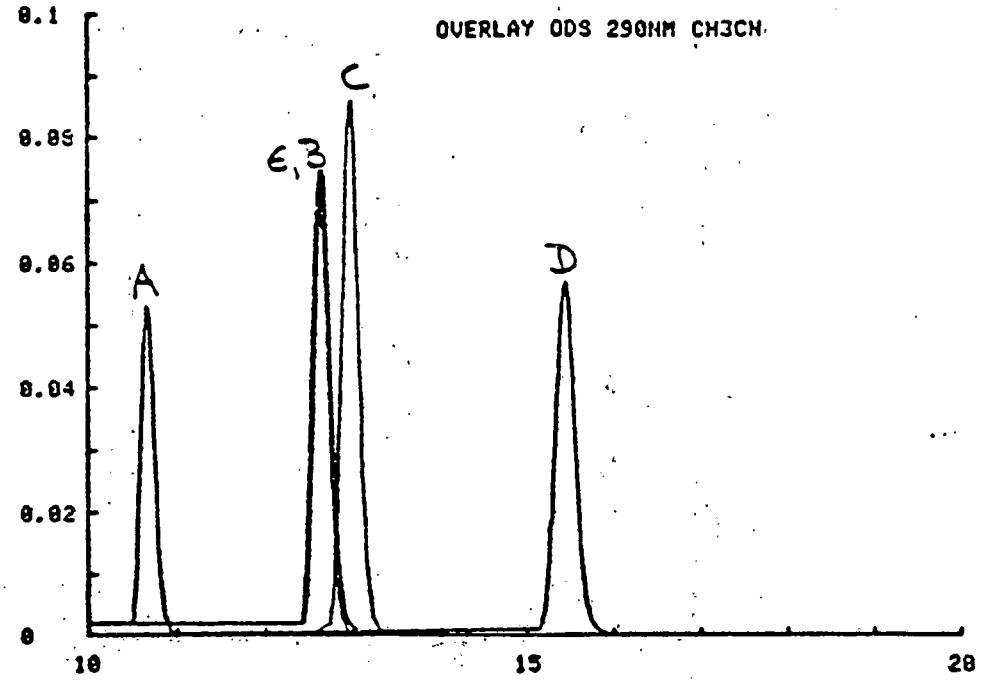


Figure 14

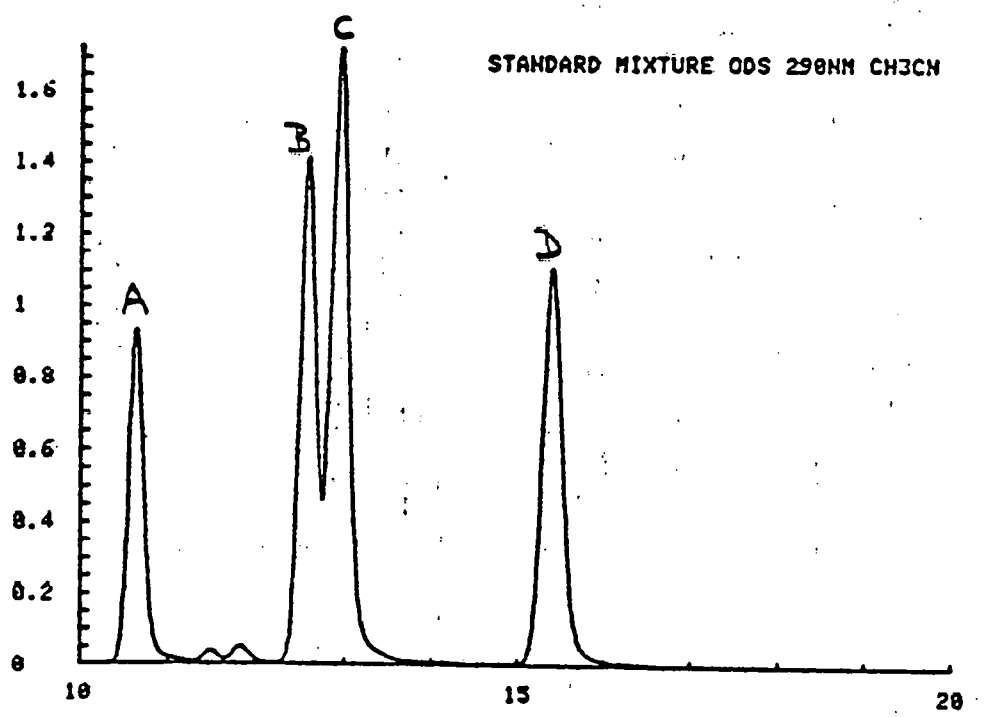


Figure 15

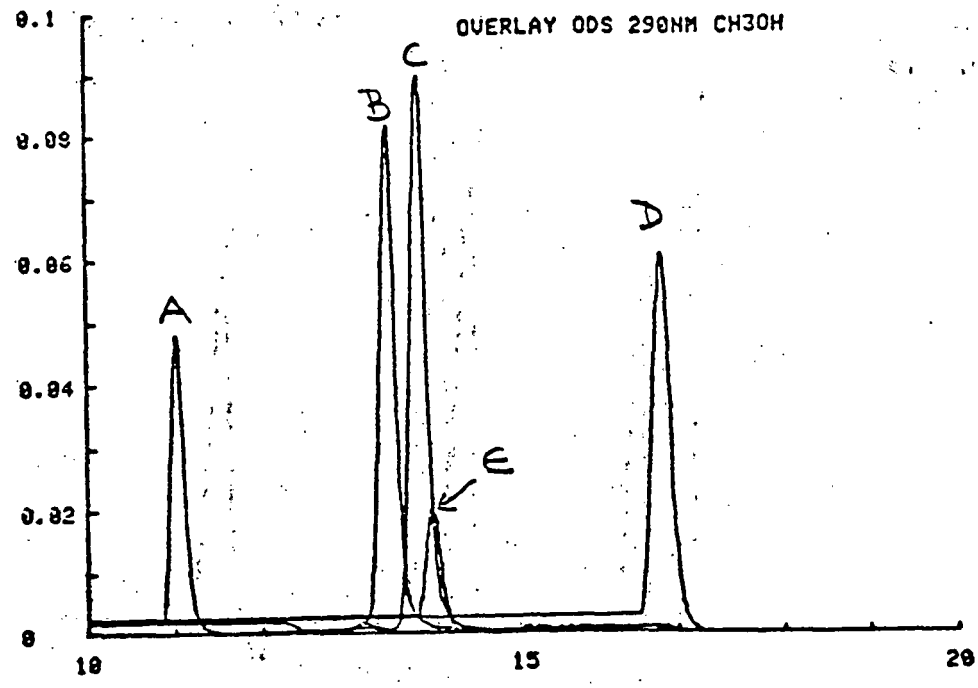
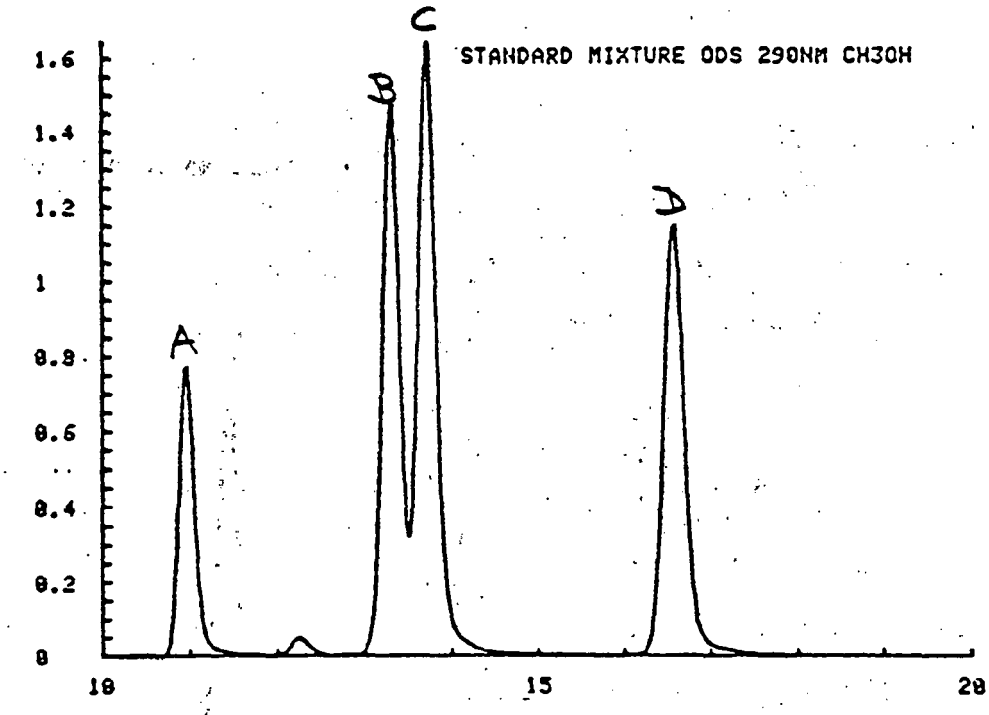


Figure 16



A chromatogram was generated by overlay of the individual chromatograms and is shown in Figure 13 and 15.* 9,10 dihydrophenanthene in CH_3CN (Figure 13) showed the same retention time as phenanthene and in CH_3CN (Figure 15) showed poor resolution from 3,3 dimethylnaphthalene. Equal proportions of all but the obtained chromatogram was identical to that generated in Figure 13 and 15, as Figure 14 and 16 shows. This confirms that there is no interaction of these components with respect to their elution times or peak shape.

The chromatogram of the standard mixture was then compared to the chromatogram of the nonpolar recycle solvent fraction. Figure 17 and 18 eluting with CH_3CN and Figure 19 and 20 eluting with CH_3OH.

The comparison of retention times at two different mobile phases give identification to:

peak #1	naphthalene	(A)
peak #5	phenanthrene	(B)
peak #11	pyrene	(D)
peak #6	2,3 dimethylnaphthalene	(C)

Identification of peak #11 in CH_3CN and CH_3OH confirms findings in Section III.

Figure 17 295 nm CH_3CN

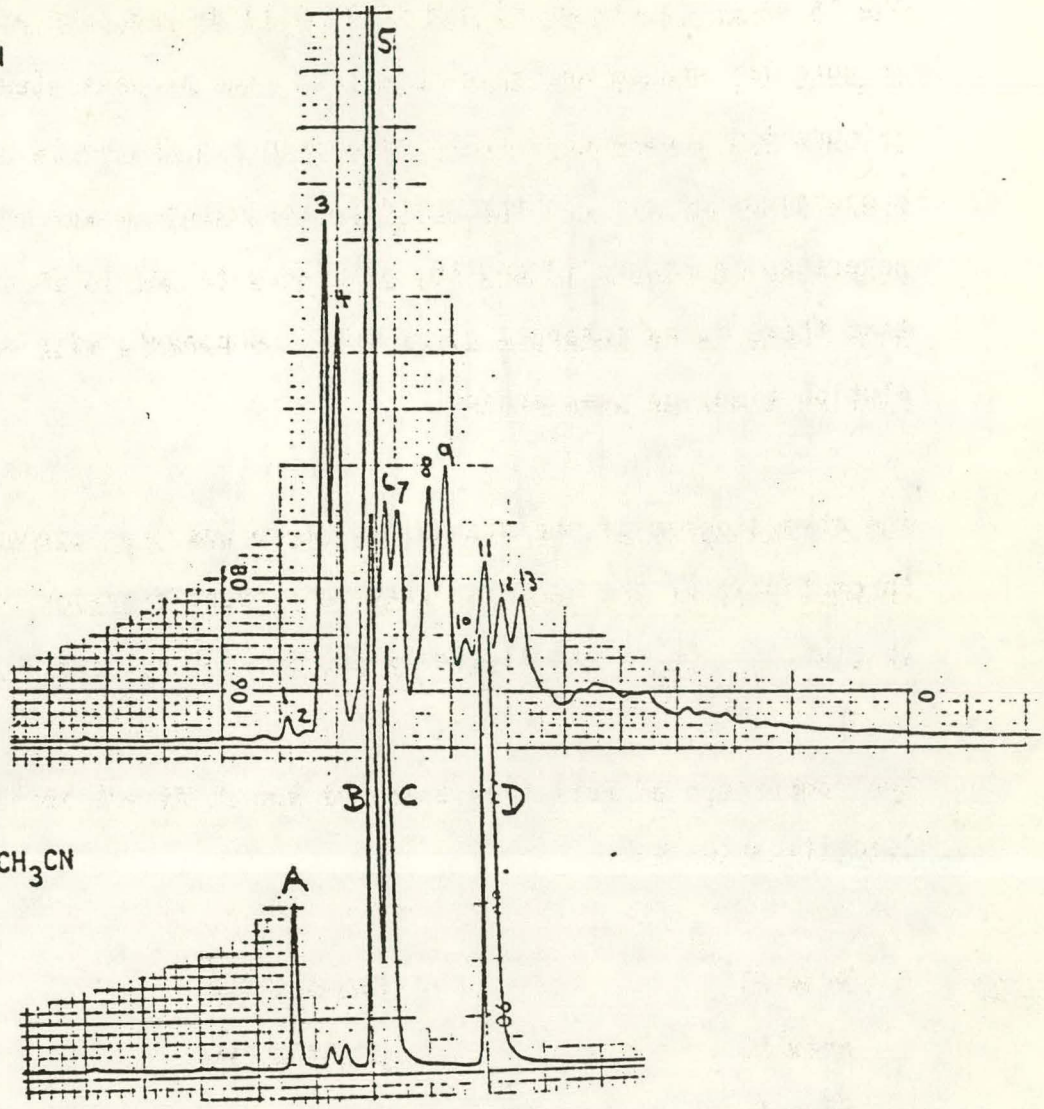


Figure 18 Standard CH_3CN

Figure 19

29 nm

CH_3OH

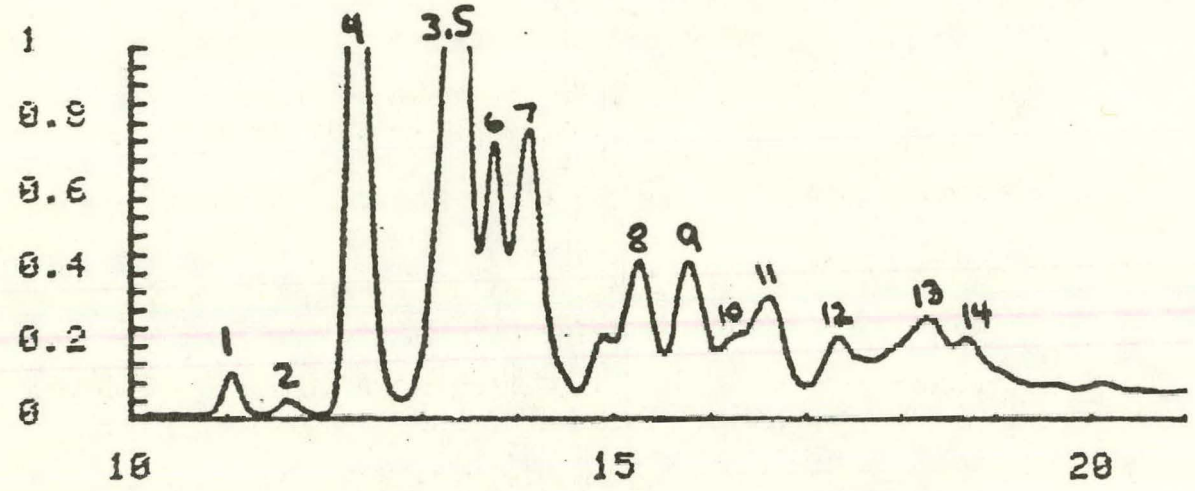
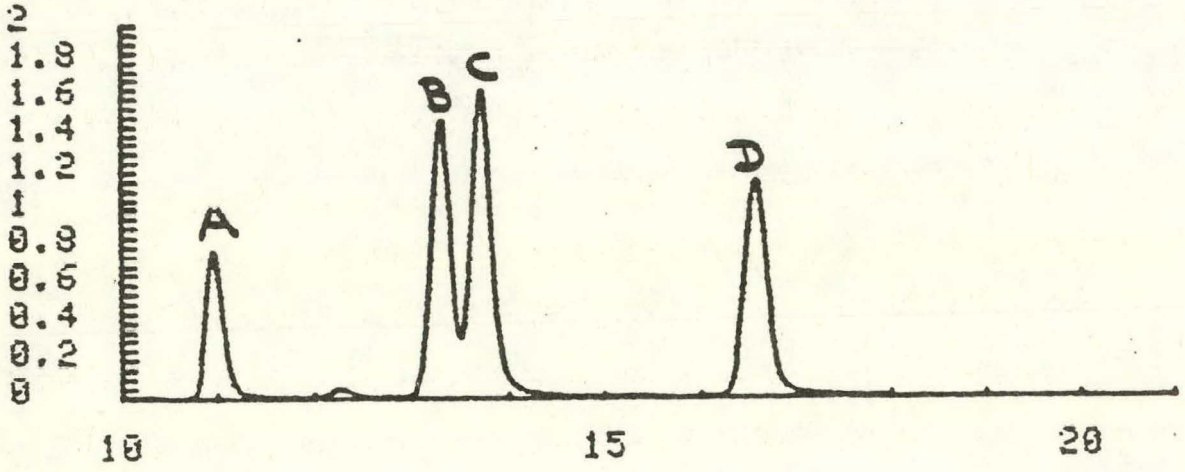


Figure 20

290 nm

CH_3OH



V. Reversed Phase HPLC of the Nonpolar Fraction of a Recycle Solvent at Different Flowrates

The nonpolar fraction was chromatographed using three flowrates.

Chromatographic conditions were:

column	ODS 5μ 250 mm x 10 mm
sample loop	20 μl
mobile phase	CH_3CN
detector	UV at 290 and 334 nm
flowrates	1.5 mL/min, 3.0 mL/min and 5 mL/min

Special attention was given to the predictability of retention times as well as to the reproducability of resolution with higher flowrates.

The chromatograms obtained at 290 nm are shown in Figures 21a and b, and at 334 nm in Figure 22a and b. It can be observed that the fingerprint of the chromatogram did not change with increase of the flowrate, i.e., all peaks found at 1.5 mL/min are found with the same relative absorbance ratios using a 3 mL/min flowrate. 5 mL/min chromatograms at 290 and 334 nm are shown in Figure 12.

The chromatograms at 290 nm were then overlayed with the same amplified chromatogram to magnify small peaks and compared on the same retention volume scale, i.e., double x-axis is scale for half flowrate. The scale is still labeled in minutes retention time. Figure 23a shows this overlayed chromatogram at 3 ml/min and Figure 23b at 1.5 mL/min. No difference in resolution and retention volume is seen. This shows

Figure 21a

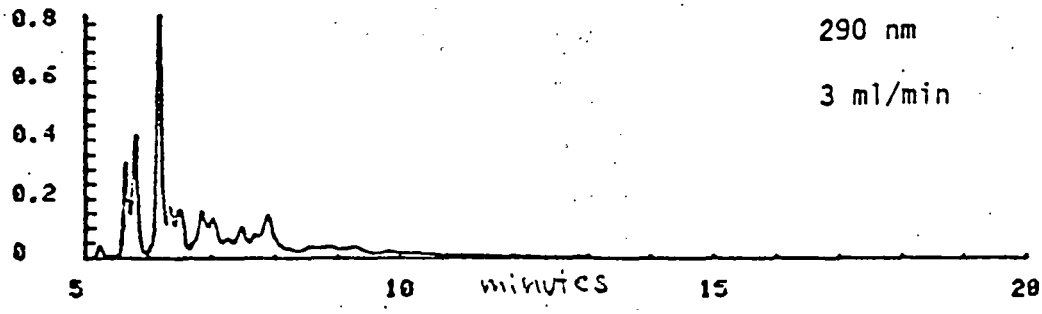


Figure 21b

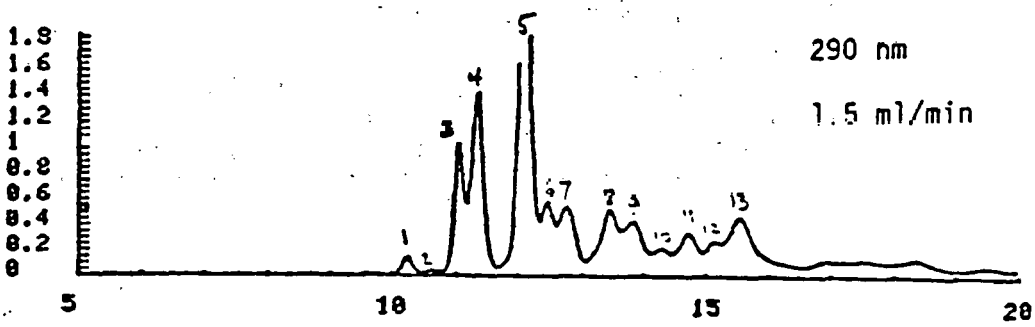


Figure 22a

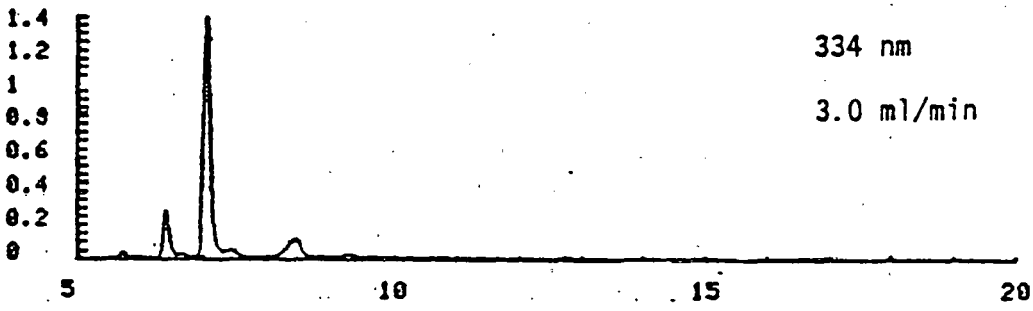


Figure 22b

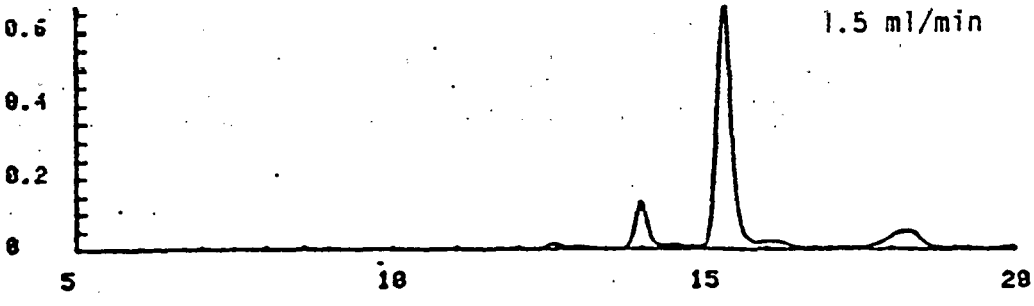


Figure 23a

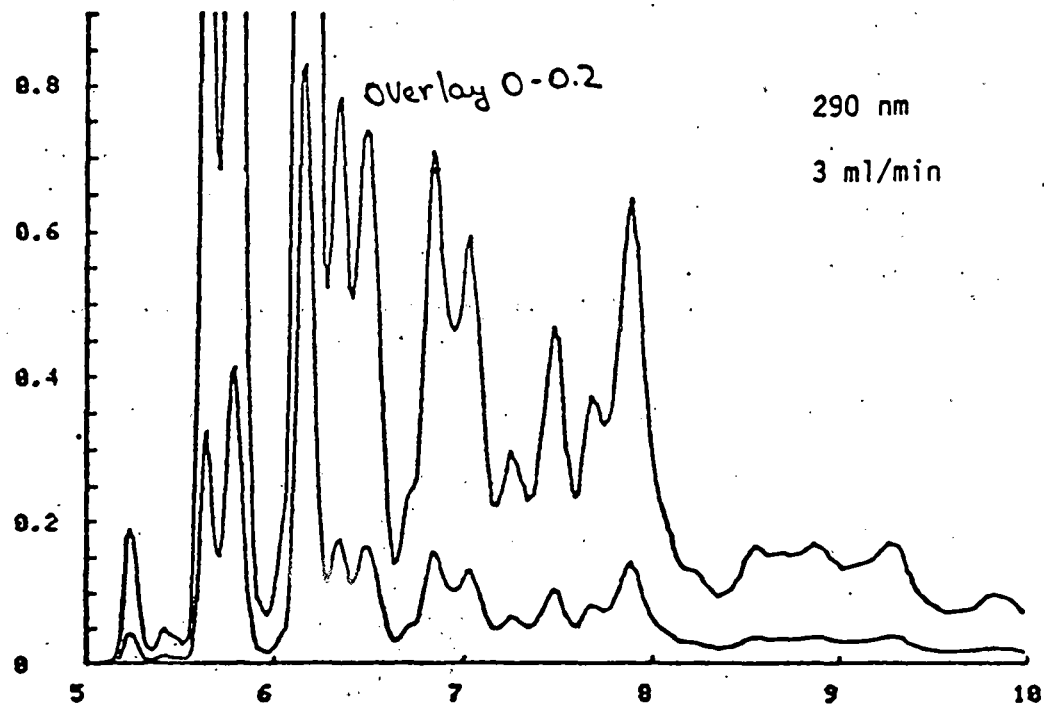
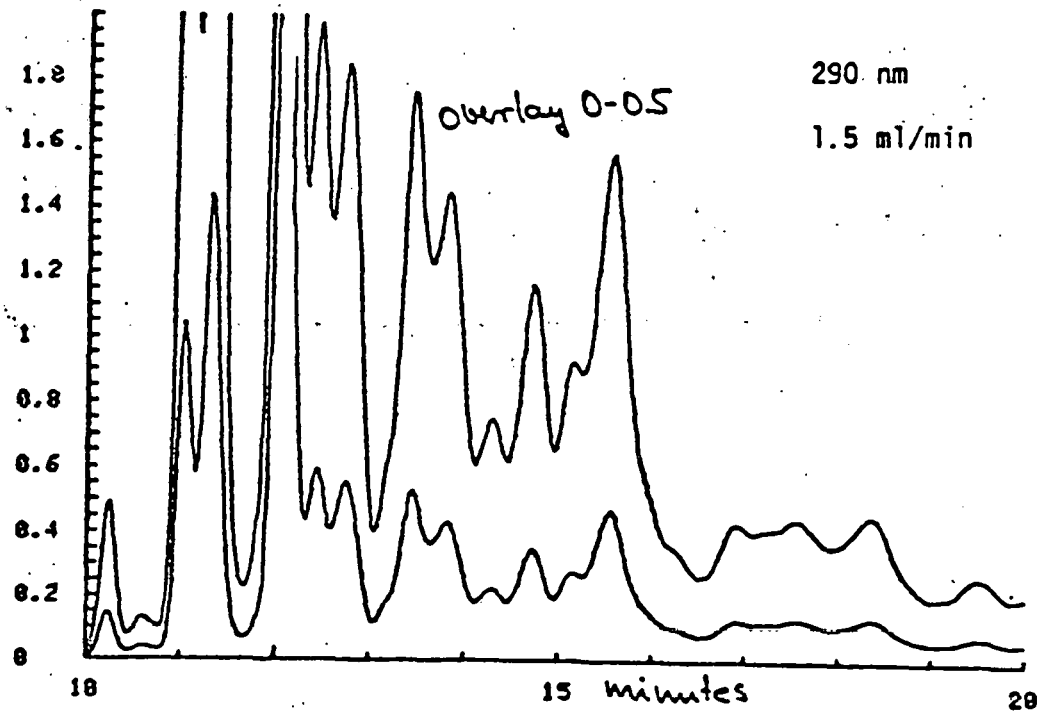


Figure 23b



that the reversed phase chromatography of the nonpolar fraction of a recycle solvent can be performed at 3x the previously evaluated flowrate and therefore will only take approximately 10 minutes per chromatogram using acetonitrile in the mobile phase.

VI. Evaluation of Sample Loop Size

The sample loop, which delivers the sample onto the HPLC column was varied from a 20 ul loop to a 100 ul loop.

Chromatographic conditions were:

flowrate	5 mL/min
mobile phase	ODS 5μ 250 x 10 mm
detector	UV at 195 nm
sample loops	20 ul and 100 ul
sample conc.	10 mg/mL and 3 mg/mL

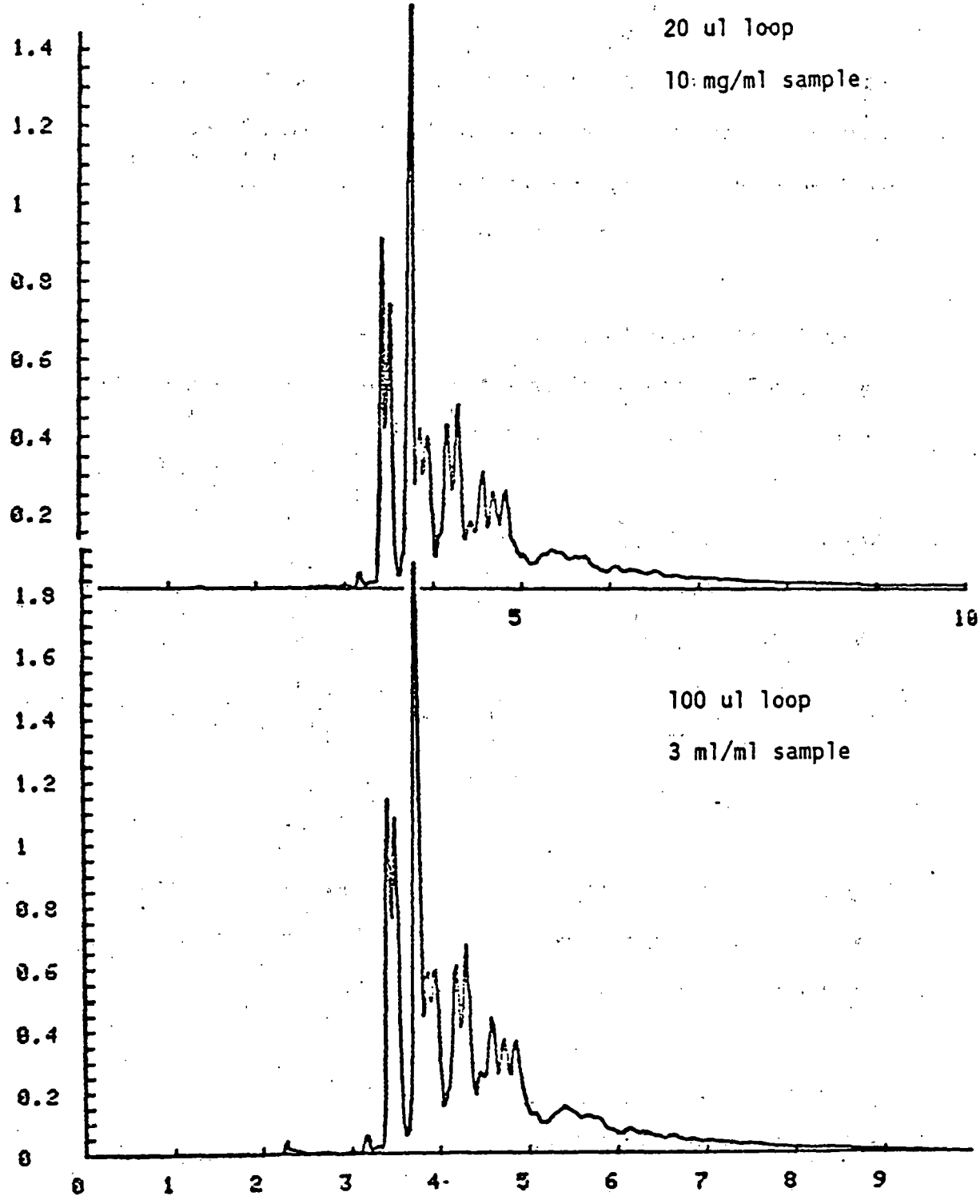
The resulting chromatograms are shown in Figure 25. It can be noticed that the range in sample volume did not effect the sharpness of peaks nor the retention times.

VII. Comparison of Chromatograms Obtained by Differential Refractometer and UV Spectrophotometer Detectors

Chromatographic conditions were:

flowrate	5 mL/min
mobile phase	CH_3CN
column	ODS 5μ 250 mm x 10 mm

Figure 25


20 ul loop
10 mg/ml sample
1.4
1.2
1
0.8
0.6
0.4
0.2
0
5
10
100 ul loop
3 ml/ml sample
1.8
1.6
1.4
1.2
1
0.8
0.6
0.4
0.2
0
0
1
2
3
4
5
6
7
8
9

sample loop	20 µl
chart speed	3 cm/min
detectors:	
differential RID	At 8x
UV-Spectrophotometer	290 nm, 0-400

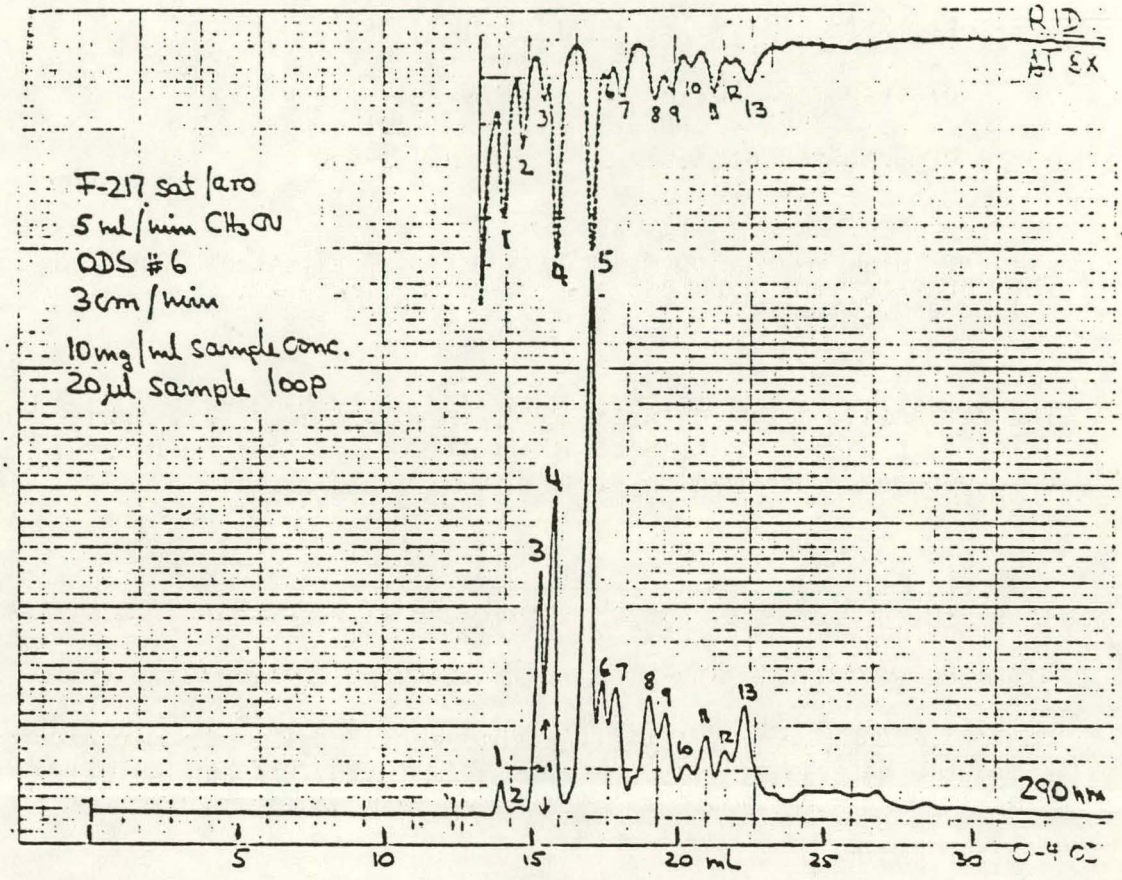
The chromatograms obtained are shown in Figure 24.

The refractive index detector (RID) response is a more true reflection on compound concentration, than the UV detector.

As shown in Figure 11 the UV absorbance of a compound fluctuates greatly with the wavelength at which it is measured. Therefore, the UV detector can be used to magnify specific components in the chromatogram or even simplify a highly complex spectrum as seen in Figure 12.

Using the RID it can be seen that peak #2, barely detected at 290 nm is of substantial concentration. This peak had been identified as naphthalene Peak #6 and #7 sharing a similar response at 290 nm seem to be of different concentrations present in the sample. Peaks #8-13 show a similar relative response at 290 nm as obtained with RID. Peaks #1 and 2, low 290 nm response high RID response, are therefore present at a significant concentration and due to their low molar absorptivity at 290 NM these compounds showed only small peaks at 290 nm. Therefore, these components are only 1-2 aromatic rings - which are compounds of low absorbance at the wavelength chosen.

Figure 24


RID
AT 8X
F-217 sat/aro
5 ml/min CH3CN
ODS #6
3cm/min
10mg/ml sample conc.
20µl sample loop
290nm
5
10
15
20 mL
25
30
0-4 OD

ANALYTICAL CAPABILITIES

INDEX OF FILE MATERIAL

1. File, "High Resolution Mass Spectroscopy Analysis of Distillate Feed and Products."

2. Interoffice Memorandum, R. F. Hamilton to E. N. Givens, "X-Ray Diffraction Method for Determining the Orientation Tendency in Calcined Coke," 29 October 1979, Project 87-0-8884.

3. Interoffice Memorandum, I. S. Kingsley to F. K. Schweighardt, "Functional Group Chromatography," 29 April 1980.

4. "Estimation of OH, NH, and NH_2 Concentrations in Methylene Chloride Soluble Materials," T. L. Slager, 7 May 1980, Project 87-0-8884.

5. File "Raw Data."

6. Documentation on Project 87-1-X023 Folders:

   A) Summary Reports October 1979-September 1980
   B) Laboratory Notebooks
   C) Analytical Data and Analysis January-June 1980
   D) Analytical Data and Analysis July-August 1980
   E) Analytical Data and Analysis September-December 1980

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