



Energy, Mines and  
Resources Canada

Énergie, Mines et  
Ressources Canada

## CANMET

Canada Centre  
for Mineral  
and Energy  
Technology

Centre canadien  
de la technologie  
des minéraux  
et de l'énergie

### THE CHARACTERIZATION OF COAL DERIVED LIQUIDS

M.A. Poirier and P.B. Van Bostelen

JULY 1982

ENERGY RESEARCH PROGRAM  
ENERGY RESEARCH LABORATORIES  
REPORT ERP/ERL 82-32(J)

This document was produced  
by scanning the original publication.

Ce document est le produit d'une  
numérisation par balayage  
de la publication originale.

### SUMMARY

Coal derived liquids (cdl) obtained from coal by supercritical gas (scg) extraction and by liquid extraction processes were analyzed by a battery of techniques. The scg-cdl were process solvent free while the cdl from the liquid processes were heavily contaminated with process solvent which could not be removed by ordinary means. The solvent contamination influenced the results of the analysis.

## I. INTRODUCTION

Raylo Chemicals Limited was awarded a contract by the Department of Energy, Mines and Resources (Canmet) for characterization studies of coal derived liquids (cdl). These studies include solvent analysis to characterize the solid and liquid products obtained from coal liquefaction processes. Canmet provided Raylo with the solvent analysis scheme to be followed, but did not provide specific procedures for carrying out the scheme. The scope of this contract does not allow for comparison of different solvent analysis schemes.

The individual components were analyzed by other means after solvent analysis. The oil was sub-divided into classes of compounds by liquid chromatography. Selected components, especially those derived from subbituminous coal by different liquefaction processes, were analyzed further by elemental analysis, average molecular weight determination and nuclear magnetic resonance (nmr) analysis. The asphaltene was sub-divided into acidic/neutral and basic components and each component was analyzed by nmr. Selected asphaltene samples were further analyzed by elemental analysis and Fourier transform infrared (FTIR). Preasphaltene and insoluble residues were similarly analyzed.

The Scientific Authority provided the cdl samples derived from coal by solvent extraction procedures while Raylo provided the cdl derived from coal by scg extraction.

The data in this Final Report was originally reported in Raylo Progress Reports I through IX, covering the work performed from August 15, 1981 to February 15, 1982. This report compiles and unifies the data and conclusions previously reported.

## II. BACKGROUND

Solvent analysis is a method frequently used to characterize the solid and liquid products obtained from coal liquefaction processes. Samples are separated into fractions according to their solubilities in several solvents. The solvent analysis scheme outlined in Figure 1, separates the cdl into four primary fractions: oil (pentane soluble), asphaltene (toluene soluble, pentane insoluble), preasphaltene (tetrahydrofuran soluble, toluene insoluble) and tetrahydrofuran (THF) insoluble material.

The solvent analysis scheme was derived from literature sources. Various other solvent analysis schemes appearing in the literature specify similar operations in a different sequence (1, 2). In some instances different solvents are used and the final products are classified in different ways such as carboid, carbene, asphaltene, resin and oil (1).

The composition of the oil derived from the solvent analysis procedure is of interest since it could be refined using conventional methods. The oil was separated into saturated, aromatic and polar material by liquid chromatography using a dual packed silica gel-alumina adsorption column. This chromatography system has been applied to the separation of high boiling petroleum distillates (3) and has been modified by the Energy Research Laboratories in Ottawa to increase the speed and efficiency of the separation (4). Heavy coal hydrogenation products have been separated using gradient elution through a dual packed adsorption column (5).

Coal liquefaction processes are often depicted as a sequential progression through a series of intermediate steps from preasphaltene to asphaltene to oil (6). Therefore, the production or genesis of asphaltene must depend on a set of environmental or process variables such as temperature, pressure, solvent and hydrogenation method. These quantities can affect the nature of the chemical and physical character of asphaltene (7). The asphaltene products derived from cdl samples were fractionated into basic and acidic/neutral fractions as a preliminary step to further study.

### III. DESCRIPTION OF SAMPLES

The data compiled in this report was obtained from analysis of the samples listed below.

#### A. Scg-cdl

Pooled cdl obtained by supercritical toluene extraction at 350 to 450°C and 1100 to 1900 psig of Forestburg subbituminous coal. This sample was heated to 200° at atmospheric pressure rendering it completely process solvent free.

#### B. Ginger

Cdl obtained from an H-coal process performed on Ginger coal (N.S.). This sample is a benzene extract of approximately 14% coal liquids in H-donor solvent. The material was heated to 200° at 14 millimeters pressure prior to solvent analysis.

#### C. SBRG-I

Material supplied by Sandwell Beak Research Group (Mississauga) derived from lignite liquefaction experiments in a ten kilogram per hour development unit include a light product, an intermediate product and a heavy product.

##### 1. Heavy product analysis (SBRG-I-H.P.):

<u>Fraction</u>	<u>Weight %</u>
Water	2.1
Distillation	
less than 205°C	2.65 includes water
205 - 275°	12.48
275 - 345°	37.80
345 - 407°	19.80
407 - 475°	6.42
residue	20.85
THF insoluble	8.5

2. Intermediate product (SBRG-I-I.P.):

Analysis is similar to that of the heavy product except that water content is 26.3 weight percent and THF insoluble is 7.5 weight percent.

Both these samples were heated to 200° at atmospheric pressure prior to solvent analysis.

D. SBRG-II

Also supplied by Sandwell Beak. The sample was derived from Alberta subbituminous coal and include a light, an intermediate and a heavy product. The total sample contains about 30 to 35% cdl, the balance being derived from the solvent, anthracene oil.

1. Light product (SBRG-II-L.P.):

This material corresponds to a light stream condensed from the gas phase off the high pressure separation pot and is totally pentane soluble.

2. Intermediate product (SBRG-II-I.P.):

This material corresponds to light oil flashed off at 180°C from the atmospheric separation pot and is totally toluene soluble and about 85% pentane soluble.

3. Heavy product (SBRG-II-H.P.):

The heavy product represents the bulk of the product (about 85%) and contains ash, unreacted coal as well as the coal and solvent derived liquids boiling at greater than 180°C. This material was heated to 200° at atmospheric pressure before solvent analysis.

E. HA (hydrogenated anthracene oil)

This material was supplied by Sandwell Beak and was the process solvent used during preliminary liquefaction experiments. The actual solvent used is very similar to hydrogenated anthracene oil. The solvent is a high boiling material having the following distillation ranges:

Less than 200°	0.5%
200 - 275°	10.5%
275 - 345°	34.9%
345 - 407°	34.9%
407 - 475°	15.6%
residue	3.1%



This material was heated to 200° at atmospheric pressure prior to solvent analysis. The material was totally soluble in toluene and 95% soluble in pentane.

#### IV. SOLVENT ANALYSIS

##### A. Distillation

Prior to carrying out solvent analysis, each of the high boiling samples described above was heated to 200° at atmospheric pressure. The Ginger sample, however, was heated to 200° at 14 mm. In the case of scg-cdl, only process solvents were removed (shown by gas chromatography) making this the only sample which is nearly totally coal derived (bibenzyl, detected in the oil, is a solvent derived contaminant). All the other cdl samples remained heavily contaminated with process solvents. The Ginger coal cdl appears to contain a substantial amount of tetralin (nmr). The heavy products of the Sandwell Beak processes lost very little weight (about 2%) during the heating process. The intermediate product of SBRG-I lost an amount which closely resembled the amount of water present. The boiling point range of the process solvent shows that little solvent will be removed during the distillation step. Materials boiling at less than 200° are usually considered part of the naphtha fraction.

##### B. Separation into Toluene Soluble and Insoluble Material

The method outlined by Mima (8) was used as described.

C. Separation into Preasphaltene and THF Insoluble Residue

The toluene insoluble material obtained in the above step was extracted with THF in a Soxhlet extraction apparatus for two hours. The extraction solvent turned colorless within one-half hour after the extraction had started.

D. Separation into Oil and Asphaltene

This separation has been extensively studied by Steffgen (9). The toluene soluble material obtained in the previous step was redissolved in toluene using a solvent to cdl ratio of three millilitres per gram. Pentane was rapidly added to the vigorously stirred solution using a pentane to toluene ratio of 20 millilitres per millilitre. The precipitated solid was collected by filtration through a Soxhlet thimble and the solid was extracted with pentane for 24 hours using a Soxhlet apparatus.

This procedure differs from the one described in reference 8 in that exhaustive pentane extraction is used. The results obtained by these two methods were compared in reference 9. Exhaustive pentane extraction decreases the apparent asphaltene content by as much as 45%.

E. Results of Solvent Analysis

The results of the above procedures are tabulated in Table I. The recovery of material from the procedure is excellent for all samples. The recovery for SBRG-II-I.P. is somewhat lower than for the other

samples due to the volatility of the material (boiling point less than 180°).

The results show that the scg-cdl are substantially different from the other groups. All the scg-cdl are soluble in supercritical toluene. Oil makes up about one-half of the total cdl, asphaltene about one-quarter and preasphaltene and insoluble residue about one-tenth each.

The other cdl samples contain relatively much higher amounts of oil. These samples, however, are heavily contaminated with process solvent. The process solvent is 95% pentane soluble, as shown by the analysis of HA, explaining the high yield of oil.

The relative amount of asphaltene isolated from the scg-cdl is larger than the amount isolated from the other cdl samples. Process solvent contamination influences the apparent amount of asphaltene isolated. Taking process solvent contamination into account, the relative amount of asphaltene isolated from all sources are similar (see Table VIII).

The yield of preasphaltene and THF insoluble material is very low for the Ginger-cdl relative to the other cdl. This material is a benzene extract and therefore the amounts of these materials would be low.

The THF insoluble material is high for the SBRG products. This can readily be attributed to the method of isolation of these products (see above).

F. Comparison of Results in Using Pentane or Heptane for the Isolation of Oil

Both scg-cdl and SBRG-II-cdl were derived from subbituminous coal. The oil component of the cdl was isolated using either pentane or heptane. The results are tabulated in Table II.

The relative amount of oil increased while the relative amount of asphaltene decreased by the same amount in going from pentane to heptane for both cdl samples. The amount of oil increase, however, was much larger for the scg-cdl than it was for the SBRG-II-H.P. cdl. There was a substantial increase in the average molecular weight of the oil obtained with heptane compared with the average molecular weight of the oil obtained with pentane for the scg-cdl. A similar increase was not observed for the oil isolated from SBRG-II-H.P. cdl.

These results show that the material defined as asphaltene (toluene soluble, pentane insoluble) is considerably more soluble in heptane than in pentane, a phenomenon also noted for bitumen derived asphaltene (10). The greater solvent power of heptane has less influence on the results of solvent analysis of the cdl contaminated by process solvent than on the results of solvent analysis of process solvent free cdl.

V. FRACTIONATION OF ASPHALTENE

A method described in the literature (11) was used for the fractionation procedure. The method involves redissolving the asphaltene isolated above in toluene. More than 98% of the scg-cdl redissolved while only 62 to 75% of the asphaltene obtained from the cdl derived by solvent extraction processes redissolved. The cdl obtained by the solvent extraction processes are contaminated with a process solvent which is 95% soluble in pentane. Removal of the pentane soluble material reduces the solvent power of toluene for asphaltene. Therefore, when the isolated asphaltene is redissolved in toluene, a certain portion will not be soluble (Table III).

The solution was treated with dry hydrogen chloride and the precipitated salts were collected. The solvent was removed to recover the acid/neutral asphaltene while the collected solid was slurried in toluene and treated with 0.3 molar sodium hydroxide solution to convert the salt into basic asphaltene. Recovery of the basic asphaltene ranges from 62 to 74% of the theoretical amount (11).

The nmr spectra for each of the fractions were taken in pyridine-d<sub>5</sub>. The integration data indicates that the insoluble material is most highly aromatic (largest aromatic/phenolic hydrogen to total hydrogen ratio - H<sub>a</sub> value) while the basic material is more aromatic than the acidic/neutral material. The spectral data is generally consistent with the elemental analysis data (see below).

## VI. LIQUID CHROMATOGRAPHY

The oils obtained from each of the above solvent separations were chromatographed on a dual packed silica gel-alumina column using the procedure described in the literature (4). The eluant was collected in ten millilitre aliquotes. The chromatography was followed by thin layer chromatography (tlc). The aliquotes of eluant which showed components having similar  $R_f$  values were pooled and the solvent was removed. The results are tabulated in Table IV.

The recovery of material is generally very good. The recovery from SBRG-II-I.P. is low due to the volatility of the material. The recovery for the scg-cdl oil is also somewhat low probably due to the large amount of polar material which results in some of this material being strongly adsorbed on the column.

Tlc showed that a number of distinct classes of compounds, usually two, were eluted with pentane. Proton nmr shows that the first distinct class of compounds eluted with pentane has a low  $H_a$  value showing that these are the saturated compounds while the second distinct class has a higher  $H_a$  value showing that these are the monoaromatic compounds. Bibenzyl appears as a component in this second fraction for the scg-cdl oil. The separation of these compounds was sharp for the scg-cdl oil but not as sharp for the cdl from the other processes. Tlc showed that relatively clean separations were obtained throughout the gradient elution.

The scg-cdl oil shows a different elution profile from the other oils. The amount eluted with pentane and 5% benzene/pentane is 31.5% of the total while for the oils from other sources this amount ranges from 61.9% for SBRG-II-I.P. to 84.7% for Ginger. The amount of polar material is 32% in the scg-cdl oil and ranges from 4.4 to 14.4% for the oil from other sources. The elution profiles for the SBRG-oils are very similar to the profile for hydrogenated anthracene oil.

The Ha values for scg-cdl oil fractions are considerably lower than for the SBRG materials. The Ha values for the bulk of the SBRG materials closely resemble those of the hydrogenated anthracene oil. The Ha values for the coal derived oil from all the processes pass through a maximum with the material eluted with 5% benzene/pentane (Table IV). After fraction B, the materials become more polar and less aromatic.

The fa values (aromatic carbon to total carbon ratio) was determined by C-13 nmr for fractions A1, A2, and E of the scg-cdl oil. These were found to be 0.24, 0.73 and 0.59 confirming the conclusion drawn from the Ha values. The fa values were not determined for other samples due to the relatively small amount of material isolated.



#### VII. NMR DATA FOR PREASPHALTENE

Proton nmr spectra of preasphaltene obtained from the cdl samples were taken in pyridine-d<sub>5</sub>. The Ha values (Table V) appear to be independent of both coal type and process parameters. There are, however, differences in the spectra of preasphaltenes isolated from cdl derived from coal by liquid extraction and from cdl derived by scg extraction (Figures 2 and 3). Figure 3 shows less resolution of the signals in both the aromatic and aliphatic regions. Aside from that, the aromatic regions are similar. The aliphatic region in Figure 3 has a prominent signal at 1.15 ppm which is virtually absent in Figure 2.

The observed differences probably arise from the response of the cdl to solvent analysis. Toluene contaminated with process solvent would have much more solvent power for all classes of cdl than pure toluene since process solvents are coal derived (like dissolves like).

#### VIII. COMPARISON OF DATA FOR SUBBITUMINOUS CDL OBTAINED BY DIFFERENT LIQUEFACTION PROCESSES

The components of subbituminous cdl were analyzed by a variety of methods.

##### A. FTIR Analysis

Diffuse reflectance Fourier transform infrared (FTIR) spectra for a number of components were obtained using the facilities at the University of Alberta.



1. THF insoluble material:

The scg-cd1 THF insoluble material is soluble in supercritical toluene since it was extracted by this process. The THF insoluble material from the SBRG process came from the vacuum bottoms and contains coal or char residues. Figures 4 and 8 are FTIR spectra of the scg-cd1 THF insoluble material and the SBRG-II heavy product THF insoluble material.

Qualitatively, Figure 4 is very similar to the rest of the scg-cd1 FTIR spectra (Figures 5 to 7) while Figure 8 is very different from all other spectra.

Figure 4 shows a strong absorbance at  $3200\text{ cm}^{-1}$  indicative of hydrogen bonded O-H and/or N-H stretch, a weak absorbance at  $3050\text{ cm}^{-1}$  indicative of aromatic C-H stretch, three absorbance bands at  $2880$ ,  $2920$  and  $2960\text{ cm}^{-1}$  associated with C-H stretching in methyl and methylene groups, a weak absorbance at  $1700\text{ cm}^{-1}$  associated with carbonyl stretch, a strong absorbance at  $1600\text{ cm}^{-1}$  probably associated with enhanced aromatic ring resonance due to OH substitution (12), an absorbance band centered at  $1460\text{ cm}^{-1}$  associated with aliphatic C-H bending, a weak absorbance at  $1380\text{ cm}^{-1}$  associated with methyl C-CH<sub>3</sub> bending, absorbance between  $1200$  to  $1300\text{ cm}^{-1}$  associated with ether linkages and a number of absorbance bands appearing in the range of  $740$  to  $900\text{ cm}^{-1}$  associated with aromatic C-H bending. The sharp absorbance at  $700\text{ cm}^{-1}$  is generally

associated with  $\text{CH}_2$  rocking when several methylene groups are linked together. This absorbance could, however, also be indicative of a monosubstituted benzene ring along with the absorbance in the 740 to 760  $\text{cm}^{-1}$  range. The 700  $\text{cm}^{-1}$  absorbance band is well defined in the spectra of the materials derived from coal by supercritical toluene extraction but is much less intense in the spectra of the materials derived by the SBRG process. This observed difference could possibly indicate benzyl substitution in the materials extracted with supercritical toluene.

The THF insoluble material derived by the SBRG process (Figure 8) shows many of the same absorbance bands noted above as well as bands at 3690, 3630, 1050, 550 and 480  $\text{cm}^{-1}$  all of which are associated with mineral matter (12). The relative intensity of the hydrogen bonded O-H and/or N-H absorbance is much smaller in Figure 8 than in Figure 4 and the ratio of the aromatic C-H stretch to aliphatic C-H stretch is much greater in Figure 8 than in Figure 4. These differences in the FTIR spectra indicate significant differences in the structural make-up of these materials.

## 2. Preasphaltenes:

The spectra of preasphaltene (Figures 5 and 9) show considerable differences in the materials derived from the different liquefaction processes. Figure 9 shows a very strong free O-H stretch at 3640  $\text{cm}^{-1}$  which is missing in Figure 5. The ratios of the aliphatic C-H stretching absorbances (2880, 2920 and 2960) are very different in

Figures 5 and 9. The relative intensity of the absorbance at  $1600\text{ cm}^{-1}$  is much smaller in Figure 9 than in Figure 5. Figure 5 shows a strong sharp absorbance at  $700\text{ cm}^{-1}$ , missing in Figure 9. The preasphaltene isolated from the cdl derived from the two liquefaction processes are different materials, corroborating the nmr data (Figures 2 and 3).

### 3. Acidic/Neutral Asphaltene:

Figures 6 and 10 are spectra of the acidic/neutral asphaltene isolated from the cdl derived by different processes. Considerable differences, mainly in the relative intensities of the absorbance bands are evident. The absorbance at  $3200$  to  $3300\text{ cm}^{-1}$  and at  $1600\text{ cm}^{-1}$  in Figure 6 are much more intense than those in Figure 10 indicating that the material isolated from scg-cdl is more phenolic than the material isolated from SBRG-II cdl. This is also evident from the nmr spectra which shows an Ha value of 0.32 for the scg material and 0.27 for the SBRG material. Common to the spectra of both material is an absorbance at  $1700$  to  $1720\text{ cm}^{-1}$  probably indicating some carboxylic acid carbonyl stretching. The position of this absorbance suggests the presence of acetic acid residues rather than benzoic acid residues. This absorbance band could also be associated with cyclic ketone carbonyl stretching.

#### 4. Basic Asphaltene:

Figures 7 and 11 are the FTIR spectra of the basic asphaltene. The basic asphaltene in Figure 11 is contaminated with silicon grease somewhat limiting the usefulness of the spectrum. Otherwise, the spectra are very similar. Both spectra show O-H or N-H stretching. The elemental analysis (see below) of the scg-cdl derived material shows that the nitrogen content for the basic and acidic/neutral materials are similar (1.84% for basic, 1.77% for acidic/neutral) but the oxygen content of the basic material (21.45%) is much greater than for the acidic/neutral material (11.59%). This data probably indicates that the basic material is amphoteric and could account for the fact that considerable material is lost during the fractionation of asphaltene into basic and acidic/neutral portions.

One notable difference between the spectra of the two materials is the absorbance band at  $700\text{ cm}^{-1}$ , intense in Figure 7 but weak in Figure 11.

#### B. Elemental Analyses

Table VI summarizes the results of the analyses of fractions of cdl obtained from subbituminous coal by scg extraction and the SBRG process.

The THF insoluble material from both sources cannot be compared, even though the results are tabulated, due to the presence of mineral matter in the SBRG material (see above).

The SBRG process derived preasphaltene is less aromatic than the scg extraction derived material (lower Ha value and larger H/C ratio). Furthermore, the SBRG process derived material has lower nitrogen and sulfur content and similar oxygen content relative to the scg extraction derived material.

The asphaltenes from both sources are similar. The fractionated SBRG asphaltene tends to have a larger H/C ratio than the corresponding scg material. The total SBRG asphaltene, however, has a lower H/C ratio, confirming the nmr data (Table III) which showed that the asphaltene which did not redissolve in toluene (38% for SBRG material, negligible for scg material) was highly aromatic.

The largest difference in the materials obtained by the two processes occurs in the pentane soluble oil. The material obtained by scg extraction is much less aromatic than the material obtained by the SBRG process. This can be attributed to the presence of process solvent (hydrogenated anthracene oil) in the SBRG material and the absence of any process solvent in the scg extraction derived material. The Ha value for the pentane soluble hydrogenated anthracene oil and the fractionated (by liquid chromatography) hydrogenated anthracene oil are very similar to the Ha values for the corresponding materials obtained for the bulk of the SBRG process cdl (Table IV). Process solvent contamination makes comparison of the cdl derived from subbituminous coal by the two different liquefaction methods invalid

since there is no method for distinguishing between coal derived and solvent derived products.

IX. MOLECULAR WEIGHTS OF OILS

Table VII summarizes the average molecular weight of oil obtained from cdl derived from coals other than subbituminous coal. The molecular weight of all the SBRG process material is very similar. The molecular weight of the oil from cdl derived from Ginger coal by an H-coal process is higher than for the oil from cdl derived by the SBRG process but not as high as the oil derived by the scg extraction process. Note that this material had been heated to 200° at 14 mm pressure prior to solvent analysis. This action will have removed the lighter materials resulting in a relatively higher molecular weight for the oil.

The amount of coal derived material in the oil can be calculated for SBRG-II-H.P. if one assumes a molecular weight of 190 for the process solvent (HA), 270 for the coal derived oil (scg) and that all the process solvent appear in the oil after solvent analysis. Letting x equal the fraction of coal derived oil in the total oil then:

$$205 = 270 x + 190 (1 - x)$$

from which  $x = 0.19$ . Therefore 19% of the oil is coal derived. Taking

this into account, the THF insoluble material represents 37.5% of the coal derived material, preasphaltene 12.2%, asphaltene 13.6% and oil 32.5%. For a similar analyses of other SBRG-cdl samples see Table VIII.

X. CONCLUSIONS

Solvent analysis is a useful method for the preliminary separation of cdl into a number of components. Process solvent, however, strongly influences the chemical and physical characteristics of the separated components and may lead to the erroneous conclusion that a given liquefaction process results in high conversion of coal to oil.

Liquid chromatography of oil on a dual-packed silica gel-alumina column results in relatively clean separations of saturated, aromatic and polar material throughout the gradient elution. Process solvents influence the elution profile of the oil.

FTIR is a powerful tool for analysis of cdl. The amounts of individual groups could be determined by computer analysis of the spectrum. FTIR could prove to be the tool capable of distinguishing between coal derived and solvent derived molecules in coal liquefaction processes.



## XI. EXPERIMENTAL SECTION

The following fractionation procedure was carried out using cdl derived from supercritical gas extraction of Forestburg subbituminous coal.

### Distillation

Coal derived liquids (9.68 g) were placed in a 25 ml tared round bottom flask and several weighed carborundum boiling chips were added. The flask was fitted with a short path distillation head (ca. 50 mm) and condensor and heated with an oil bath to  $210 \pm 10^\circ\text{C}$ . The distillate consisted of pyridine and toluene (gc analysis), solvents used to pool the cdl. Yield of distillate 3.90 g; yield of solvent free residue 4.98 g (92% recovery).

### Fractionation into Toluene Soluble and Insoluble Materials

The residue from the distillation was slurried with 20 ml of toluene and transferred to a 25 x 80 mm Soxhlet thimble which had been washed with toluene, dried at  $100^\circ\text{C}$  for 0.5 hr, cooled and allowed to equilibrate with the atmosphere until there was no further change in weight. The distillation flask was washed with four additional 20 ml portions of toluene and the washings were transferred to the Soxhlet apparatus through the thimble. An additional 100 ml of toluene was added to the Soxhlet apparatus and the residue was extracted for 24 hours. The thimble was removed and treated as described above. The yield of toluene insoluble material was 1.09 g (21.9%).



The toluene was removed from the extract by rotary evaporation followed by subjecting the sample to 0.01 mm vacuum until no further weight change was observed. The yield of toluene soluble material was 3.89 g (78.1%).

#### Fractionation into Preasphaltene and THF Insoluble Material

The toluene insoluble material left in the Soxhlet thimble was re-extracted in the Soxhlet apparatus with 100 ml of tetrahydrofuran (THF) for two hours. The thimble and contents were dried at 60°C for 0.5 hour in a vacuum desiccator. The thimble was cooled under vacuum, removed from the desiccator and allowed to equilibrate with the atmosphere. The yield of THF insoluble material was 0.50 g (10.0%).

The THF was removed by rotary evaporation followed by subjecting the sample to 0.01 mm vacuum until there was no further change in weight. Yield of THF soluble material was 0.50 g (10.0%).

#### Fractionation into Oil and Asphaltene

The toluene soluble material (3.89 g) was redissolved in 12 ml of toluene (ca. 3 ml toluene per gram of toluene soluble material). The solution was vigorously stirred and 240 ml pentane (20 ml pentane per ml of toluene) was rapidly added. After the pentane addition, the mixture was allowed to stand for 0.5 hour, then the solid was collected by filtration through a 25 x 80 mm soxhlet thimble which had been washed with pentane, dried at 60°, cooled and weighed. The flask was washed with two 20 ml portions of pentane and washings were added to

the Soxhlet apparatus through the thimble. The solid was extracted with pentane for 24 hours. The thimble was then dried as described above. The yield of asphaltene was 1.20 g (24.1%).

The pentane was removed as described to yield 2.50 g (50.2%) oil.

#### Fractionation of Asphaltene into Acid/Neutral and Basic Components

A portion of the asphaltene (0.80 g) was redissolved in 20 ml toluene in a glass centrifuge tube. The tube was placed on a rotary shaker for one hour and the undissolved solid was centrifuged to the bottom of the tube. The toluene solution was decanted from the solid and the solid was washed twice with an additional 10 ml toluene. The solid was dried and weighed to leave 0.013 g (1.6%) of undissolved asphaltene.

Hydrogen chloride was passed through the combined toluene solution for four hours. The tube was centrifuged and the toluene solution containing the acid/neutral component was decanted. The solid was washed twice with 10 ml portions of toluene followed by centrifuging and decanting each time. The washes were combined with the solution, the toluene removed by rotary evaporation and the solid dried at 0.01 mm to leave 0.40 g (50.0%) acid/neutral asphaltene.

The collected solid was slurried in 10 ml toluene and 10 ml 0.3 molar sodium hydroxide solution was added. The phases were separated and the aqueous phase was extracted 3 times with 10 ml toluene. The combined extracts were dried over anhydrous sodium sulfate and toluene

was removed by rotary evaporation. The solid was dried at room temperature under 0.01 mm vacuum to leave 0.25 g (31.6%) basic asphaltene.

#### Liquid Chromatography

The bottom of a vertically clamped 40" x 1/2" O.D. 316 SS tube was connected, using Swagelok fittings, to a 4" length 1/8" O.D. SS tube fashioned into a U-tube. This was connected to a 1/8" union tee, one inlet of which was fashioned as an injector port using a neoprene septum while the branch was connected to a Model B-100-S Eldex Laboratories metering pump with a length of 1/16" SS tubing. The bottom of the column was plugged with a Pyrex wool plug and 37 grams of Fisher Reagent ACS 28 - 200 mesh silica gel activated at 250°C for 20 hours was packed into the column. This was followed with 47 grams of Fisher Certified 80 - 200 mesh Basic Brockman Activity I alumina activated at 400°C for 20 hours. The top (outlet) of the column was fitted with a Pyrex wool plug and connected with Swagelok fittings to a 1/16" exit tube. Pentane was pumped through the packed column and the flow rate was adjusted to deliver 3 ml/min. The chromatography column was wrapped with heating tape and the temperature on the outside of the column was monitored using a thermometer.

Oil from scg-cdl was warmed to 50°C using a water bath to make it sufficiently mobile and drawn into a syringe. The syringe and oil was weighed. The oil was injected onto the column, pentane was drawn into

the syringe to rinse it, the pentane was also injected onto the column and the syringe was dried and weighed showing that 0.920 g oil had been placed on the column. The pump was started and the oil was eluted in succession with 250 ml pentane (fraction A), 300 ml 5% benzene/pentane (fraction B), 300 ml 15% benzene/pentane (fraction C), 100 ml benzene (fraction D), 50 ml 60% methanol, 20% benzene, 20% ether (fraction E), and 100 ml methanol (fraction F). The column was then heated to 100° and eluted with 100 ml pyridine (fraction G). The heat was removed and the column was eluted with 100 ml toluene (fraction H). Finally 300 ml pentane was passed through the column to prepare it for the next injection.

The eluant was collected in 10 ml aliquotes using a Buchler Fracto Mette 200 collector. The aliquotes were spotted on 20 x 20 cm 0.25 mm thickness silica gel 60F<sub>254</sub> plates (Merck) developed with pentane/benzene in a 97:3 ratio. The developed plates were viewed under long and short wave ultraviolet light. The aliquotes which showed components having similar R<sub>f</sub> values were pooled, the solvent was removed and the residue dried under 0.01 mm vacuum at room temperature. The results were fraction A1 - 0.140 g (15.2%), A2 - 0.099 g (10.8%), B - 0.051 g (5.5%), C - 0.030 g (4.2%), D - 0.062 g (6.7%), E - 0.295 g (32.0%), F - 0.035 g (3.8%), G - 0.019 g (2.1%), H - 0.030 g (3.3%). The total recovery was 0.77 g (83.6%).

XII. REFERENCES

1. I. Schwager and T.F. Yen, *Fuel*, 57, 100 (1978).
2. F.K. Schweighardt and B.M. Thames, *Anal. Chem.*, 50, 1381 (1978).
3. D.E. Hersch, R.L. Hopkins, H.J. Coleman, F.O. Cotton and C.J. Thompson, *ibid.*, 44, 915 (1972).
4. H. Sawatzky, A.E. George, G.T. Smiley and D.S. Montgomery, *Fuel*, 55, 16 (1976).
5. R.J. Pregmire, D.M. Grant, K.W. Zilm, L.L. Anderson, A.G. Oblad and R.E. Wood, *ibid.*, 56, 295 (1977).
6. B.C. Bockrath and F.K. Schweighardt, "Chemistry of Asphaltene", J.W. Bunger and N.C. Li, ed., ACS Advances in Chemistry Series, 195, 29 (1981).
7. T.F. Yen, *ibid.*, 195, 39 (1981).
8. M.J. Mima, H. Schultz and W.E. McKinsty, "Analytical Methods for Coal and Coal Products", C. Karr Jr., Ed., Vol. 1, p.557 (1978).
9. F.W. Steffgen, K.T. Schroeder and B.C. Bockrath, *Anal. Chem.*, 51, 1164 (1979).
10. E.W. Funk, *Can. J. Chem. Eng.*, 57, 333 (1979).
11. B.C. Bockrath, C.L. Delle Donne and F.K. Schweighardt, *Fuel*, 57, 4 (1978).
12. P.R. Solomon, United Technologies Research Centre, East Hartford, unpublished results.

TABLE I

Results of solvent analysis for various samples of cd1<sup>a)</sup>.

Fraction	scg-cd1	Ginger	% of Initial Sample		SBRG-II		HA
			SBRG-I H.P.	SBRG-II I.P.	SBRG-II H.P.	SBRG-II I.P.	
THF Insoluble	10.0	0.6	11.0	9.9	15.7	---	---
Preasphaltene	10.0	5.0	4.2	3.5	5.1	---	---
Asphaltene	24.1	14.4	7.4	7.5	5.7	1.2	2.0
Oil <sup>b)</sup>	50.2	80.1	77.9	77.9	71.7	86.6	94.7
% Material Recovery	94.3	100.1	100.5	98.8	98.2	87.7	96.7

a) See text for sample description.

b) For all samples except scg-cd1, the oil is heavily contaminated with process solvent. For results taking the quantity of process solvent into account, see Table VIII.

TABLE II

Comparison of the results of solvent analysis of cdl using pentane or heptane for oil extraction.

Fraction <sup>a)</sup>	scg-cdl		SBRG-II-H.P.	
	<u>Pentane</u>	<u>Heptane</u>	<u>Pentane</u>	<u>Heptane</u>
Asphaltene	24.1	14.6	5.7	3.4
Oil	50.2	60.0	71.7	74.3
Molec. Wt. of oil <sup>b)</sup>	267	302	205	206

a) % of total cdl.

b) By VPO

TABLE III

Fractionation and nmr integration data for asphaltene isolated from cdl samples.

Asphaltene	scg		Ginger		SBRG-I-I.P.		CdI Sample <sup>a)</sup> SBRG-I-H.P.		SBRG-II-I.P.		SBRG-II-H.P.	
	%	Ha	%	Ha	%	Ha	%	Ha	%	Ha	%	Ha
Total	100	0.37	100	--	100	0.52	100	0.51	100	0.58	100	0.53
Insoluble	1.6	--	31.2	0.44	24.3	0.59	25.2	0.57	--	--	38.0	0.61
Basic	31.6	0.37	31.4	0.42	30.2	0.46	41.6	0.53	--	--	37.4	0.43
Acid/neutral	50.0	0.32	35.9	0.37	31.3	0.44	27.1	0.36	--	--	26.6	0.28
% Recovery	83.2		98.5		85.3		93.9		--		102	

a) % represents percent of total asphaltene.



TABLE IV

liquid chromatography and proton nmr integration data of pentane soluble cdI.

raction <sup>a)</sup>	scg-cdI		Ginger		SBRG-I-I.P.		Source <sup>b, c)</sup> SBRG-I-H.P.		SBRG-II-I.P.		SBRG-II-H.P.		HA	
	%	Ha	%	Ha	%	Ha	%	Ha	%	Ha	%	Ha	%	Ha
M <sup>d)</sup>	100	0.24	100	0.46	100	0.67	100	0.70	100	0.55	100	0.73	100	0.74
1	15.2	0.07	28.2	0.11	15.6	0.54	7.0	0.23	23.0	0.39	20.8	0.43	17.4	0.41
2	10.8	0.33	29.1	0.38	21.2	0.75	21.7	0.69	18.9	0.79	30.8	0.80	9.9	0.70
3	--	--	--	--	--	--	30.5	0.88	11.5	0.79	--	--	--	--
4	--	--	--	--	--	--	--	--	5.7	0.86	--	--	--	--
1	5.5	0.28	27.4	0.83	21.1	0.87	14.9	0.88	2.8	0.93	25.2	0.88	21.0	0.88
2	--	--	--	--	10.5	0.86	--	--	--	--	--	--	24.8	0.88
	4.2	0.19	9.2	0.47	5.6	0.83	3.5	0.63	0.3	--	4.1	0.78	6.0	0.95
	6.7	0.19	2.8	0.41	3.3	0.65	2.4	--	0.3	--	3.8	0.68	3.6	0.96
	32.0	0.25	4.4	0.30	14.4	0.57	13.6	0.62	9.1	0.51	11.8	0.60	9.5	0.69
	3.8	0.18	0.5	--	2.1	--	1.5	--	0.9	--	1.8	--	1.4	0.67
	2.1	0.13	2.9	0.09	1.0	--	0.9	--	0.9	--	1.1	--	1.5	--
	3.3	--	0.2	--	1.0	--	0.9	--	--	--	0.2	--	0.9	0.13
Recovery	83.6		104.7		95.8		97.1		73.4		99.6		96.1	

i) Fractions eluted with: A1, 2, 3, 4 - pentane; B1, 2 - 5% benzene/pentane; C - 15% benzene/pentane; D - benzene; E - 60% methanol/20% benzene/20% ether; F - methanol; G - pyridine at 100°C; H - toluene.

j) See text for source description.

k) % is percent of total sample placed on column.

l) SM = Starting oil.

TABLE V

Proton nmr integration data for preasphaltene isolated from various cdl samples.

<u>Cdl Sample</u>	<u>Ha</u>
scg (SB)	0.32
Ginger (NS)	0.32
SBRG-I intermediate (L)	0.25
SBRG-I heavy (L)	0.33
SBRG-II heavy (SB)	0.19

a) Letters in brackets represent the coal rank the cdl were derived from: SB = subbituminous; NS = Nova Scotia bituminous; L = lignite.

TABLE VI

Comparison of elemental analysis, nmr and vapour phase osmometry data for fractions of cdl derived from subbituminous coal by different liquefaction methods.

Sample	% Yield	Elemental Analysis					H/C	O/C	Ha	VPO
		%C	%H	%N	%S	%O				
THF insoluble										
scg	10.0	75.11	5.32	2.22	0.77	16.58	0.85	0.17	--	--
SBRG	15.7	57.22	2.37	0.04	0.94	39.43	0.50	0.52	--	--
Preasphaltene										
scg	10.0	76.74	6.14	2.04	0.77	14.31	0.96	0.14	0.32	--
SBRG	5.1	78.19	7.92	1.24	0.30	12.35	1.22	0.12	0.19	--
Asphaltene										
scg	24.1	78.60	6.46	1.37	0.56	13.01	0.99	0.12	0.37	--
SBRG	5.7	78.08	4.88	2.32	0.50	14.22	0.75	0.14	0.53	--
Basic asphaltene										
scg	31.6	70.14	5.90	1.84	0.67	21.45	1.01	0.23	0.37	--
SBRG	37.4	63.55	5.84	1.82	0.45	28.34	1.10	0.33	0.43	--
Acidic/Neutral asphaltene										
scg	50.0	78.48	7.53	1.77	0.63	11.59	1.15	0.11	0.32	576
SBRG	26.6	79.79	8.45	0.79	0.90	10.07	1.27	0.09	0.28	--
Oil										
scg	50.2	82.64	9.46	0.47	0.54	6.89	1.37	0.06	0.25	267
SBRG	71.7	90.51	6.49	0.73	0.65	1.61	0.86	0.01	0.73	205
Pentane A										
scg	15.2	82.48	12.07	0.12	0.33	5.00	1.76	0.05	0.07	--
SBRG	20.8	87.20	9.87	0.05	--	--	1.36	--	0.43	215
Pentane B										
scg	10.8	86.01	9.07	0.17	0.60	4.15	1.27	0.04	0.33	--
SBRG	30.8	90.92	6.12	0.04	0.69	2.23	0.81	0.02	0.80	187
5% Benzene/Pentane										
scg	5.5	86.51	8.94	0.20	0.86	3.49	1.24	0.03	0.28	--
SBRG	25.2	93.52	5.57	0.07	0.72	0.12	0.74	0.001	0.88	196
Benzene (scg)	6.7	83.30	8.32	0.74	0.66	6.98	1.20	0.06	0.19	--
15% Benzene/Pentane (SBRG)	4.1	91.78	5.63	0.30	0.79	1.50	0.74	0.01	0.78	272
MeOH/Et <sub>2</sub> O/Benzene 3:1:1										
scg	32.0	78.60	8.25	1.04	0.48	11.63	1.26	0.11	0.25	282
SBRG	11.8	82.34	6.13	4.67	0.79	6.07	0.89	0.06	0.60	228

- a) Performed by Canadian Microanalytical Services Ltd., Vancouver, B.C.
- b) Obtained by difference.
- c) Performed at University of Alberta.
- d) Percent of total cdl.
- e) Contains mineral matter by FTIR
- f) Percent of total asphaltene.
- g) Percent of total oil.

TABLE VII

Average molecular weight for pentane soluble oil obtained from cdl derived from coals other than subbituminous coal.

<u>Sample</u>	<u>Coal</u>	<u>Molecular Weight</u>
Ginger coal	Nova Scotia bituminous	234
SBRG-I-intermediate product	Lignite	194
SBRG-I-heavy product	Lignite	197, 200
Hydrogenated anthracene oil	---	192

a) Duplicate determination.

TABLE VIII

Results of solvent analysis for various samples of cdl corrected for solvent contamination<sup>a)</sup>

Fraction	% of Solvent Corrected Sample			
	scg-cdl	SBRG-I-H.P.	SBRG-I-I.P.	SBRG-II-H.P.
THF Insoluble	10.0	34.1	36.5	37.5
Preasphaltene	10.0	13.0	13.0	12.2
Asphaltene	24.1	22.9	27.9	13.6
Oil	50.2	30.0	17.8	32.5
Portion coal derived <sup>b)</sup>	1.0	0.125	0.062	0.19

a) See text for basis of calculation.

b) Portion of isolated oil which is considered coal derived on the basis of average molecular weight - see text and Table VII.

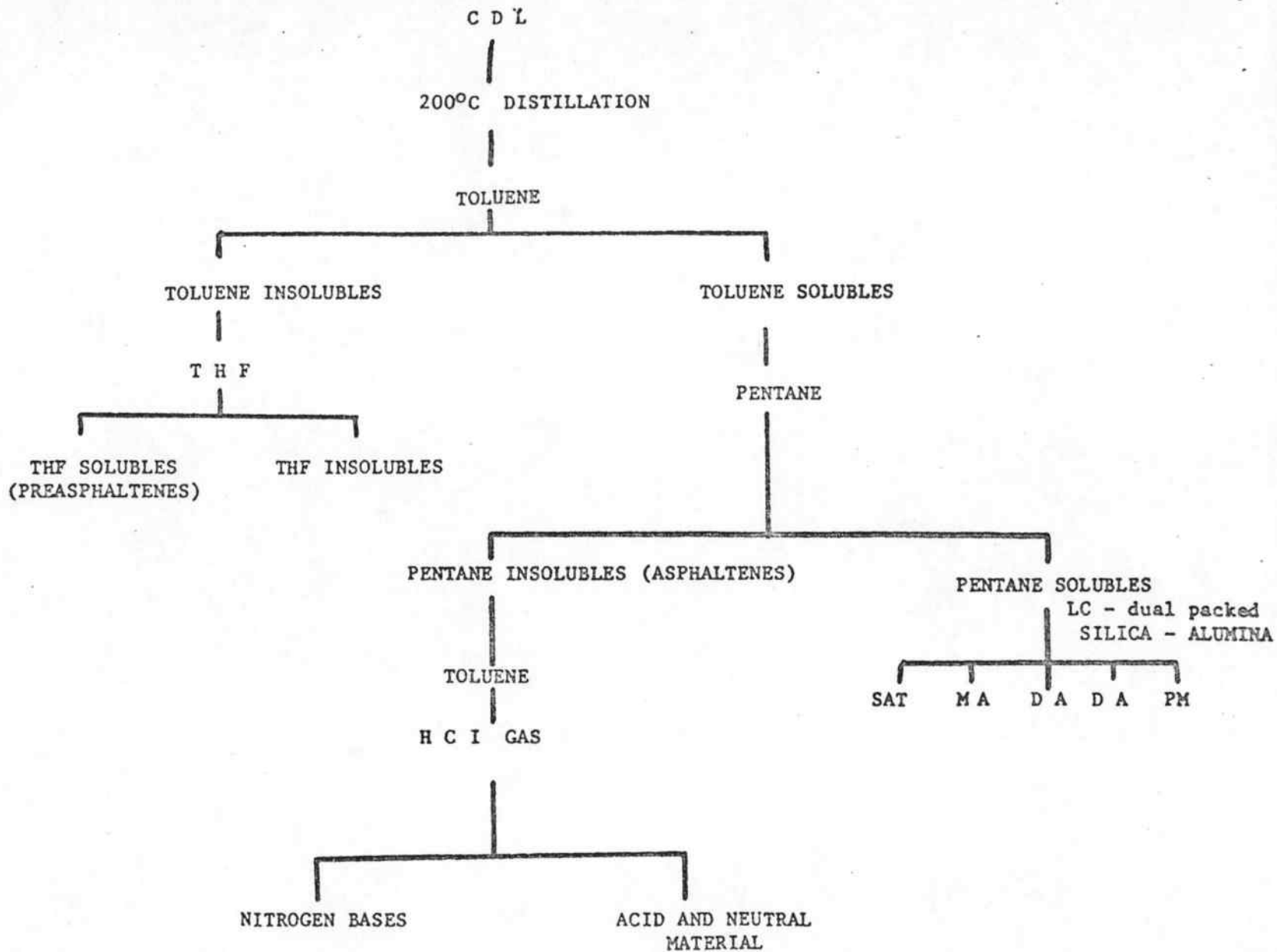


Figure 1: Separation scheme for cdl characterization supplied by Canmet.

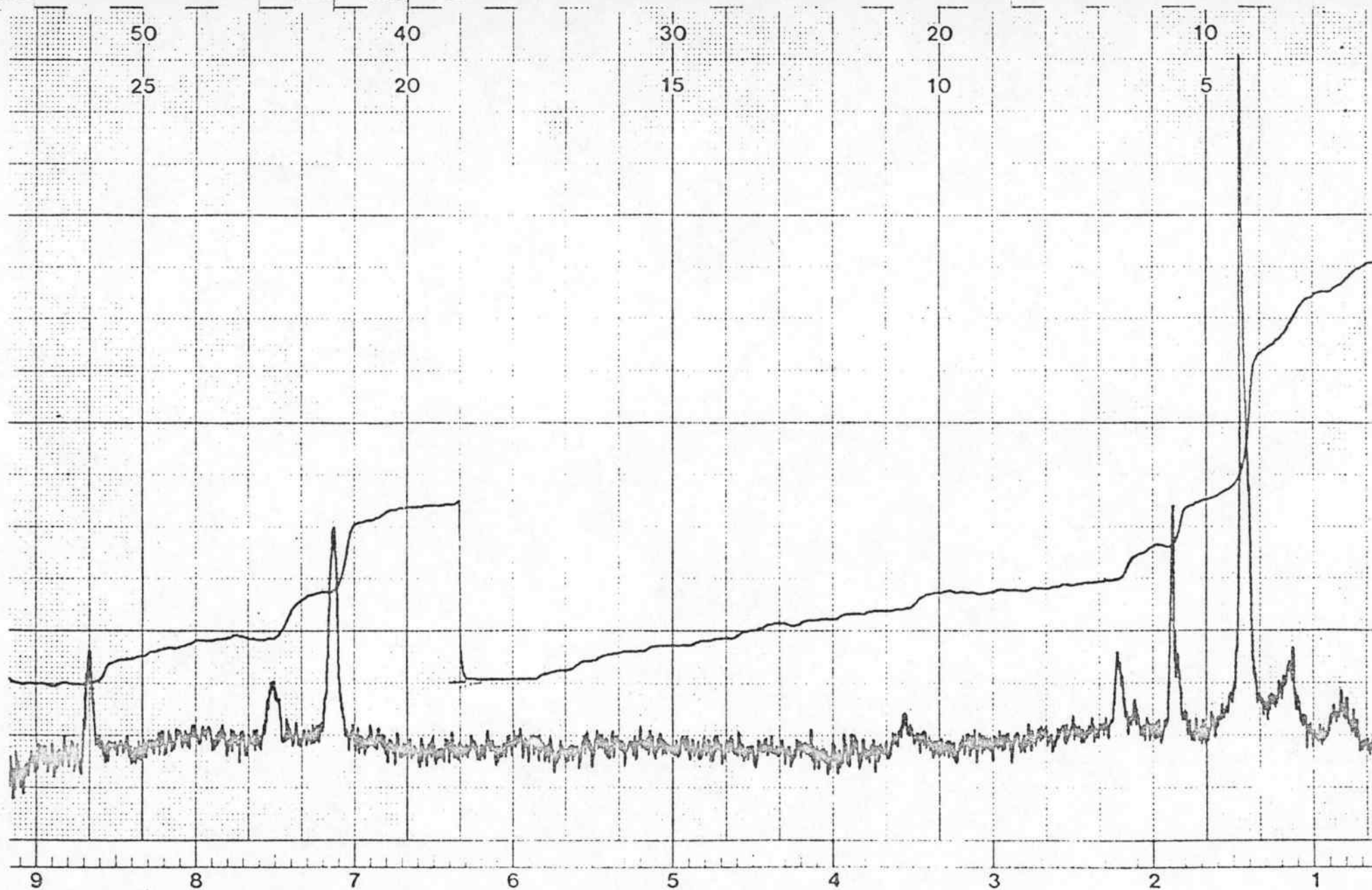


Figure 2 : Nmr spectrum of preasphaltene isolated from SBRG-I heavy product. This spectrum is typical for preasphaltenes isolated from cdl obtained by the SBRG process.

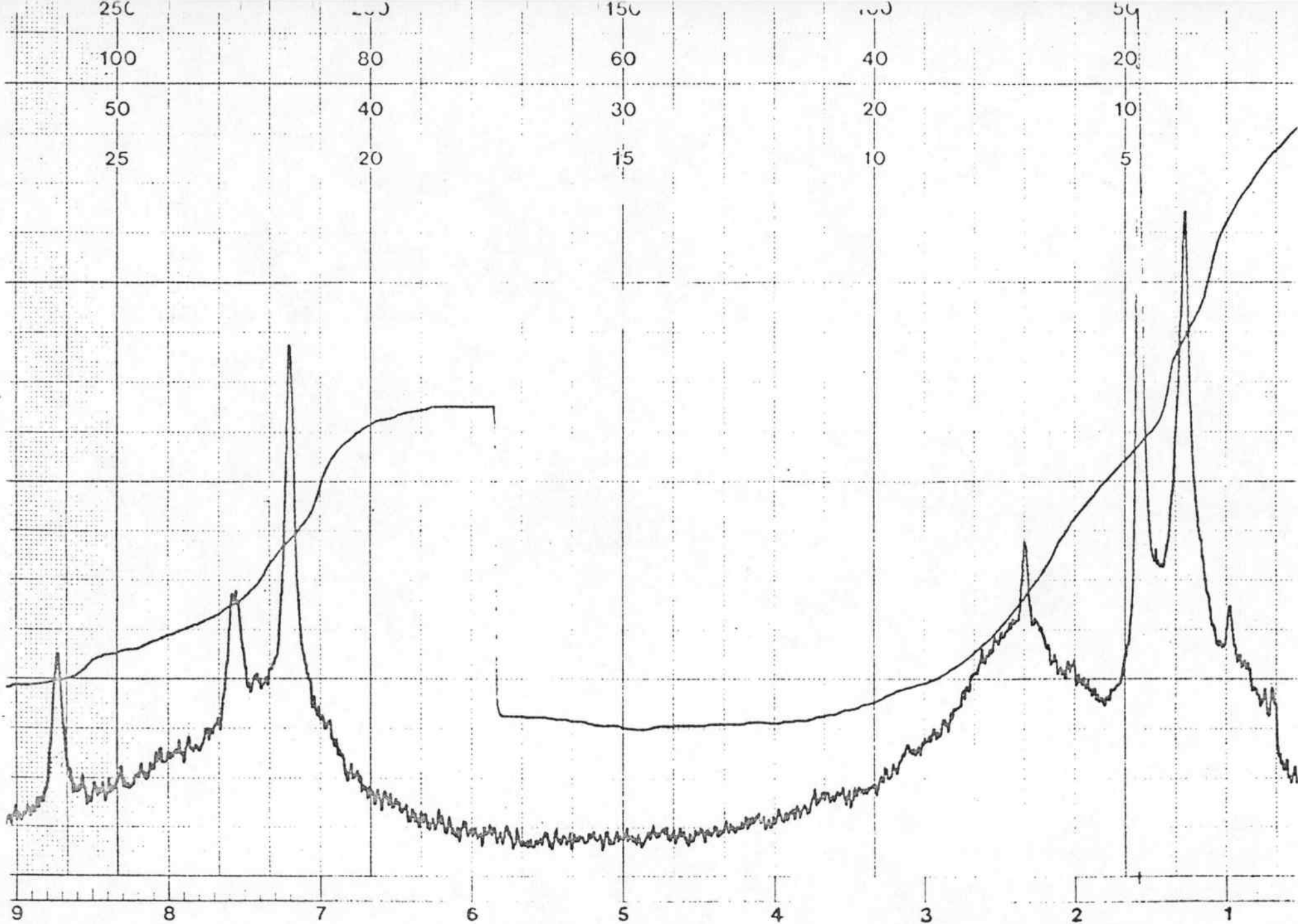
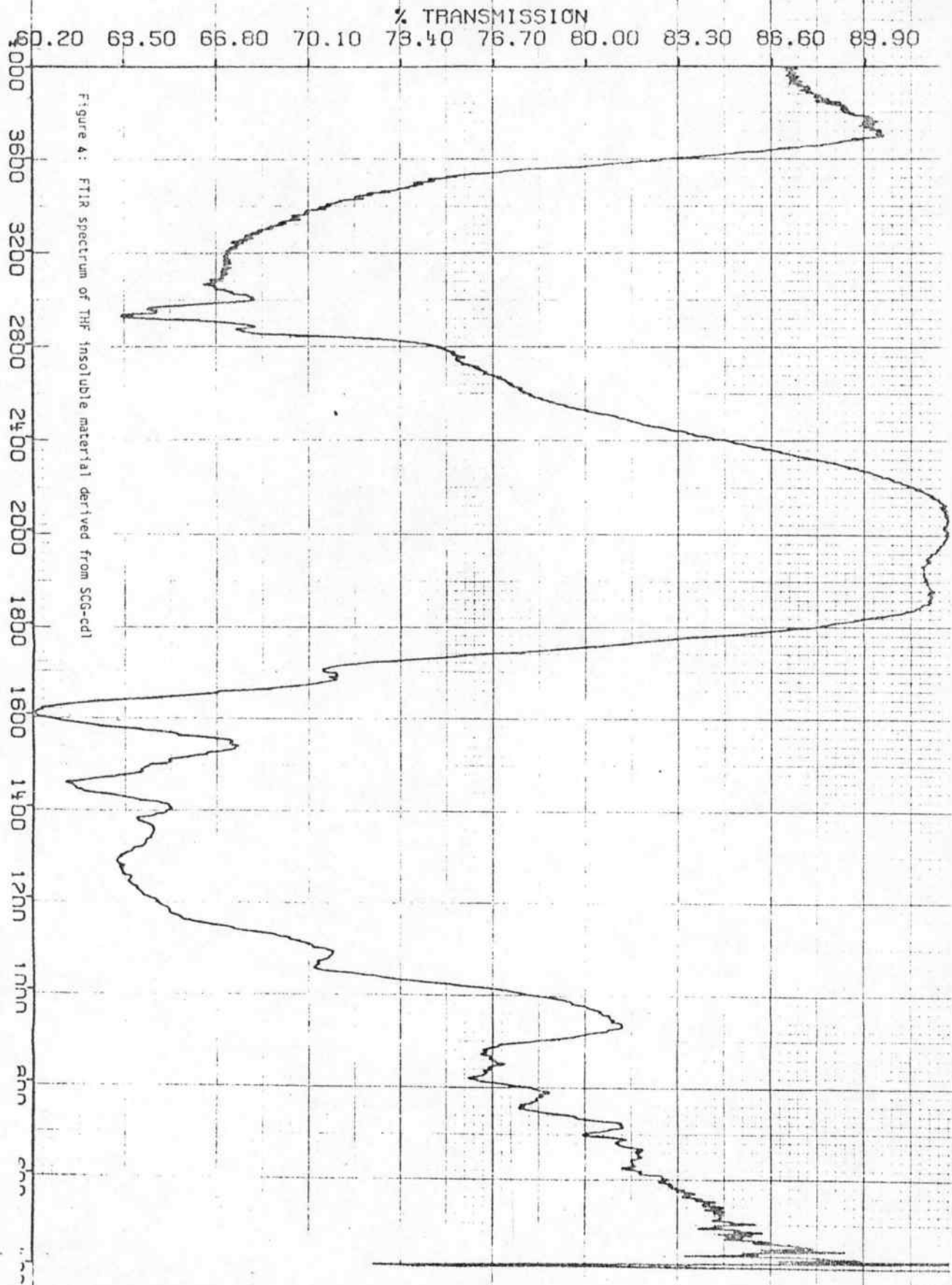


Figure 3 : Nmr spectrum of preasphaltene isolated from cdl obtained from subbituminous coal by supercritical toluene extraction.





RAYLO ■ CDL-1980-2 ■ DIFFUSE IN KBR  
 03/05/82 09:42:08

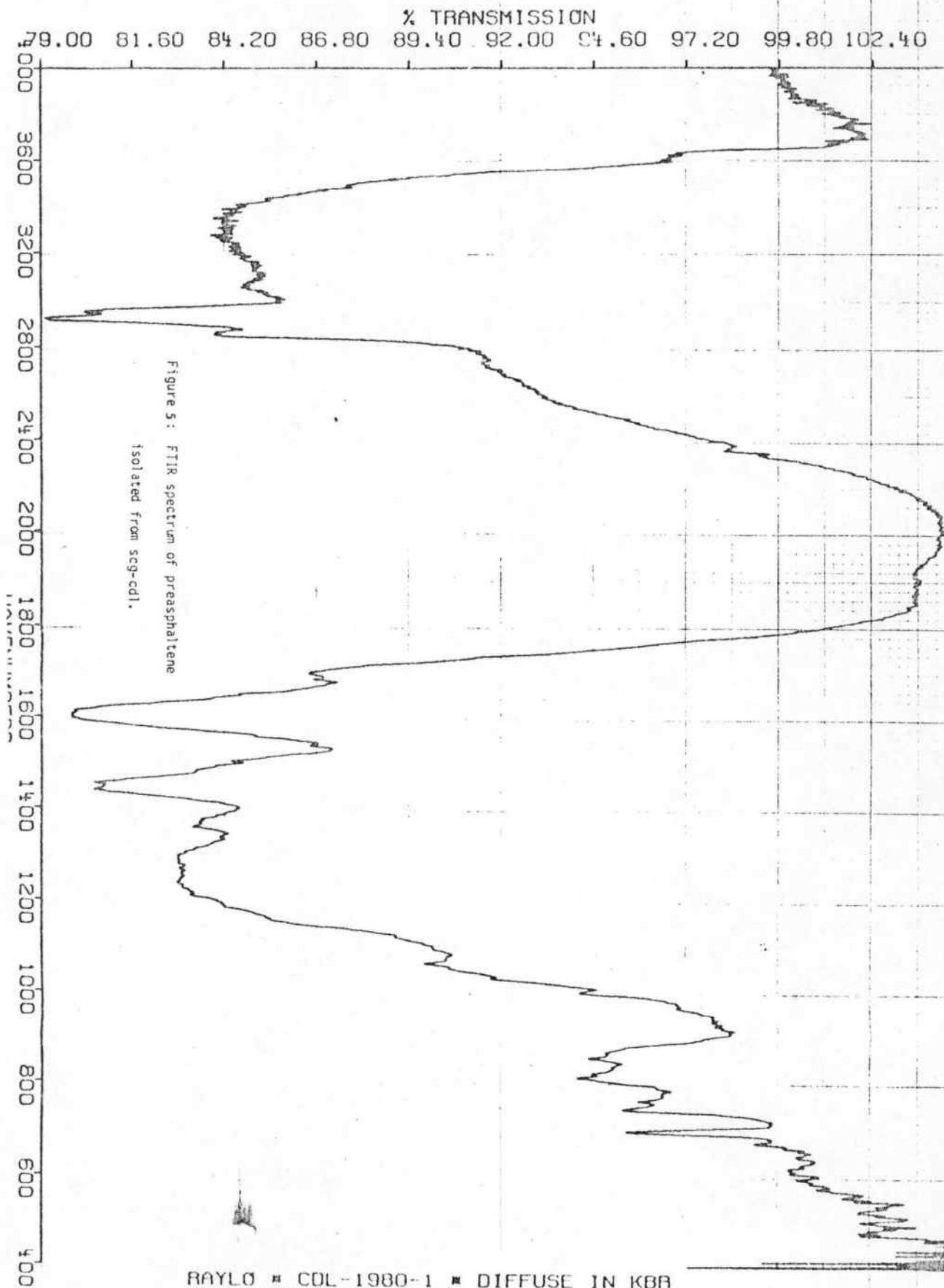


Figure 5: FTIR spectrum of preasphaltene isolated from scg-cdl.

RAYLO ■ COL-1980-1 ■ DIFFUSE IN KBR  
03/05/82 09:54:51

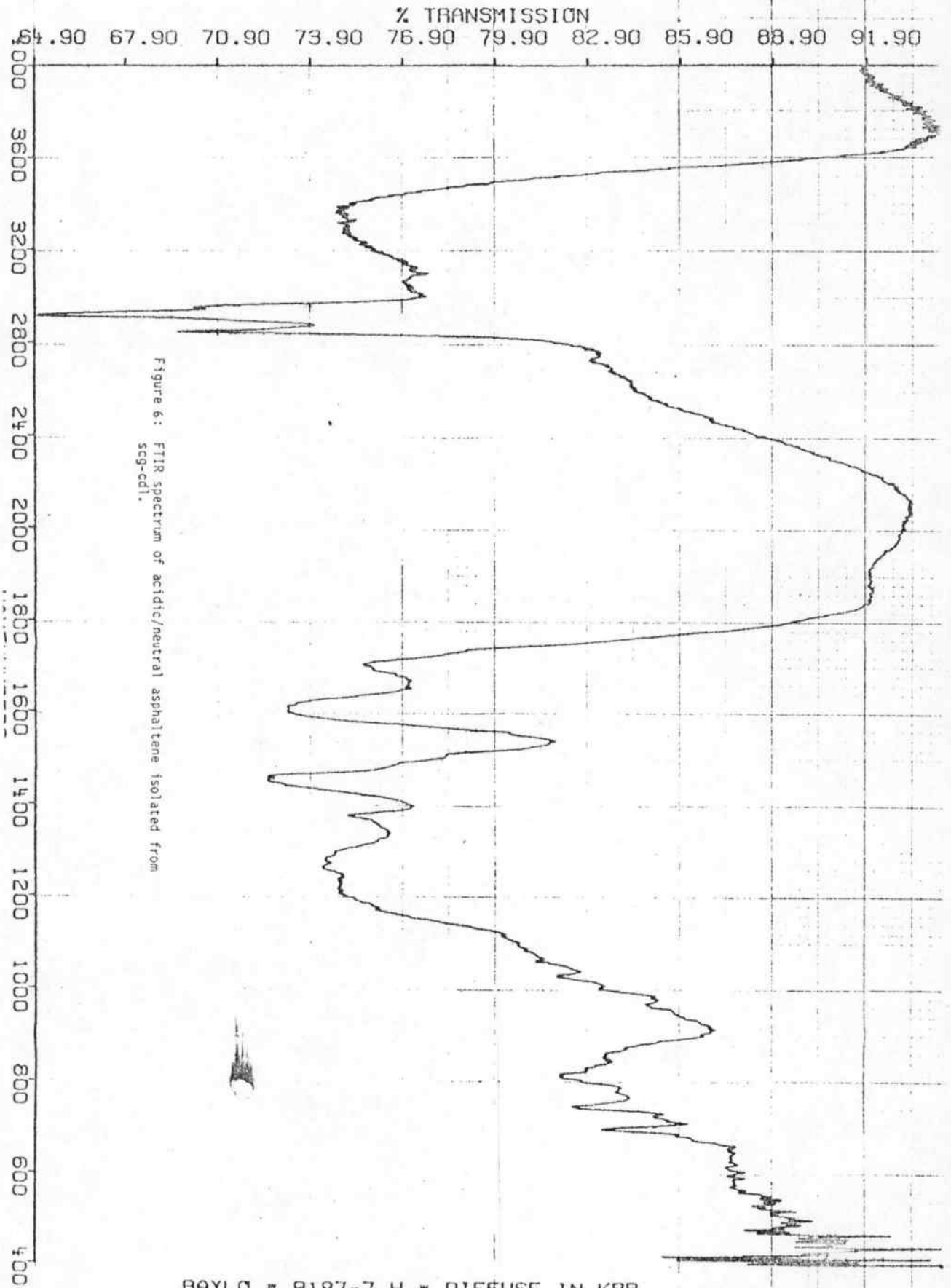


Figure 6: FTIR spectrum of acidic/neutral asphaltene isolated from scg-cdl.

RAYLO \* A187-7 H \* DIFFUSE IN KBR  
 03/05/82 09:35:13

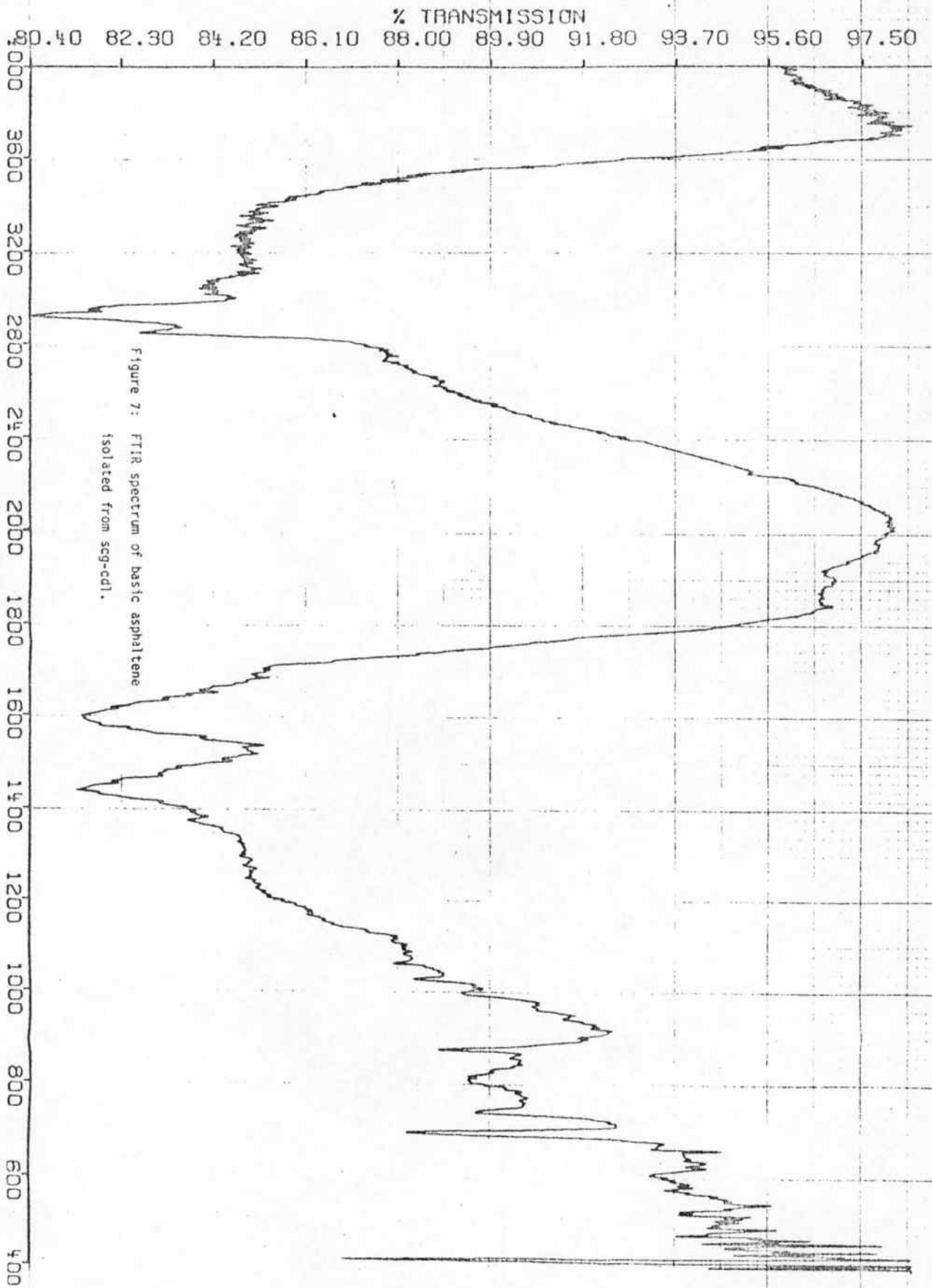


Figure 7: FTIR spectrum of basic asphaltene isolated from scg-cdl.

RAYLO \* R187-7 G \* DIFFUSE IN KBR  
03/05/82 09:30:43

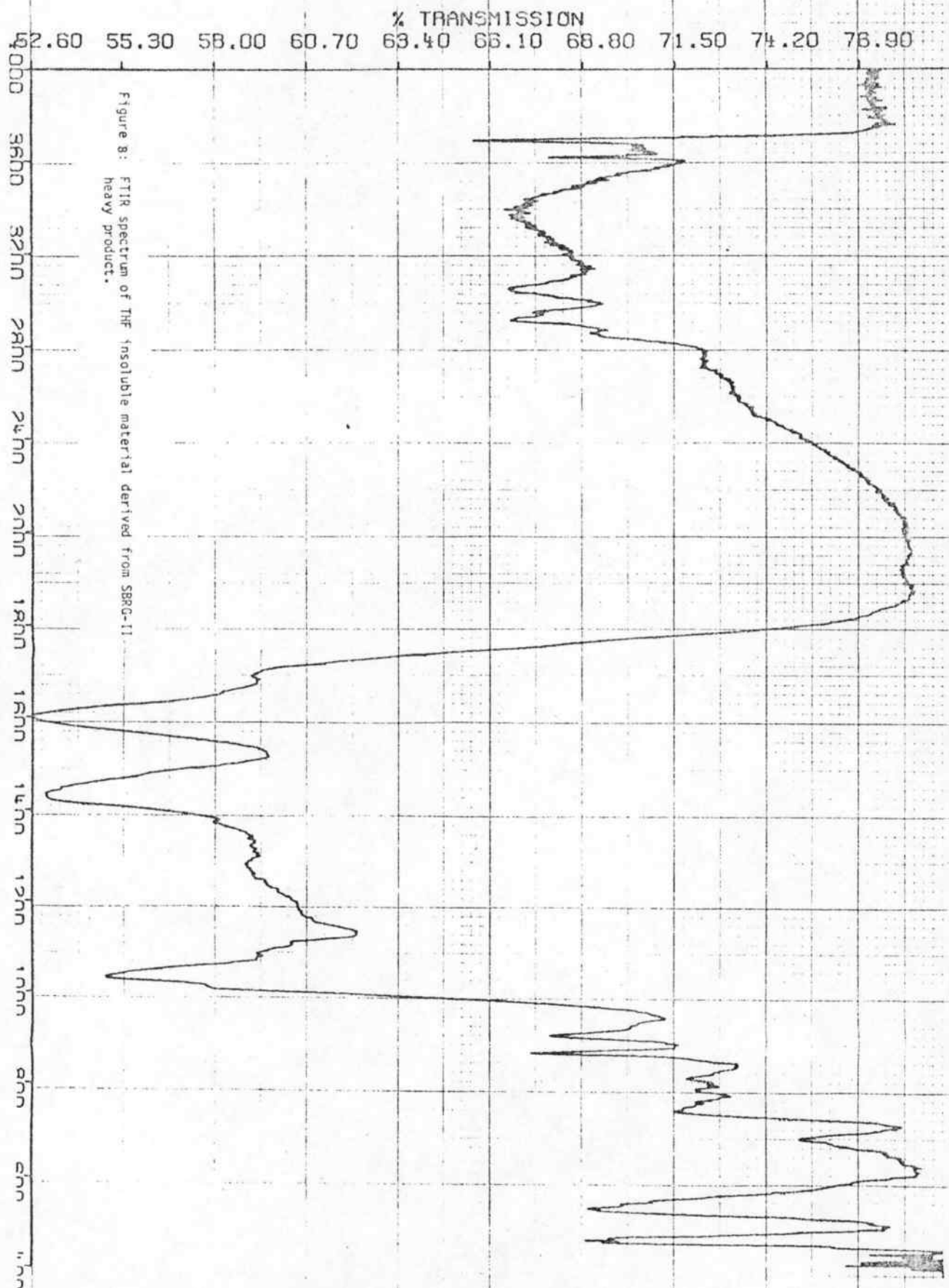


Figure 8: FTIR spectrum of THF insoluble material derived from SBRC-11 heavy product.

RAYLO \* SBRC-11-HF-2 \* DIFFUSE IN KBR  
 03/05/82 09:47:30

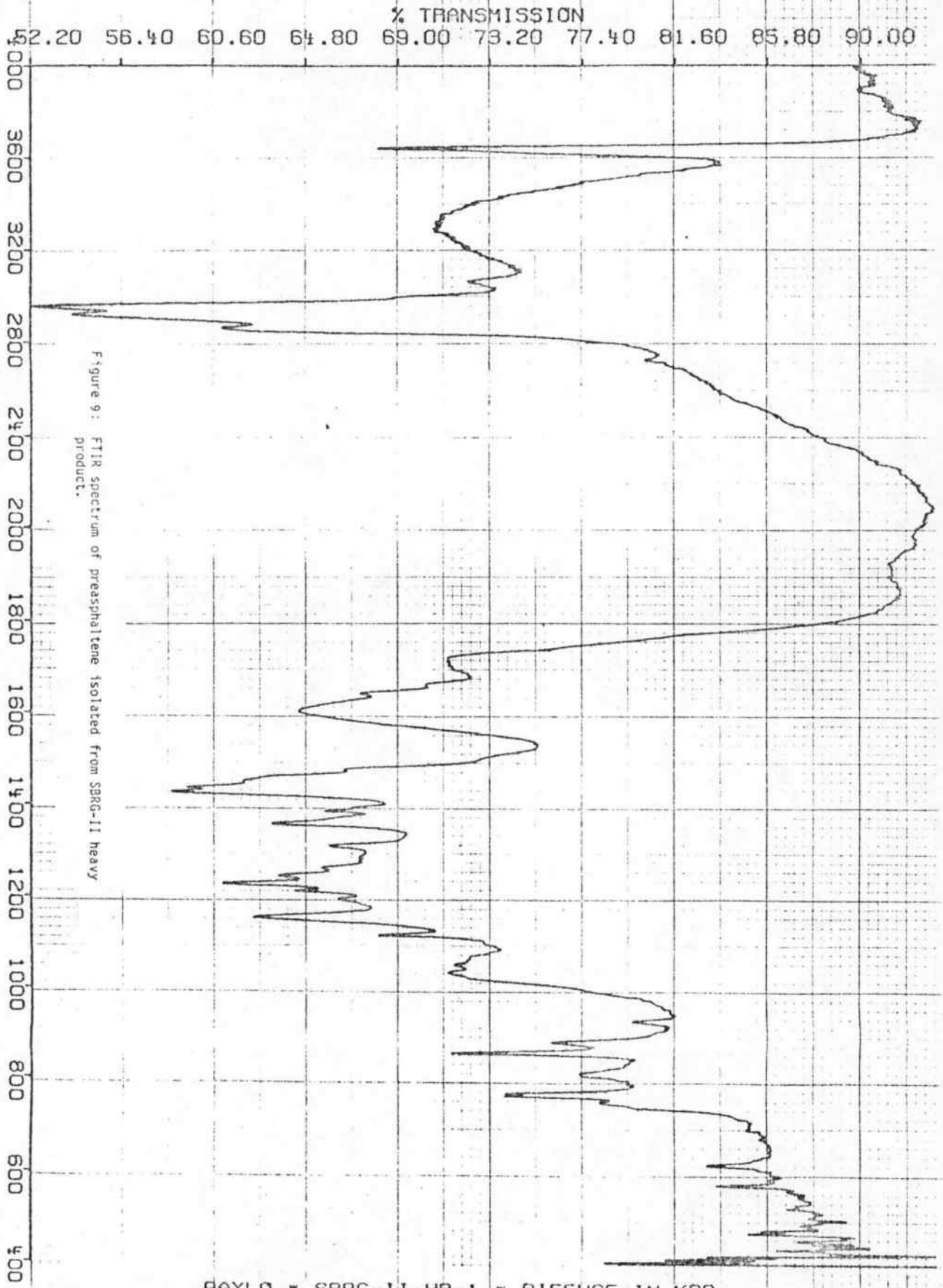


Figure 9: FTIR spectrum of preasphaltene isolated from SBRG-II heavy product.

RAYLO \* SBRG-II-HP-1 \* DIFFUSE IN KBR  
 03/05/82 09:51:10



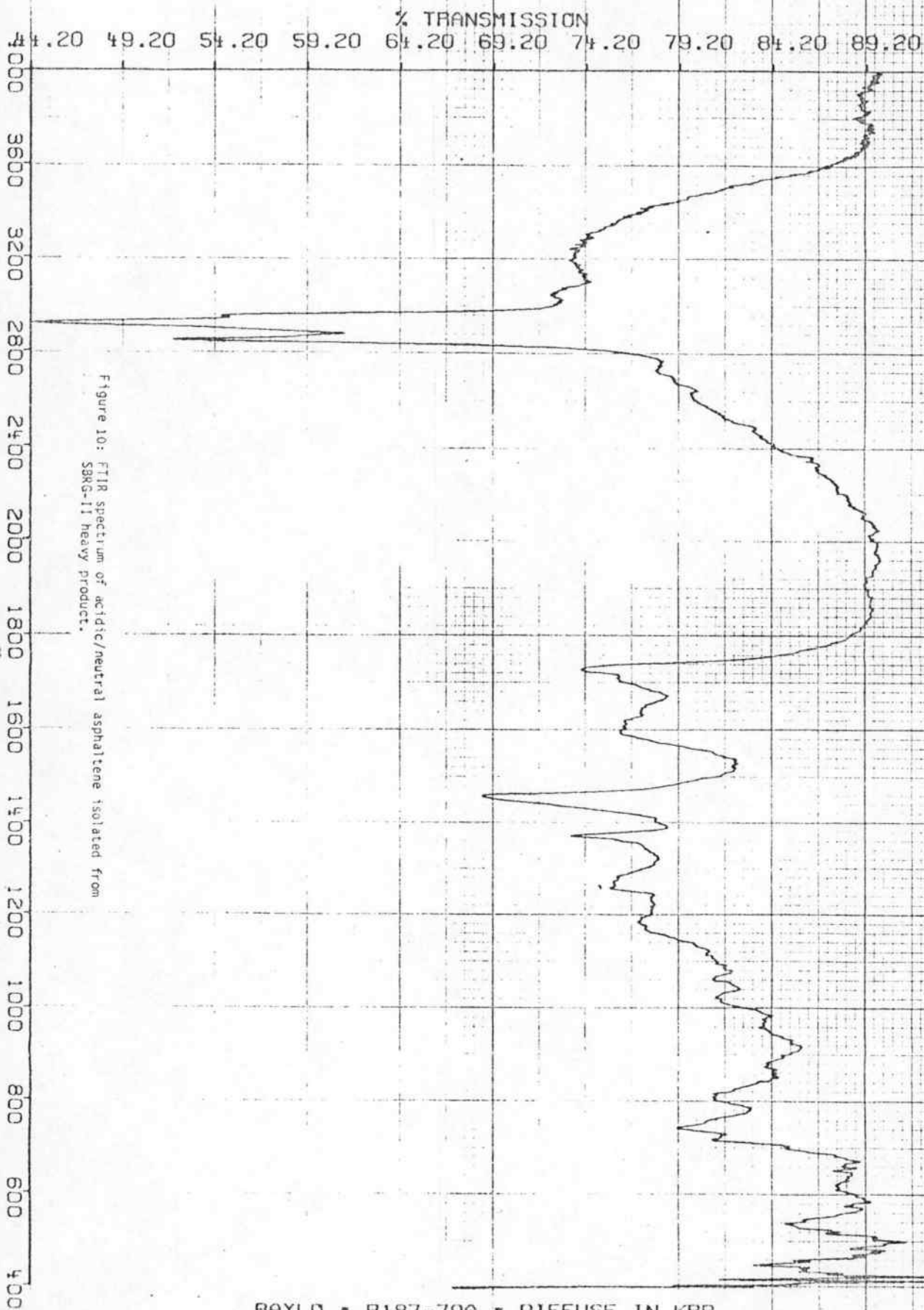


Figure 10: FTIR spectrum of acidic/neutral asphaltene isolated from SBRG-11 heavy product.

RAYLO \* R187-79A \* DIFFUSE IN KBR  
03/05/82 09:25:44

% TRANSMISSION

72.60 75.10 77.60 80.10 82.60 85.10 87.60 90.10 92.60 95.10

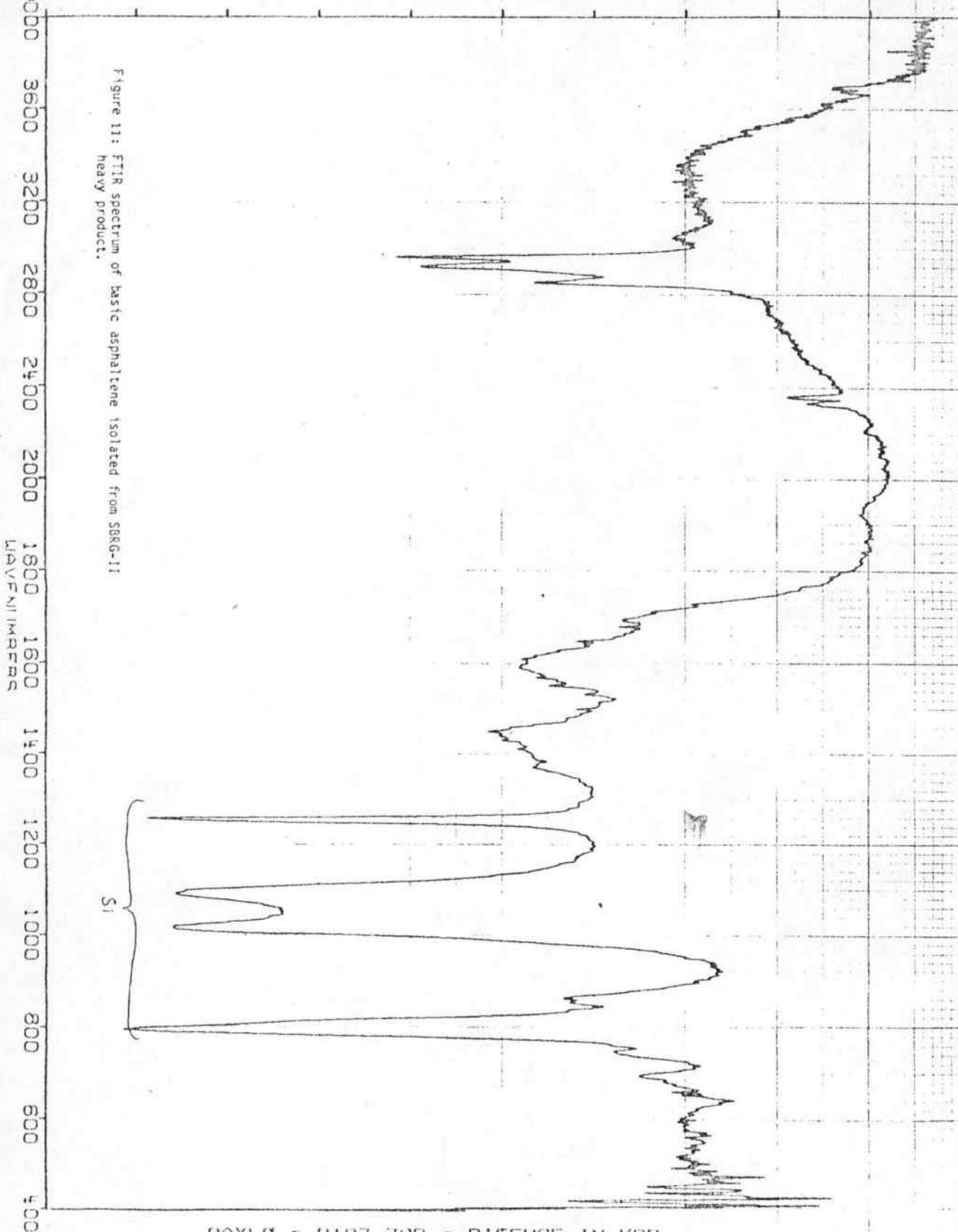


Figure 11: FTIR spectrum of basic asphaltene isolated from SRG-II heavy product.

RAYLO \* R187-79B \* DIFFUSE IN KBR  
03/05/82 09:17:19