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Canada Centre for Mineral and Energy Technology
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CHEMICAL CHARACTERIZATION OF A NUMBER OF RESIDUAL PITCHES

M.A. POIRIER AND E.S. DAS

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ENRGY RESEARCH PROGRAM
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REPORT ERP/ERL 83-25 (TR)

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CHEMICAL CHARACTERIZATION OF A NUMBER OF RESIDUAL PITCHES

(Distillation Residue Boiling Above 524°C)

SUMMARY

This work conducted jointly by the United Technology and Science Inc. (UTS) [a member of the Proctor and Redfern Group] and the Ontario Research Foundation (ORF) describes the separation and chemical characterization of twelve residual pitch samples (distillation residue boiling above 524°C) provided by the Energy Research Laboratory (ERL) of the Canadian Institute of Minerals and Energy Technology (CANMET).

Two schemes were used for the separation of pitches - one scheme based on physical method of separation into maltene and asphaltene fractions by means of precipitation with n-pentane and n-heptane, and the second scheme based on chemical method of separation of pentane maltenes into acids, bases and neutral hydrocarbons type fractions by ion-exchange and liquid solid chromatography (LSC). Methods for characterization included gel permeation chromatography (GPC), infra-red (IR) spectroscopy and elemental, porphyrin and metal analysis.

Methods were developed for the determination of average molecular weights [weight average molecular weight (Mw) and number average molecular weight (Mn)], polydispersity (Mw/Mn) and molecular weight distribution (MWD) in pitch samples by GPC using Ultra-Styragel columns, UV detection and computer MWD program for automation. Mono-disperse polystyrene standards of known molecular weight were used for calibration and therefore the average molecular weights determined by GPC represented relative molecular sizes of the pitches.

Prior to deasphaltening, the samples were separated into benzene solubles and insolubles. Of the twelve pitches, sample #2 contained the highest (28%) and samples #5 and 8 yielded only traces of benzene insolubles. The amount of insolubles in the remaining nine samples ranged between 4-9%.

Deasphaltening studies with both pentane and heptane indicated that the asphaltene content in the pitch samples increased in the following order: #11, 8, 5, 1, 6, 3, 10, 12, 2, 4, 7 and 9. As expected, pentane precipitated more asphaltene than heptane in all pitch samples. Sample #2 with the higher heptane asphaltene was the only exception to this.

GPC studies have shown that the average molecular weights and polydispersity in the pitch samples and in their maltenes and asphaltenes fractions decreased in the following order: #5, 1, 8, 11, 3, 7, 4, 6, 2, 12, 10 and 9. Interestingly, the first four whole pitch samples with low asphaltene content displayed high Mw values of about 3200, 2700, 1400 and 1100 respectively. Mw of the second seven samples in the above series ranged between ∿ 700-300, and the high asphaltene pitch sample #9 exhibited the lowest Mw (∿ 260) and polydispersity. Mn values obtained with all pitch samples were in the medium to low hundreds. As expected, both pentane- and heptane-asphaltenes displayed higher weight average molecular weights and polydispersity than the whole pitches. Conversely, Mw values were lower in both maltenes types than in the whole pitches. These differences in Mw values were more pronounced in samples #5, 1, 8 and 11 than others. No appreciable differences were observed in average molecular weights and MWD between the two asphaltene fractions in any one of the pitch samples.

All pitch samples were characterized by a decrease in H/C ratio and an increase in hetero atom (N, S) content in both of their pentane- and heptane-asphaltenes. In addition, nine samples were also characterized by very high oxygen content in both asphaltene fractions. Asphaltenes of three samples (7, 9 and 11) contained no oxygen. No marked difference in H/C ratio and hetero atom (N,S,O) distribution was noticed between the two asphaltene fractions in each sample. Four samples (#1, 5, 8 and 11) were characterized by their high H/C ratios and absence of any nitrogen in the whole pitch, benzene solubles and in their two maltenes fractions. As expected, nitrogen was concentrated more in the asphaltene than in the maltene. Nitrogen contents in pentane asphaltenes were slightly higher than in heptane asphaltenes in the majority of the pitch samples. All pitch samples contained high sulfur. The highest sulfur values were observed with samples #1, 3 and 5 and in all their fractions. Sulfur content was relatively low only in two samples, #11 and 12.

The acid, base and neutral hydrocarbon fractions isolated by the ion-exchange chromatography of the pentane maltenes of the twelve pitch samples were analyzed for molecular weights and MWD by GPC. The results indicated that the average molecular weights of the ion-exchange eluates decreased in the order similar to that recorded for the whole pitches and their maltene fractions: #5, 1, 8, 11, 3, 7, 4, 6, 2, 12, 10 and 9. Pentane eluates of all samples displayed lower molecular weight values and the cyclohexane eluates of four samples #5, 1, 8 and 11 had slightly higher values than the corresponding maltenes. The three acid- and three base subfractions exhibited molecular weight values higher than the maltenes in all samples. This was more pronounced in samples #5, 1, 8 and 11 than others. Between the three acid subfractions, the highest Mw, Mn and Mw/Mn values were observed with A-3 fractions. Three base subfractions showed no appreciable differences. All ion-exchange eluate fractions were also characterized by elemental analysis.

The compound type fractions (saturates, monoaromatics, diaromatics, polyaromatics and polar polyaromatics) isolated by LSC of the ion-exchanged maltenes were characterized by % wt. distribution and elemental analysis.

The ion-exchange eluate fractions of pitch samples were analyzed for major functionalities by IR Spectroscopy. A number of model compounds was studied to obtain molar extinction coefficients of functional groups that would be similar to those of the acidic and basic compound types expected in the eluate fractions. The only major functional groups identified in the eluate fractions were carboxylic acid and pyrrolic type of compounds. Carboxylic acids were identified and quantitated in all A-3 acid subfractions of the twelve pitch samples except sample #2. A-3 fraction of sample #5 showed the highest carboxylic concentration expressed as millimoles benzoic acid/g residual pitch. Pyrrolic compounds were concentrated in the A-2 subfractions of all samples except samples #1, 5, 8 and 11. These four samples had pyrrolic compounds concentrated in either pentane eluates or A-1 acid subfractions. These samples also contain the least amounts of pyrrolic compounds when expressed as millimoles carbazole/g residual pitch. Of the three base subfractions, no pyrrolic compounds were identified in C-3 base subfractions and only traces were identified in the other two subfractions.

Other parameters studied in the characterization of residual pitch samples and their pentane- and heptane-asphaltenes included distribution of trace metals (V, Ni, Fe) and porphyrin. Pitch asphaltene samples showed wide variation in iron contents. The highest concentration was observed with sample #1 (∿ 1300-1500 ppm). Only two samples #9 and 10 which contained no porphyrin showed very low concentrations of iron (∿ 3 ppm). The asphaltenes of most of the pitch samples were characterized by substantial amounts of V and Ni. Sample #3 with the highest porphyrin content gave the highest concentration of V and Ni (∿ 1500-1600 ppm V and ∿ 450 ppm Ni). Three other samples, #1, 5 and 8, with high porphyrin content also exhibited high V and Ni concentration. A comparatively low value of V and Ni were observed with porphyrin free pitch samples #9 and 10. The above indicated that a decrease in metals content, vanadium in particular was accompanied by a decrease in porphyrin content with most of the pitch samples. Similar distribution of metals was observed in both pentane- and heptane-asphaltene fractions of each of the twelve pitch samples.

In conclusion, methods have been developed for the separation and characterization of residual pitches. The various characterization data generated in the study provided information for studying compositional differences between pitch samples.

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CHEMICAL CHARACTERIZATION OF A NUMBER OF RESIDUAL PITCHES
(Distillation Residue Boiling Above 524°C)

1. INTRODUCTION

This report on the above characterization study is submitted to DSS Consignee, the Department of Energy, Mines and Resources, CANMET, Energy Research Laboratories, Ottawa, Ontario. The work was carried out jointly by the United Technology & Science, Inc. (UTS) of Proctor and Redfern Group and the Ontario Research Foundation (ORF), with ORF acting as subcontractors for UTS.

Sample preparation (initial fractionation and deasphaltening) and ion-exchange chromatographic part of the work was carried out at UTS, and studies on the other aspects of the project were performed by ORF.

1.1 Objective

The objective of the work is the separation and characterization of twelve residual pitch samples provided by the Energy, Mines and Resources (CANMET). The chemical properties of the pitch dictate the behaviour of this fraction during upgrading in terms of yields and quality of products as well as operational problems, e.g. coke formation, catalyst poisoning. Therefore, knowledge of the types and distribution of major structural and functional groups in the residual pitches is needed for effective utilization of the pitches by upgrading to lower boiling distillates. In addition, such knowledge is also necessary for other economic uses for these residual pitches, e.g. heat and power generation, building and road construction, additives in the production of coke briquettes. The objective as specified in the RFP is as follows:

> "Hydrocracking processes are conducted with the purpose of optimizing pitch conversion (conversion of the residual fraction +524°C to lower boiling distillates). The chemical properties of the pitch dictate the behaviour of this fraction during upgrading in terms of production of distillates as well as their coking propensity. The objective of this study is to determine the chemical differences between the pitch from various sources and to correlate these differences to the product properties, response to upgrading parameters, and behaviour of these pitches in other utilizations."

1.2 Statement of Work

The work statement on the chemical characterization of the twelve CANMET residual pitch samples was specified in the RFP. This was further modified by the Scientific Authority. The modified work program is as follows:

1) Fractionation of the pitch into benzene-solubles and insolubles; and separate deasphaltening of the benzene solubles with n-pentane and n-heptane.

2) Quantitative separation of the "acids" and "bases" from the pentane maltenes on anion and cation exchange resins.

3) Quantitative separation of the pentane maltenes that have been pretreated with ion-exchange resins into compound type concentrates of saturates, aromatics and polar material on silica-alumina liquid chromatographic columns.

4) Determination of porphyrin in the benzene solubles and metals (V, Ni, Fe and Sb) in the pentane- and heptane-asphaltenes; and elemental analysis (C,H,N,S,O) of pitches and their fractions.

5) Molecular size characterization by gel permeation chromatography of pitches and their maltenes and asphaltenes fractions, and their pentane maltene ion-exchange eluate fractions.

6) Characterization of the most acidic and most basic fractions for each pitch sample by infra-red spectroscopy.

2. METHODOLOGY

The overall objective of this study was to provide a comparative study of chemical characteristics of twelve pitch samples. Pitch was defined as distillation residue above 524°C. The pitch samples supplied by EMR/CANMET were identified by numbers (Sample #1 - Sample #12). Methods used for the present characterization study were partly based on the recommended procedures developed at CANMET, namely, ion-exchange chromatography (IEC), liquid-solid chromatography (LSC), porphyrin analysis and infra-red spectroscopy. A fractionation and analytical scheme for the characterization of residual pitches is shown in Figure 1.

2.1 Isolation of Benzene Solubles and Deasphaltening with n-Pentane and n-Heptane

Each pitch sample was fractionated in benzene soluble and benzene insoluble fractions by extraction with benzene. About 80 g of the pitch sample was dissolved in 350 mL benzene (Baker-Analytical grade) with stirring at room temperature until the sample was completely dissolved. The solution was then allowed to stand for 24 hours and filtered; the insoluble fraction was washed with 50 mL of benzene, dried under vacuum and weighed. The soluble fraction was recovered by evaporating most of the solvent in a rotary evaporator; the last traces of benzene solvent were removed in the spinning band distillation column at 50°C and 2 mm Hg. Results are shown in Table 1.

The benzene soluble fraction from each pitch sample was fractionated into maltene and asphaltene fractions by deasphaltening with n-pentane and n-heptane in separate experiments. Asphaltenes were precipitated by adding about twenty volumes of solvent (glass distilled HPLC grade, Burdick-

Jackson) to one volume of the benzene soluble with occasional shaking for 24 hours at room temperature. The asphaltenes were first separated by filtration, and then extracted with solvent in a Soxhlet extractor until the solvent was colourless. The asphaltenes from the extractor were then air-dried and the weight recorded. The Soxhlet extract and the main maltene filtrate were combined and the solvent removed under reduced pressure at 50°C followed by distillation in the spinning band distillation column at 50°C and 2 mm Hg to recover the maltene fraction. The weight of this fraction was then recorded. Table 2 summarizes the amount of pitch benzene solubles used, and the yield of maltene and aspahltene obtained in deasphaltening with n-pentane and n-heptane.

2.2 Separation of the Acids and Bases from Pentane Maltenes by Ion-Exchange Chromatography

The maltene fractions obtained with n-pentane from each pitch were separated into three acid fractions and three base fractions by chromatography on ion-exchange resins. Published procedure developed at Energy Research Laboratory, EMR/CANMET, was used for ion-exchange column chromatographic work.[1]

The anion exchange and the cation exchange resins were exhaustively cleaned prior to use. The following procedures were used:

Rohm and Hass Amberlyst A-27 reagent grade macroreticular strong base (type 1) anion exchange resins (500 g) were washed with 3 x 600 mL methanolic HCl solution (10% volume aqueous HCl in methanol) and rinsed with about 6 L of distilled water until the washings were neutral to litmus paper. The resin was then activated with 600 mL of 10% KOH solution in methanol for one hour with intermittent stirring, and the resin washed with about 6 L of distilled water until the washings were neutral. The resin was then subjected to Soxhlet extraction for 25 hours with 2.5 L each of the following solvents in the following order: methanol, benzene and pentane. The extracted resin was then dried for 24 hours at 40°C in a vacuum oven.

As cation exchange resin, Rohm and Hass Amberlyst A-15 reagent grade macroreticular strong acid resin was used. This resin was cleaned as follows: 500 g of the resin placed in an ice bath were washed with 4 x 600 mL 10% KOH solution in methanol at ambient temperature with intermittent stirring and rinsed with 4 x 500 mL methanol. The washed resin was then subjected to Soxhlet extraction (25 x 20 g) for 24 hours with 25 x 200 mL of methanol. The resin was then activated by slow addition of one litre methanolic HCl solution (10% by volume aqueous HCl in methanol) for one hour with constant stirring using a magnetic stirrer. The resin was washed with about 6 L of distilled water until the washings were neutral. The resin was then subjected to Soxhlet extraction for 24 hours with 2.5 L each of the following solvents in the following order: methanol, benzene and pentane. The extracted resin was then dried for 24 hours at 40°C in a vacuum oven.

The column chromatographic system was set up as follows: Two stainless steel columns (10 mm I.D. x 100 cm each) - one packed with about 40 g cleaned Amberlyst A-27 anion exchange resin in OH^- form and the other packed with about 50 g cleaned Amberlyst A-15 cation exchange resin in H^+ form were connected initially in series during adsorption (ion-exchange) mode and then disconnected for separate operation during the desorption (elution) mode. The bed volume in each column was about 75 mL. A pumping system (Model Milton Roy Instrument Mini-Pump) was used to deliver the solvents through the columns at 2 mL/min flow rate.

The ion-exchange chromatographic separations were carried out by dissolving the pentane maltenes (5-10 g) in a minimum amount of 20 mL pentane-cyclohexane mixture (15:5), introducing to the column system via a separatory funnel, and then eluting immediately with the solvent systems in the following order:

Ion-exchange columns in series

Pentane (360 mL)}
Cyclohexane (200 mL)} Maltenes less "acids" and "bases".

Columns disconnected

Anion exchange resin column

Benzene (150 mL) - Acid Subfraction (A-1) }
Benzene - 40% MeOH (120 mL) - Acid Subfraction (A-2) } "Acids"
Benzene - 20% HOAC (150 mL) - Acid Subfraction (A-3) }

Cation exchange resin column

Benzene (120 mL) - Base Subfraction (C-1) }
Benzene - 40% MEOH (80 mL) - Base Subfraction (C-2) }
Benzene - 37% MeOH } "Bases"
- 8% Isopropylamine (140 mL) }
- Base Subfraction (C-3) }

The pentane and cyclohexane eluates, anion eluates and the cation eluates were collected, and the solvents were removed using a rotary evaporator under reduced pressure at 35°C, and Kuderna-Danish evaporative concentrator, and the weights recorded. Each sample was run with fresh batches of activated resins and each sample was run in duplicate. However, for duplicate experiments, both anion and cation exchange resins from the first experimental run were exhaustively washed with large volumes of benzene prior to use.

2.3 Hydrocarbon Type Separation of Ion-Exchanged Maltenes by Liquid-Solid Chromatography

The pentane and cyclohexane eluates from the ion-exchange chromatography contained maltenes less "acids" and "bases." They were combined and the maltenes were separated into compound type concentrates of saturates, monoaromatics, diaromatics, polyaromatics and polar polyaromatics on a dual-packed silica gel-alumina liquid solid chromatographic system (LSC) developed by the USBM-API Project 60 and modified at the CANMET EMR Laboratory.[2] The procedures used were as follows:

A stainless steel column, 10 mm x 100 cm was packed top-half with about 25 g activated silica (Davidson Grade 12, 28-200 mesh, activated at

25°C for 24 hours) and bottom half of the column packed with about 35 g activated alumina (ALCOA F-20, 38-200 mesh, activated at 400°C for 20 hours). The unfilled space at the top was filled with glass beads, and both ends of the column were plugged with glass wool.

A solution of the ion-exchanged pentane maltene fraction of the pitch sample in pentane-cyclohexane (1:1 v/v) (∿ 1.0 g in 15 mL) was then placed at the top of the column and the solvents listed in Table 28 were used for the consecutive elution of the hydrocarbon types. A Milton Roy pumping system (LDC Mini-Pump) was used to deliver solvents through the column.

The fractions of the column effluents were collected in test tubes and solvents evaporated using rotary evaporator under reduced pressure at 35°C, and Kuderna-Danish evaporative concentrator. After most of the solvents were evaporated, the fractions were transferred quantitatively to pre-weighed vials using appropriate solvents. The solvents were removed, and the vials were reweighed to determine the weight of the fraction.

2.4 Porphyrin Determination in Benzene Soluble Fraction

The benzene soluble fractions of the twelve pitch samples were analyzed for porphyrins following a published procedure[3] with slight modification. The isolation and analytical scheme is shown in Figure 2. Porphyrin isolated in a large scale experiment from ∿ 80 g benzene soluble of pitch sample #8 was used as reference standard and absorbance values in the UV/VIS wavelength at between 400-410 nm was used to measure the porphyrin content.

2.5 Metal Analysis in Asphaltene Fractions

Both pentane- and heptane-asphaltenes fractions of the pitch samples were analyzed for V, Ni and Fe. The procedure used is as follows: The samples were digested with aqua regia and sulfuric acid, and then diluted to known volume for analysis by DC Plasma Emission Spectrophotometry (Model 3A

Spectrametrics/Beckman). Atomic absorption spectrophotometry was used to verify the Fe and Ni results.

2.6 Elemental Analysis

The twelve pitch samples and their fractions (benzene solubles, maltenes, asphaltenes, ion-exchange eluates, hydrocarbon compound type fractions) were analyzed for C,H,N and S. C,H,N were analyzed using Perkin Elmer Model 240 and Hewlett-Packard Model 165B instruments. Sulfur was determined by oxygen flask method. Oxygen was determined by difference. Elemental analysis was performed by The Guelph Chemical Laboratory, Guelph, Ontario.

2.7 Molecular Weight Distribution by Gel Permeation Chromatography

Gel permeation chromatography (GPC) was used to determine the average molecular weights (Mw and Mn) and the molecular size or the molecular weight distribution (MWD) of the pitches and their fractions. MWD measurements were made using two GPC systems - one system using 500Å and 100Å Ultrastyragel columns (Waters Associates) in series [System #1] and the other system with 1000Å and 100Å Ultrastyragel columns (Waters Associates) in series [System #2]. Tetrahydrofuran (THF) [Burdick & Jackson HPLC grade without any inhibitor] was used at 1 mL/min flow rate as the mobile phase. The concentrations of the samples in THF were limited to 0.1-0.25% in order to avoid "concentration effects" on the peak positions in the chromatograms. The solutions were prefiltered through 0.5 μm Fluoropore filter (Millipore Corporation) prior to injection. The GPC conditions for both systems #1 and #2 are shown in Table 3.

2.8 Infra-red Spectroscopy

The absorbance of eighteen (18) model compounds and the ion-exchange eluate fractions in the regions of 3800-3200 cm^{-1} and 1900-1450 cm^{-1} were obtained in methylene chloride or in unstabilized THF solution with the use of Perkin-Elmer 267 Infra-red Spectrophotometer. Two different sets of scanning conditions were used: M-1-7 and 5X-1-7. The first set of conditions gives moderate scan and chart speeds, fast pen response and wide slits to permit good records in areas of stronger solvent absorbance. The second set of conditions gives a slow scan speed and a faster chart speed which expands the wave number scale five times so that band absorbance is not changed, but band wave number may be measured more accurately. A 0.5 mm thickness cell was used.

The wave number scale was calibrated with polystyrene, and band positions were measured on M-1-7 records. For quantitation of pyrrolic, carboxylic acid and aromatic functions, band absorbance was measured on 5X-1-7 records using the Baseline Method (ASTM E.168). This method was modified for shoulder bands whose baselines extended from adjacent absorbance minima instead of from fixed wave numbers. In the case of carboxylic acids, both the monomer and the dimer bands were measured from a single baseline. For pyrrolic functions the absorbance of carbazole was used as a reference. The absorbance of benzoic acid as a reference was used for quantitation of carboxylic acids in the ion-exchange eluate fractions.

3. RESULTS & DISCUSSION

Pitch residuals are mainly composed of maltenes and asphaltenes. Molecules comprising both the asphaltene and maltene fractions in the pitch are broadly distributed with respect to molecular weight, aromaticity, polarity (acids, bases), heteroatom content (O,N,S) and hydrocarbon functionality, and there is substantial overlap between asphaltenes and maltenes with respect to the above functionalities. However, such functionalities whether in asphaltene or in maltene fractions are unique properties of a residual pitch sample and are useful for characterizing and differentiating pitch samples from various sources.

This report deals with our separation and characterization work for studying compositional differences in twelve (12) CANMET residual pitch samples. Separation methods used in this study involved solvent fractionations, ion-exchange chromatography (IEC) and liquid-solid chromatography (LSC), and techniques used in characterization included GPC for determination of average molecular weights and molecular weight distribution (MWD), IR for functional group analysis, porphyrin analysis and elemental analysis for H/C ratio, heteroatoms (N, S, and O) and metals (V, Ni and Fe) distribution in pitch samples and their various fractions.

3.1 Molecular Size Characterization by Gel Permeation Chromatography

One major objective in the present study was the molecular size characterization of the pitch samples by GPC. The theory and mechanism of GPC are well known and are described in various publications.[4,5,6] It is a liquid chromatographic technique which separates molecules according to their size. In such a technique, the sample is introduced into the mobile phase and separated on a column packed with rigid porous microparticulates (e.g. polystyrene-divinylbenzene). Separation is accomplished by repeated exchange of the sample molecules between the mobile bulk solvent and the stagnant solvent within the pores of the column packing. Thus, the pore size of the column packing particles determines the range of molecular size which can be separated. Sample molecules with the largest size (highest molecular weight) elute out from the column first followed by the smaller molecules. Two important elution limits are defined for every column, and are called total exclusion and total permeation limits. Sample molecules which are too large to access any of the column packing pores elute from the column at the total exclusion limit. Sample molecules small enough to access all pore volume elute at the total permeation limit. Between these two limits is the separation-range of the column.

In the present study, initially various GPC columns, e.g. μ-Styragels and Ultra-Styragels were evaluated for proper pore size selection in order that the chromatographic separation of the pitch samples ranges within the exclusion and permeation limits of the column. Two GPC systems were finally adopted - System #1 with 500Å and 100Å Ultra-Styragel in series and System #2 with 1000Å and 100Å Ultra-Styragel column in series. The Ultra-Styragels are the newest types of GPC column packings from Waters Associates. These controlled pore size "ultra" microparticulate columns gave slightly better resolution of the pitch samples than the μ-Styragels under identical chromatographic conditions. GPC conditions for both Systems #1 and #2 are shown in Table 3.

Pitch is not a single molecular weight compound. Instead, it represents a mixture of molecular weights (molecular size) with a particular molecular weight distribution (MWD). Since the components in pitch materials consist of a distribution of molecular weights, only average molecular weights can be measured. The molecular weight averages that are normally measured are: weight average molecular weight, Mw, and number average molecular weights, Mn. Mw is normally determined from light scattering measurements and it provides information on the strength of the material. High molecular weight species particuarly influence the value of Mw. Mn is frequently determined by one of the colligative property methods such as vapour pressure osmometry, boiling point elevation and others. It provides information on the pliability of the material. The value of Mn is influenced mostly by species at the lower end of MWD.

Average molecular weights can be calculated using the following equations:

$$Mn = \Sigma\,(MiNi)/\Sigma\,(Ni) \;.......\; \text{Eq.(1)}$$

$$Mw = \Sigma\,(NiMi^2)/\Sigma\,(NiMi) \;....\; \text{Eq.(2)}$$

where

Ni = the number of moles having molecular weight Mi.

GPC is becoming an important tool to determine the Mw, Mn and MWD. GPC will produce well resolved peak whose whose total area is proportional to weight or concentration of the solute. This definition also holds true for area slices. If a given peak is sliced in equal increments then the area and the amplitude of that slice are proportional to the solute species eluting during that time that slice is taken. Any given slice or integral has a defined retention volume or retention time (with a constant flow GPC system).

Using a standard calibration curve (log molecular weight of standards against retention times or retention volumes of the standards), one can extrapolate back the molecular weight for that area slice. This gives a value of Mi for area slice i. If the area slice i is used to represent Ni, then the above equations (Eq. 1 and 2) become:

$$Mn = \Sigma\, Area_i / \Sigma\, (Area_i/Mi) \ldots\ldots\ldots \quad Eq.(3)$$

$$Mw - \Sigma\, (Area_i Mi)/\Sigma\, Area_i \ \ldots\ldots\ldots \quad Eq.(4)$$

It would be a tedious process if the average molecular weights from the GPC curves are calculated manually. In the present study, a Spectra-Physics 4100 computing integrator equipped with Autolab GPC MWD software, Spectra-Physics MWD 5.0 (written in Basic) was used for data acquisition and reduction. It provided calibration [log molecular weight of standard vs eluation time (Beckman HPLC used was constant flow pumping system)], acquisition of MWD data in area slices, processing of the acquired data to calculate Mw, Mn and Mw/Mn (polydispersity) and generated MWD normalized and cumulative curves.

In order to determine the average molecular weights and MWD from a GPC chromatogram, it is necessary to derive a calibration curve that represents the relationship between retention or elution time and molecular weight. In the present work, the calibration of the instrument was performed with narrow distribution samples of polystyrene (Mw/Mn = ∿ 1) of known molecular weights. For the molecular size characterization of pitch samples and their fractions in GPC System #1 (see conditions in Table 3), two calibration curves shown in Figures 3 (see Table 4 for retention time data) and 4 (see Table 5 for retention time data) were used. Calibration curve used in GPC System #2 (see conditions in Table 3) for characterization of pitch samples is shown in Figure 5 (see Table 6 for retention time data). One must bear in mind that the MWD data obtained by GPC do not represent actual absolute values of molecular weights of pitch samples, since the system has been calibrated using monodisperse polystyrene standards. Thus, the average molecular weights determined by GPC represents relative molecular size only. However, a comparison of differences in molecular size between pitch samples and their fractions is possible by the calibration method used in the present study.

A typical MWD-GPC profile showing area slices, MWD data, Mw, Mn and Mw/Mn values and MWD normalized and cumulative curves is presented in Figure 6. This was obtained with pitch sample #4 in GPC System #1 using calibration curve #2 shown in Figure 4. MWD-GPC profiles of the twelve pitch samples in both GPC Systems #1 and #2 are given in the Appendix (24 profiles). Profiles of thirteen (13) fractions (2 maltenes, 2 asphaltenes and 9 ion-exchange eluates) of six individual pitch samples #1-#6 in GPC System #1 are also in the Appendix (78 profiles).

Average molecular weight values (Mw, Mn) and the polydispersity index, Mw/Mn of the twelve pitch samples are listed in Table 7. Values from duplicate runs in each system shown in the table indicate good reproducibility. Mw, Mn and Mw/Mn in pitch samples were found to decrease in the following order: 5, 1, 8, 11, 3, 7, 4, 6, 2, 12, 10, 9. Sample #5 showed the highest Mw (∿ 3200) among the pitch samples followed by samples #1 (Mw ∿ 2700), #8 (Mw ∿ 1400), #11 (Mw ∿ 1100), and #3 (Mw ∿ 700). Mw of five pitch samples, namely #7, 4, 6, 2, and 12 ranged between 500-350. The lowest weight average molecular weight (Mw ∿ 300) was found in samples #10 and #9. These two samples also showed the lowest polydispersity (Mw/Mn ∿ 1.8). Number average molecular weights (Mn) in most of the pitch samples were in the low hundreds, e.g. Mn (∿ 200) in samples #3, 7, 4, 6, 2, and 12; Mn (∿ 150) in samples #10 and 9. Samples with high Mw, namely #5, 1, 8 and 11 also showed low Mn values (∿ 500-400).

MWD-normalized curves (plot of % weight fraction vs log MW) of the twelve (12) pitch samples are compared and are presented in Figure 7. It clearly shows the differences in MWD between the pitch samples.

3.2 Deasphaltening and Characterization of Pitch Maltenes and Asphaltenes

After separation of the benzene insolubles, the pitch samples were subjected to physical separation into maltenes and asphaltenes by the addition of n-pentane. Similar separation of the pitch benzene solubles were also made with n-heptane. The % distribution of benzene insolubles, pentane- and heptane-maltenes and asphaltenes in the twelve pitch samples is presented in Table 8.

Of the twelve samples, nine samples gave varying amounts ranging between 4-9% of benzene insolubles. Sample #2 contained the highest amount (∿ 28%). Only traces of insolubles were found in samples #5 and #8.

As shown in Table 8, the highest yield of pentane asphaltene (conversely the lowest yield of maltene) was observed with sample #9 which was about 67%. Seven samples (#7, 4, 2, 12, 10, 3 and 6) yielded pentane asphaltene in the 35-48% range, whereas the yield of the insoluble precipitate from samples #1 and 5 was almost identical (∿ 28%). Samples #8 and 11 gave the lowest yield (∿ 11-14%). Trends similar to the above were also observed with the yield of heptane asphaltenes for all samples except sample #2. It is interesting to note that the samples with an increase in asphaltene content show a decrease in average molecular weights and less wider MWD (i.e. decrease in polydispersity, Mw/Mn). For example, sample #9 with the highest asphaltene (∿ 67%) displayed lowest average molecular weights (Mw = 261, Mn = 148, Mw/Mn = 1.76). On the contrary, samples #1, 5, 8 and 11 with low asphaltene content gave high values of molecular weights, e.g. sample #1 (asphaltene content ∿ 28%) gave Mw = 2563, Mn = 470 and Mw/Mn - 5.21.

The yield of insoluble asphaltenes is known to decrease with the increasing carbon number of the precipitating agent.[7] For example, it is known that n-pentane precipitates more asphaltenes than n-heptane. In our deasphaltening studies, eleven pitch samples gave yields of asphaltenes higher in pentane than in heptane. The only exception was pitch sample #2 which showed heptane asphaltene yield higher than pentane asphaltene (cf. 47.00 and 37.70%). The % decrease observed in the heptane asphaltene yield of the pitch samples is as follows: #11 (34.64), 8 (23.66), 7 (19.55), 5 (19.26), 10 (16.18), 9 (12.99), 1 (11.87), 12 (5.68), 3 (4.24), 4 (3.31), 6 (2.84) [#2 - % increase of 24.69%].

It is generally believed that the amounts of asphaltene precipitated depend not only on the n-alkanes solvents, but also on the initial composition of the residual pitch materials, e.g. ratio of polar to non-polar compounds and ratio of low molecular weight to high molecular weight compounds in the pitches.[8] With higher alkanes, e.g. n-heptane, one would expect to have both less polar materials of higher molecular weight and more polar materials of lower molecular weight precipitated as asphaltenes. With lower alkanes such as pentane, in addition to the above, both less polar and lower molecular weight materials are included in the precipitate and the total amount of pentane asphaltene precipitate increases more than the heptane asphaltenes.

That precipitated pentane- and heptane-asphaltenes contain high molecular weight pitch components is reflected on their average molecular weights data shown in Tables 9-20. These tables also contain data for the corresponding pentane- and heptane-maltenes. The MWD-normalized curves generated by GPC of pentane- and heptane-maltene and asphaltene fractions of twelve residual pitch samples are illustrated in Figures 8-19. The results in Tables 9-20 clearly show the high average molecular weight values obtained with both types of asphaltenes in all pitch samples. The MWD curves in Figures 8-19 which show a wider molecular weight distribution of the asphaltenes also illustrate this. As expected, in all cases, the pentane- and heptane-soluble maltenes showed average molecular weights lower than the parent pitch materials. This is due to the removal of high molecular weight compounds from pitches in the precipitated asphaltenes. Similar to the pattern observed with the whole pitch samples, the Mw, Mn and the polydispersity of maltenes and asphaltenes fractions of all pitch samples were found to decrease in the following order: 5, 1, 8, 11, 3, 7, 4, 6, 2, 12, 10 and 9.

Some differences were expected in the average molecular weights between the pentane- and heptane-asphaltenes fractions and between the corresponding maltene fractions of individual pitch samples, particularly for samples (e.g. 11, 8, 7, 5, 10, 9 and 1) which showed substantial % decrease of asphaltenes in n-heptane. The two asphaltene fractions in any of the pitch samples failed to show any appreciable difference between them in molecular weights and MWD. However, the heptane maltenes of the above mentioned samples gave average molecular weight values higher than the corresponding pentane maltenes, e.g. for sample #5: heptane maltene- Mw = 1597, Mn = 533; pentane maltene - Mw = 1199, Mn = 483. Small differences in samples #9 and 10 are not noticeable because of the very low molecular weight values in these samples. As expected with samples #12, 3, 4 and 6 which showed very little difference in % asphaltene yield between pentane and heptane, no changes in molecular weights were observed between the two maltene fractions. Sample #2 with higher heptane asphaltene than pentane asphaltene shows no difference between the asphaltenes and between the maltene fractions in molecular size.

Both pentane- and heptane-asphaltenes were also characterized by a decrease in H/C ratio and an increase in heteroatom (N, S) content. This was observed with all pitch samples. In addition, both asphaltenes of nine samples (#1, 2, 3, 4, 5, 6, 8, 10 and 12) showed a very high oxygen content. Five of the above nine samples, namely #2, 3, 4, 10 and 12 also showed a high oxygen content in the whole pitch and the corresponding benzene soluble fractions. Three samples #7, 9 and 11 contained no oxygen in the pitch and in any of their fractions. The results of the elemental analysis (C, H, N, S and O) of the twelve pitch samples, their benzene solubles, pentane-maltenes and asphaltenes and heptane-maltene and asphaltenes are shown respectively in Tables 21-26. No marked differences were observed in H/C ratio and heteroatom (N, S, O) contents between the two asphaltene fractions in each pitch sample. Four samples #1, 5, 8 and 11 were characterized by their high H/C ratio and absence of nitrogen in the pitch and in their benzene solubles, and two maltene fractions with the exception of sample #11 which showed some nitrogen in the two maltene fractions. (These samples also gave higher average molecular weights and higher maltene than other samples). Only eight pitch samples #2, 3, 4, 6, 7, 9, 10 and 12 and their benzene soluble fraction showed nitrogen content ranging between 1-3%. As expected, nitrogen was concentrated more in the asphaltene fractions than in maltene fractions. For instance, all pentane- and heptane-asphaltene fractions from all pitch samples contained nitrogen, whereas nitrogen was found only in the three pentane maltene samples (#6, 9 and 11) and seven heptane maltenes (2, 6, 7, 9, 10, 11 and 12) and the nitrogen content was low. Interestingly, nitrogen contents in pentane asphaltenes were found slightly higher than in heptane asphaltenes with majority of the pitch samples.

All pitch samples showed different distribution of sulfur. With the exception of two samples (#11 and 12), all samples showed high sulfur content between ∿ 4-8.3% in the pitch, benzene solubles, maltenes and asphaltenes fractions. The high sulfur values were observed with samples #1, 3 and 5 in all their fractions. Only two samples #11 and 12 and their fractions contained low sulfur. Both pentane- and heptane-asphaltenes showed higher sulfur than the corresponding maltenes in all pitch samples. No marked difference was observed in sulfur content between the pentane- and heptane-maltenes and between the pentane- and heptane-asphaltenes in each sample.

3.3 Fractionation of Pitch Maltenes by Ion-Exchange and Liquid Solid Chromatography and Characterization

In order to obtain information on the compositional differences in compound types between the pitch samples, initially a quantitative separation of the pitch maltenes into three acid and three base fractions was performed by anion- and cation exchange chromatography. The neutral pentane and cyclohexane combined eluates from IEC were then separated into hydrocarbon types by silica-alumina LSC. The above separation schemes are shown in the flow chart in Figure 1. Studies were made to characterize the IEC anion-, cation-, pentane- and cyclohexane eluates fractions by % yield, MWD by GPC, elemental analysis and infra-red spectroscopy. Compound types from LSC studies were characterized by determining % distribution and by elemental analysis.

Table 27 shows the weight % distribution of the pentane and cyclohexane eluates fractions, three acid subfractions (anion eluates) and three base subfractions (cation eluates) of twelve pitch maltene samples. Table 28 shows a similar weight % distribution of compound types (saturates, mono-aromatics, diaromatics, polyaromatics and polar polyaromatics) obtained by LSC of the combined pentane and cyclohexane ion-exchange eluates. An LSC chromatogram of pitch maltene sample #1 is shown in Figure 20. (This chromatogram was used as a reference for processing of other pitch samples by LSC). A per cent by weight distribution of all fractions, namely benzene insolubles, asphaltenes, ion-exchange eluates and compound types isolated from pitch samples is given in Table 29. Elemental analyses of the ion-exchange eluates and compound types are shown in Tables 30-33 and Table 34 respectively.

Distribution of nitrogen and sulfur heteroatoms in the whole pitch samples are shown in the four tables (Tables 35, 36, 37 and 38). Tables 35 and 36 respectively show the nitrogen content (Wt. %) of all pitch fractions, and the amount of nitrogen (g) that each fraction contributed to 100 g pitch sample. Similarly, sulfur content (Wt. %) of all pitch fractions and the amount of sulfur (g) that each fraction contributed to 100 g pitch sample are given in Tables 37 and 38 respectively.

As shown in Tables 27 and 29, the ion-exchange pentane eluates containing neutral and polar components represent the highest fraction of the pitch maltenes. This was observed with all pitch samples. The cyclohexane eluates represented amounts ranging between a low of 2% to a high value of 10.5%. The three acid subfractions combined amounted to 11.75, 19.02, 6.90, 15.46, 4.86, 6.35, 6.39, 3.96, 10.65, 6.96, 3.68 and 6.37% of the pitch maltene samples #1 - 12 respectively. The respective yield (Wt. %) of the three base subfractions combined are as follows: 12.96, 12.47, 16.78, 16.17, 14.09, 16.40, 14.91, 9.82, 6.97, 10.34, 9.5 and 17.23. Between the three acid subfractions, subfraction A-3 was the lowest fraction in all pitch samples. Except in subfraction A-3, all subfractions from both anion and cation eluates showed wide variation in yields and nitrogen contents between the twelve pitch samples, and no definite patterns were observed. The acid and base subfractions in each sample also showed similar wide variations.

The ion-exchange eluates gave average molecular weight data which are in accord with the values observed with the pitch samples and their maltene fractions. The data shown in Table 39 (compiled from data shown in Tables 9-20) clearly indicate this. The molecular weights of the eluates decrease in the order similar to that noted for pitch and maltene samples: 5, 1, 8, 11, 3, 7, 4, 6, 2, 12, 10 and 9. As expected, the acid and base free pentane eluates show a slightly lower value than the corresponding maltenes. Higher values in the cyclohexane eluate fractions of the four samples, #5, 1, 8 and 11, indicate the presence of high molecular weight pitch components in this eluate. No marked differences were observed in molecular weights between pentane maltenes, pentane eluates and cyclohexane eluates in the last eight samples in Table 39, namely #3, 7, 4, 6, 2, 12, 10 and 9.

An interesting observation was made with GPC-MWD studies with the three acid and three base subfractions. These subfractions gave molecular weight data which are higher than the maltene fractions. This was more prominent in samples #5, 1, 8 and 11 than others. This is in agreement with the reported Mn values (determined by VPO) in acid and base subfractions from similar ion-exchange studies with asphaltenes of heavy crudes.[9] Between the three acid fractions, the highest Mw, Mn and Mw/Mn values were observed in subfraction A-3 of pitch samples. No marked difference in MWD and polydispersity was observed in the three base subfractions within each pitch sample. However, an exception was the C-3 fraction of sample #11 which showed a very low Mw (604) [cf. Mw-C1 fraction (1120), Mw-C2 fraction (1342)]. This could not be explained.

A comparison of the molecular weight distribution of the ion-exchange eluate fractions of pitch sample #1 is shown in the MWD normalized curves in Figure 8. The MWD profiles of the ion-exchange eluate fractions of six pitch samples (#1-6) are given in the Appendix.

Table 28 shows the compound type distribution (Wt. %) in pentane deasphaltene maltenes of the twelve pitch samples after ion-exchange chromatography. The recoveries of the hydrocarbons on the average ranged between 85-95% of the acid and base free maltenes in the combined pentane and cyclohexane eluates. Per cent by weight distribution data of various fractions in the residual pitch samples (Table 29) indicate that the proportions of saturates, monoaromatics, diaromatics, and combined polyaromatics and polar polyaromatics decrease in the following order:

→ decreasing saturates : #11, 8, 12, 5, 1, 10, 4, 2, 7, 3, 6, 9
→ decreasing monoaromatics : #11, 8, 5, 1, 12, 7, 10, 4, 3, 2, 6, 9
→ decreasing diaromatics : #8, 5, 11, 1, 12, 3, 4, 10, 7, 2, 6, 9
→ decreasing polyaromatics + polar polyaromatics : #8, 1, 5, 11, 7, 10, 3, 4, 12, 6, 2, 9

The above order of compound types distribution is found to be closely related to the decrease in the maltene content in the pitch samples, e.g.

→ decreasing maltenes/increasing asphaltene : #8, 11, 1, 5, 7, 4, 12, 3, 10, 6, 2, 9

Elemental analysis of ion-exchange eluates (Tables 30-33) indicate that atomic H/C ratio in the eluate fractions decrease in the following order:

H/C Ratio	Combined Pentane & Cyclohexane Eluate	Anion Eluate			Cation Eluate		
		A-1	A-2	A-3	C-1	C-2	C-3
Decreasing ↓	#11	5	5	5	5	1	1
	2	1	1	8	1	5	11
	8	11	11	2	8	2	5
	5	8	8	11	11	8	2
	1	3	3	1	4	11	8
	4	4	4	10	12	12	6
	10	6	12	6	2	4	3
	7	2	2	4	6	3	12
	12	12	6	12	3	6	4
	6	7	7	3	10	7	7
	3	10	9	7	7	9	10
	9	9	10	9	9	10	9

A pattern is noted in the H/C values of the acid and base subfractions between the pitch samples. Nitrogen and sulfur were generally found to be evenly distributed among the acid and base ion-exchange eluate fractions, and they are not concentrated in any one subfraction. Large amounts of oxygen are found in all acid subfractions but specially in subfraction A-3 which contained carboxylic acids (see Infra-red Section). Base subfractions, C-3 of samples #1 and 2, also contained large amounts of oxygen. Other C-3 fractions (#4, 5, 6, 10, 11) showed small amounts of oxygen, whereas C-3 fractions of the other five pitch samples (#3, 7, 8, 9, 12) failed to show any oxygen. With some exception, C-1 and C-2 fractions of most of the samples showed varying amounts of oxygen. As expected, the combined pentane and cyclohexane eluate of the majority of samples showed no nitrogen nor oxygen.

Elemental analysis of the compound types from LSC studies (Table 34) showed no nitrogen in the saturate, monoaromatic, diaromatic, and polyaromatic fractions. Polar polyaromatic fractions of only four samples (#2, 3, 5 and 6) showed the presence of nitrogen. Sulfur was found more concentrated in the polyaromatic and polar polyaromatic fractions. It was found to be evenly distributed in the mono- and diaromatic fractions. No sulfur was found in saturate fractions with the exception of two samples (#1 and 6) which contained only traces of sulfur.

3.4 Major Functional Groups Analysis of Ion-Exchange Eluate Fractions by Infra-red Spectroscopy

The spectroscopic technique most widely used in analyzing major functional groups in the acid, base and neutral fractions present in high boiling residuals is infra-red spectroscopy.[10,11,12] Previous work with high boiling distillate and residue of crude oil has identified compound types such as carboxylic acids, phenols, amides, and carbazoles as the major components of the acid fractions in asphaltene. Identification of compound types such as pyridine benzologs, carbazole and amides has also been reported as the major component in the base fraction of petroleum heavy ends.

In order to gain information on the compositional differences between pitch samples, analytical studies of major functional groups in the ion-exchange eluates of deasphaltened maltenes by infra-red spectroscopy were undertaken in the present study.

Model Compounds Studies

Initially, the quantitative infra-red spectra of model compounds (see Table 40) were recorded to obtain molar extinction coefficient of functional groups that would be similar to those of the acidic and basic compound types expected in the ion-exchange eluate fractions. The spectra of the model compounds in CH_2Cl_2 and in THF are shown in Figures 21-24. Solution concentrations, functional groups bands position and intensities are given in Table 40.

Carbazole and 2-methyl indole - examples of pyrrolic compounds have characteristic N-H group absorption at about 3470 cm^{-1} but show considerable variation in band position and intensity for ring vibrations around 1600 - 1500 cm^{-1}. The 1500 cm^{-1} band is usually least sensitive to structural change. A straight line absorbance calibration (see Figure 36) for pyrrolic compounds was obtained with carbazole at about 3470 cm^{-1}. An amide model compound such as benzamide in CH_2Cl_2 shows asymmetric and symmetric NH_2 group absorption at about 3530 and 3410 cm^{-1}. This compound in both CH_2Cl_2 and THF shows a C=O group absorption about 1685 cm^{-1} and the absorptivity was strongest in the latter solvent.

Infra spectra of five model carboxylic acids in CH_2Cl_2 showed two or three absorption bands around 1700 cm^{-1} with some variations in band position. The most prominent band is assigned to dimers and the next strongest band is assigned to monomers. In THF, benzoic acid gives a single band about 1720 cm^{-1} with strong absorptivity. Figure 35 is the absorbance calibration for the benzoic acid doublet in CH_2Cl_2. The carboxylic O-H group is inter- or intramolecularly bonded and its absorption band is therefore broad with its maxima ranging from 3480-3500 cm^{-1}. This was observed with all carboxylic acid model compounds.

The seven phenolic model compounds with free (unassociated) O-H groups have a single band in positions ranging from 3400-3650 cm^{-1} depending on the rest of the structure.

Three other N-hetero aromatics type model compounds, acridine, phenanthridine, and 5,6-benzoquinoline showed several bands in the ring vibration region around 1600 and 1500 cm^{-1} with substantial variation in relative intensity. These compounds showed no common band at about 1605 cm^{-1} where most of the pitch fractions showed absorption.

Pentane and Cyclohexane Fractions

The infra-red spectra of the pentane and cyclohexane eluates of twelve pitch samples are shown in Figures 25-27. IR spectral data showing concentration, absorbance, band position and quantitation of major functional groups are given in Tables 41-52 respectively for pitch samples #1-12.

Spectra of most of the pentane and the cyclohexane eluate fractions were generally similar, with a sharp peak at about 3470 cm^{-1} which was assigned to pyrrolic N-H functionality. In addition, scan between 3800-3200 region also showed presence of trace of water. There was also considerable similarity in the 1900-1450 cm^{-1} region with the principal absorption being a broad band at about 1605 cm^{-1}. Both pentane and cyclohexane eluates of pitch sample #1 showed evidence of free carboxylic acid OH at about 3500 cm^{-1}. The cyclohexane eluates of pitch samples #4, 5 and 11 had a sloping baseline in the same region which might indicate bonded acids. Weaker bands near the water bands in these five fractions (pentane and cyclohexane eluates of #1, and the three cyclohexane eluates of #4, 5 and 11) may be due to phenol but further study is needed for the characterization. Four of the above five fractions (pentane and cyclohexane eluates of #1, and two cyclohexane eluates of #4 and 5) also showed absorption bands at about 1770 and/or 1720 cm^{-1} which were stronger than their absorption at about 1605 cm^{-1}. IR spectra of the cyclohexane eluate fraction of pitch #11 was somewhat different in the region between 1700-1750 cm^{-1}. This could not be explained.

Acid Subfractions

The infra-red spectra of the three acid subfractions in the anion exchange eluate of twelve pitch samples are shown in Figures 28-32. IR spectral data showing concentration, absorbance, band position and quantitation of major functional groups are given in Tables 41-52 respectively for pitch samples #1-12.

The only sharp peak other than that due to water (contaminant) in the infra-red spectra of all three subfractions of the twelve pitch samples occurred at 3470 cm^{-1} in the 3800-3200 cm^{-1} scan. This peak was assigned to pyrrolic N-H functionality. This band appeared in all A-1 and A-2 fractions, but only in a few of the A-3 fractions. All A-3 fractions had a broad band at about 3400 cm^{-1} assigned to carboxylic acids. There was no evidence of primary amides or free phenols in any of the acid subfractions.

The strongest band in the 1900-1450 cm^{-1} region occurred at about 1605 cm^{-1} in the CH_2Cl_2 solutions of A-1 and A-2 fractions of ten of the pitch samples with the exception of #4 and #5. The A-1 and A-2 fractions of pitches 4 and 5 also showed this band, but other bands at about 1770 and/or 1720 cm^{-1} were stronger. The width (sharpness) of the band at 1605 cm^{-1} varied considerably in the A-1 and A-2 fractions of the various pitch samples. Clearly the 1605 cm^{-1} band is composite and is generally indicative of aromaticity. The A-3 fractions had very strong absorption in the 1900-1450 cm^{-1} region showing several absorption bands. The band at about 1775 cm^{-1} in A-3 fractions of pitch samples #7 and 12 disappeared on dilution of the CH_2Cl_2 solutions (Figure 30), but a band at this position was present in A-3 fractions of pitch samples #4, 5 and 6 which were not diluted further (Figure 28). When the A-3 fractions were dissolved in THF, the principal band between 1800 and 1650 cm^{-1} was strong and sharp at about 1720 cm^{-1} (see Figure 31). It was assigned to carboxylic acid. Presumably bands between 1800 and 1650 cm^{-1} in the CH_2Cl_2 solution result from various forms of carboxylic acid, i.e. dimer, monomer, complex with pyridine ring, etc. Even the A-3 fractions of pitch samples #11 and 8 which have no strong bands between 1800 and 1650 cm^{-1} in CH_2Cl_2 show a significant acid peak at about 1720 cm^{-1} in THF. The strong band at about 1560 cm^{-1} may represent an amino acid salt in the A-3 fractions of pitch samples #11 and 8. Two sharp, weak bands below 1650 cm^{-1} in all A-3 fraction spectra are assigned to aromatic ring vibrations. These bands closely resemble those of benzoic acid. Infra-red spectra of the A-3 fraction of sample #2 in CH_2Cl_2 is somewhat different from other A-3 fractions. This is shown in Figure 32.

Base Subfractions

The infra-red spectra of the three base subfractions in the cation exchange eluate of twelve pitch samples are shown in Figures 33-34. IR spectral data showing concentration, absorbance, band position and quantitation of major functional groups are given in Tables 41-52 respectively for pitch samples #1-12. In the 3800-3200 cm^{-1} region, spectra of base subfractions in methylene chloride showed a peak at about 3470 cm^{-1} which was assigned to pyrrolic N-H groups. This was observed in most of the C-1 and C-2 fractions of the twelve pitch samples. Absorption of C-3 fractions in this region of the spectrum was very weak, but many samples appeared to contain some pyrrolic compounds. Only C-3 fractions of pitch samples #1 and 5 showed the possible presence of other components in this region.

In the 1900-1450 cm^{-1} region, methylene chloride solutions of all base subfractions showed an absorption maximum at about 1605 cm^{-1}. This was a broad composite band apparently related to aromaticity. In most base subfractions, this was the strongest absorption band, but the following fractions also showed stronger or other prominent bands: 1770 and/or 1720 cm^{-1} bands (C-1, C-2 and C-3 fractions of #5; C-1 and C-2 fractions of #4; C-2 and C-3 fractions of #2, and C-2 fraction of #1), and an extremely strong 1560 cm^{-1} band (C-3 fraction of #1).

Carboxylic Acid Compounds in A-3 Acid Subfractions

Tables 41-52 give the absorbance values of bands at about 1695 and 1735 cm^{-1} in A-3 acid subfractions of all pitch samples. This was assigned to carboxylic acid functionality. The absorbance of benzoic acid (see calibration curves in Figure 35) as a reference was used for quantitation of carboxylic acids in the A-3 fractions. It is possible that some forms of carboxylic acid would be missed in the measurement since absorbance was measured only in CH_2Cl_2 solution. The acids were measured in A-3 fractions of all pitch samples except #2.

Of the twelve pitch samples, nine samples (#1, 3, 4, 5, 6, 7, 8, 11 and 12) showing the presence of carboxylic acid showed no measurable amount of pyrrolic compounds. The A-3 fractions of samples #9 and 10 showed both carboxylic acid and pyrrolic compounds, and the acid concentration was higher than that of the pyrrolic compounds. The A-3 fraction of sample #2 showed pyrrolic compound but no carboxylic acid.

A-3 fraction of pitch sample #7 showed the highest carboxylic acid concentration expressed as benzoic acid ($\sim$ 4 mmoles/g fraction. However, when expressed as wt. % of residual pitch, highest concentration is shown by the A-3 fraction of sample #5 (0.02 mmole/g residual pitch).

Pyrrolic Compounds in Pitch Ion-Exchange Eluate Fractions

The absorbance values of the band at about 3470 cm^{-1} for all ion-exchange eluates fractions of the pitch samples are shown in Tables 41-52. This band was assigned to pyrrolic compounds. For quantitation of pyrrolic functions in eluate fractions, the absorbance of carbazole (see calibration curve in Figure 36) was used as a reference. The concentration of pyrrolic compounds in each fraction is expressed in millimoles of carbazole per gram of fraction.

It is evident from the results shown in Tables 41-52 that acid sub-fraction A-2 has the highest concentration of pyrrolic compounds (when expressed as mmole carbazole/g fraction) compared to other fractions of the same pitch for pitch samples #2, 3, 4, 6, 7, 9, 10 and 12. Other pitch samples (#1, 5, 8 and 11) did not show this clear distinction. In those samples, the pyrrolic compounds are found evenly distributed between the

A-1 and A-2 fractions. For example, their pyrrolic fractions contents expressed as mmoles carbazole/g fraction are as follows: #1 (A-1, 0.310; A-2, 0.337), #5 (A-1, 0.224; A-2, 0.107), #8 (A-1, 0.306; A-2, 0.294) and #11 (A-1, 0.362; A-2, 0.363).

Concentrations of pyrrolic compounds in ion-exchange eluate fractions expressed as millimoles of carbazole per 100 g residual pitches are shown in Table 53. The results indicate that most of the pyrrolic compounds in all pitch samples except #1, 5, 8 and 11 are concentrated in either pentane eluate or acid subfraction A-1. Total pyrrolic content was found highest in sample #4, and the samples #1, 5 and 8 had the least. Most of pyrrolic compounds of samples #5, 8 and 11 were concentrated in the pentane eluate. Acid subfraction A-1 showed the highest concentration of pyrrolic compounds in sample #1.

3.5 Analysis of Porphyrins and Metals (V, Ni, Fe) in Pitch Fractions

Porphyrins of petroleum origin and a number of trace metals are known to be associated with the heavy components of petroleum.[13,14] Of the various trace metals, V, Ni and Fe are the most abundant and show the highest concentration in the asphaltenes. Porphyrins are known to be distributed in both maltene and asphaltene fractions of oils. The above suggests that these metals and porphyrin content may be useful parameters for the characterization of petroleum heavy ends. These parameters were utilized for characterizing residual pitch samples in the present study.

Analysis and distribution of porphyrins in the twelve pitch samples were performed with their benzene solubles containing both maltene and asphaltene fractions. The method of isolation of porphyrins is shown in the flow chart in Figure 2. The UV-VIS spectral scan between 300-510 nm of the chloroform extracts of the processed benzene soluble fractions of the twelve samples are shown in Figure 37. As shown in the figure, an absorption maximum at between 400-410 nm is observed with most of the pitch samples. Previous work has identified this absorption as due to petroporphyrin.[3] No absorption was observed with samples #9, 10 and 12. For calibration and quantitation, porphyrin isolated from one of the pitch samples (sample #8) was used as a reference standard. A calibration curve is shown in Figure 38.

The distribution of porphyrins in the pitch benzene soluble fraction is presented in Table 54. Only three samples #1, 3 and 5 showed very high concentrations of porphyrin which ranged between 1-2%. No porphyrin was noted in samples #9, 10 and 12. Five samples showed very low concentrations (between 0.136 - 0.388%) and only trace amounts (0.036%) were found in sample #2.

Metal contents were determined in both pentane- and heptane-asphaltenes of pitch samples. Their distributions are presented in Table 55. Results indicate similar distribution of metals in both pentane- and heptane-asphaltenes. For example, in most cases both asphaltenes in each of the twelve samples were characterized by similar Fe content. Similar distributions were also observed with V and Ni content and V/Ni ratios in the two asphaltenes of each sample.

Distribution of iron between pitch samples showed wide variation in most samples. The highest concentration was in sample #1 (∿ 1300-1500 ppm). This was followed by samples #7 and 3 with ∿ 400-450 and ∿ 200-250 ppm respectively. Only two samples #9 and 10 showed a very low concentration (∿ 3 ppm).

The asphaltenes in most of the pitch samples were characterized by substantial amounts of V and Ni. The highest concentration of V and Ni was found in samples #3 (e.g. ∿ 1500-1600 ppm V and ∿ 450 ppm Ni). Porphyrin concentration was also highest with this sample. V and Ni content was found comparatively low in the asphaltenes of three pitch samples, namely #9, 10 and 12. As noted previously, no porphyrin was found with these three samples. The above distribution suggests a close relationship between the two metals, vanadium in particular and porphyrins in the pitch samples. The decrease in the V content in the two asphaltenes of pitch samples is found to be closely related tothe decrease in porphyrin content in pitch benzene soluble fractions, e.g.

$$\xrightarrow[\text{heptane asphaltene}]{\text{V decreasing}} \#3, 1, 5, 8, 7, 4, 11, 6, 2, 9, 10, 12$$

$\frac{\text{V decreasing}}{\text{pentane asphaltene}} \rightarrow$ #3, 1, 5, 8, 7, 4, 6, 2, 11, 10, 9, 12

$\xrightarrow{\text{Porphyrins decreasing}}$ #3, 1, 5, 8, 6, 11, 4, 7, 2, 9, 10, 12

Studies in the past have indicated that high sulfur content in crude oils correlates with high vanadium and porphyrin content and high ratios of vanadium to nickel.[15] However, no such correlation was observed with most of the high sulfur pitch asphaltenes examined in the present study. Only the three high sulfur samples (#1, 3 and 5) contained high amounts of vanadium and porphyrins and have high ratios of vanadium to nickel (see Tables 54 and 55). The only pitch asphaltene sample (#12) which is low in sulfur contained, as expected, the lowest amount of vanadium and no porphyrin, and has the lowest vanadium to nickel ratio less than unity. The other eight high sulfur asphaltenes samples contained vanadium and porphyrin which did not correlate with their sulfur contents.

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TABLES

TABLE 1

% Benzene Solubles and Insolubles in Residual Pitches

Sample #	Weight of Sample (g)	Weight of Benzene Insolubles (g)	Weight of Benzene Solubles (g)	% Benzene Insolubles	% Benzene Solubles
1	80.0	3.15	76.85	3.93	96.06
2	80.0	22.65	57.35	28.31	71.69
3	80.0	5.99	74.01	7.48	92.52
4	80.0	4.10	75.90	5.13	94.87
5	80.0	0.73	79.27	0.91	99.09
6	75.3	2.19	73.11	2.91	97.09
7	80.0	1.89	78.11	2.36	97.64
8	89.8	0.56	89.24	0.62	99.38
9	77.8	3.77	74.03	4.84	95.16
10	74.9	4.44	70.46	5.93	94.07
11	86.9	6.28	80.62	7.23	92.77
12	76.1	6.61	69.49	8.68	91.32

TABLE 2

Yield of Maltene and Asphaltene in Deasphaltening of Pitch Benzene Solubles with n-Pentane and with n-Heptane

Sample #	n-Pentane					n-Heptane				
	Weight of Sample (g)	Weight of Asphaltene (g)	Weight of Maltene (g)	% Asphaltene	% Maltene	Weight of Sample (g)	Weight of Asphaltene (g)	Weight of Maltene (g)	% Asphaltene	% Maltene
1	50.30	14.65	34.94	29.13	69.46	10.21	2.62	7.53	25.66	73.75
2	36.00	18.93	17.06	52.58	47.39	8.89	5.83	2.99	65.58	33.63
3	50.60	25.16	25.40	49.72	50.20	10.04	4.78	5.19	47.61	51.69
4	45.60	17.42	28.00	38.20	61.40	9.18	3.39	5.78	36.93	62.96
5	54.00	15.84	36.30	29.33	67.22	10.6	2.51	7.00	23.67	66.03
6	43.10	21.37	16.80	49.58	38.98	9.01	4.34	3.50	48.17	38.84
7	44.20	15.97	25.50	36.13	57.69	9.77	2.84	6.66	29.07	68.17
8	56.70	7.93	46.90	13.99	82.72	12.08	1.29	10.50	10.68	86.92
9	48.60	34.35	13.20	70.68	27.16	10.18	6.26	3.70	61.49	36.35
10	53.95	25.97	25.10	48.14	46.52	8.80	3.55	4.00	40.34	45.45
11	53.00	6.12	45.10	11.55	85.09	9.41	0.71	8.40	7.55	89.27
12	31.20	13.33	16.60	42.72	53.21	9.63	3.88	5.60	40.29	58.15

TABLE 3

GPC Conditions (System 1 and System 2) in MWD Determinations of Residual Pitch Samples

GPC Parameters	System No. 1	System No. 2
Instrument	Beckman Model 112 HPLC	Beckman Model 112 HPLC
Columns	500Å Ultrastyragel + 100Å Ultrastyragel 7.8 mm I.D. x 30 cm (Waters Associates)	1000Å Ultrastyragel + 100Å Ultrastyragel 7.8 mm I.D. x 30 cm (Waters Associates)
Mobile Phase	Tetrahydrofuran	Tetrahydrofuran
Flow Rate	1.00 mL/min	1.00 mL/min
Injection Volume	10 μL	20 μL
Temperature	Ambient	Ambient
Detector	UV @ 254 nm 0.2 AuFs (Schoeffel Model SF 770)	UV @ 254 nm 0.32 AuFs (Beckman Model 153)
Chart Speed	0.5 cm/min	0.5 cm/min
Data System	Spectra Physics SP 4100 SP MWD-5 Program	Spectra Physics SP 4100 SP MWD-5 Program
Molecular Weight	Polystyrenes (2.2 x 10^3, 955, 570), Styrene monomer (104), Benzene (78) [for samples 2, 3, 4, 6, 7, 9, 10, 12]; above standards plus polystyrenes (35 x 10^3, 17.5 x 10^3 and 4 x 10^3) [for samples 1, 5, 8 and 11]	Polystryrenes (35 x 10^3, 17.5 x 10^3, 4 x 10^3, 2.2 x 10^3, 955, 570), Styrene monomer (104), Benzene (78)

TABLE 4

Molecular Weight/Retention Time Data of Standards for Calibration Curve #1 (Figure 3) in GPC System #1

```
[redacted].AUD1200
LOAD"CAL"

TEST
      ERROR   36
!SIZE 0
 4953.

GPC Calibration File  1.
Press 'ENTER' to skip entry
Ref Ret Time(Rp):
Area Slice Width (mins)(Ta): .1
Initial delay (mins)(Id):
End of Run (mins)(ER): 25
Baseline Times(mins)(Bb,Eb): 9,24
Data Proc Times(Bp,Ep): 9.5,23.5
FILE NAME? CANMET RESIDUAL PITCHES
TIME FUNCTIONS...
RUN TIME:TT?
Universal Calibration (Y/N)(Uc): N
Standards Table...
Elution Time(RT): 13.31
Mol.Wt.(Mw): 2200
Elution Time(RT): 14.54
Mol.Wt.(Mw): 955
Elution Time(RT): 15.45
Mol.Wt.(Mw): 570
Elution Time(RT): 16.19
Mol.Wt.(Mw): 400
Elution Time(RT): 16.79
Mol.Wt.(Mw): 300
Elution Time(RT): 17.88
Mol.Wt.(Mw): 200
Elution Time(RT): 20.53
Mol.Wt.(Mw): 104
Elution Time(RT): 21.04
Mol.Wt.(Mw): 78
Elution Time(RT): 11.22
Mol.Wt.(Mw): 35000
Elution Time(RT): 11.64
Mol.Wt.(Mw): 17500
Elution Time(RT): 12.84
Mol.Wt.(Mw): 4000
Elution Time(RT):
FIT Type(0=Pt to Pt,1=linear,2=quad,3=cubic)(Ft): 3
Cal Plot(Y/N): Y
END OF DIALOG
```

TABLE 5

Molecular Weight/Retention Time Data of Standards for Calibration Curve #2 (Figure 4) in GPC System #1

```
 READY

BAUD 1200
LOAD "CAL"
TEST
     ERROR   36
!SIZE 0
 4953.

GPC Calibration File  1.
Press 'ENTER' to skip entry
Ref Ret Time(Rp):
Area Slice Width (mins)(Ta): .1
Initial delay (mins)(Id):
End of Run (mins)(ER): 34
Baseline Times(mins)(Bb,Eb): 10,24
Data Proc Times(Bp,Ep): 11.5,23.5
FILE NAME? UTS RESIDUAL PITCHES
TIME FUNCTIONS...
RUN TIME:TT? 10
FUNCTION:TF? NE
RUN TIME:TT?
Universal Calibration (Y/N)(Uc): N
Standards Table...
Elution Time(RT): 13.31
Mol.Wt.(Mw): 2200
Elution Time(RT): 14.54
Mol.Wt.(Mw): 955
Elution Time(RT): 15.45
Mol.Wt.(Mw): 570
Elution Time(RT): 20.53
Mol.Wt.(Mw): 104
Elution Time(RT): 16.19
Mol.Wt.(Mw): 400
Elution Time(RT): 16.79
Mol.Wt.(Mw): 300
Elution Time(RT): 17.88
Mol.Wt.(Mw): 200
Elution Time(RT): 21.04
Mol.Wt.(Mw): 78
Elution Time(RT):
FIT Type(0=Pt to Pt,1=linear,2=quad,3=cubic)(Ft): 3
Cal Plot(Y/N): Y
END OF DIALOG
```

TABLE 6

Molecular Weight/Retention Time Data of Standards for Calibration Curve #3 (Figure 5) in GPC System #2

```
BAUD 1[illegible]
LOAD"C _[illegible]
      ERROR  100
LOAD"CAL"
TEST
      ERROR   36
!SIZE
 4953.
GPC Calibration File  1.
Press 'ENTER' to skip entry
Ref Ret Time(Rp):
Area Slice Width (mins)(Ta): .1
Initial delay (mins)(Id):
End of Run (mins)(ER): 24
Baseline Times(mins)(Bb,Eb): 9,23.5
Data Proc Times(Bp,Ep): L0.5,23
FILE NAME? CANMET RESIDUAL PITCHES
TIME FUNCTIONS...
RUN TIME:TT?
Universal Calibration (Y/N)(Uc): H
Standards Table...
Elution Time(RT): 11.48
Mol.Wt.(Mw): 35000
Elution Time(RT): 12.41
Mol.Wt.(Mw): 17500
Elution Time(RT): 14.08
Mol.Wt.(Mw): 4000
Elution Time(RT): 14.71
Mol.Wt.(Mw): 2200
Elution Time(RT): 15.96
Mol.Wt.(Mw): 955
Elution Time(RT): 16.76
Mol.Wt.(Mw): 570
Elution Time(RT): 17.76
Mol.Wt.(Mw): 400
Elution Time(RT): 18.62
Mol.Wt.(Mw): 300
Elution Time(RT): 20.13
Mol.Wt.(Mw): 200
Elution Time(RT): 21.80
Mol.Wt.(Mw): 104
Elution Time(RT): 22.27
Mol.Wt.(Mw): 78
Elution Time(RT):
FIT Type(0=Pt to Pt,1=linear,2=quad,3=cubic)(Ft): 3
Cal Plot(Y/N): Y
```

TABLE 7

GPC-MWD of Twelve Residual Pitch Samples

Whole Pitch Sample No.	System No. 1			System No. 2		
	Mw	Mn	Mw/Mn	Mw	Mn	Mw/Mn
1	2563	470	5.450	2709	679	3.990
	(2691)*	(515)	(5.213)	(2686)	(674)	(3.986)
2	384	186	2.058	478	207	2.301
	(398)	(169)	(2.351)	(461)	(206)	(2.274)
3	674	214	3.149	917	326	2.811
	(672)	(197)	(3.403)	(906)	(321)	(2.821)
4	466	223	2.087	580	251	2.309
	(463)	(218)	(2.123)	(581)	(251)	(2.316)
5	3304	510	6.468	3188	658	4.839
	(3216)	(532)	(6.038)	(3213)	(657)	(4.884)
6	429	192	2.234	527	231	2.279
	(412)	(196)	(2.102)	(597)	(248)	(2.409)
7	490	228	2.143	587	284	2.067
	(475)	(211)	(2.242)	(589)	(281)	(2.096)
8	1362	445	3.057	1484	510	2.908
	(1315)	(439)	(2.995)	(1508)	(510)	(2.956)
9	261	148	1.757	306	174	1.750
	(263)	(148)	(1.757)	(314)	(177)	(1.771)
10	290	163	1.778	328	178	1.845
	(267)	(148)	(1.799)	(310)	(171)	(1.815)
11	1188	418	2.839	1138	464	2.450
	(1087)	(410)	(2.648)	(1132)	(465)	(2.433)
12	380	184	2.066	413	218	1.889
	(347)	(196)	(1.818)	(357)	(218)	(1.889)

* MWD data from duplicate GPC runs are in parantheses.

TABLE 8

% Distribution of n-Pentane- and n-Heptane-Maltene and Asphaltene Content, and Benzene Insoluble Content in Twelve Residual Pitch Samples

Fraction	#1	#2	#3	#4	#5	#6	#7	#8	#9	#10	#11	#12
Benzene Insoluble	3.94	28.31	7.48	5.12	0.91	2.91	2.36	0.62	4.84	5.93	7.23	8.68
Pentane Maltene	66.73	33.97	46.44	58.25	66.61	37.49	56.33	82.20	25.85	43.77	78.94	48.59
Pentane Asphaltene	27.97	37.70	46.00	36.24	29.07	48.14	35.28	13.90	67.26	45.28	10.71	39.02
Total Recovery	98.64	99.98	99.92	99.61	96.59	88.53	93.96	96.72	97.95	94.98	96.88	96.29
Benzene Insoluble	3.94	28.31	7.48	5.12	0.91	2.91	2.36	0.62	4.84	5.93	7.23	8.68
Heptane Maltene	70.84	24.11	47.83	59.74	65.44	37.72	66.56	86.38	34.59	42.76	82.82	53.11
Heptane Asphaltene	24.65	47.01	44.05	35.04	23.47	46.77	28.38	10.61	58.52	37.95	7.00	36.80
Total Recovery	99.43	99.43	99.36	99.90	89.82	87.40	97.30	97.61	97.95	86.64	97.05	98.59

TABLE 9

MWD of Residual Pitch No. 1 and Its Various Maltene and Asphaltene, and Ion-Exchange Extract and Eluate Fractions

CANMET Residual Pitch No. 1	GPC System No. 1			GPC System No. 2		
	Mw	Mn	Mw/Mn	Mw	Mn	Mw/Mn
Whole Pitch	2563 (2691)	470 (515)	5.450 (5.213)	2709 (2686)	679 (674)	3.990 (3.986)
Deasphaltening*						
Pentane Maltene	1202 (1174)	488 (480)	2.463 (2.443)	1105 (1099)	541 (537)	2.040 (2.048)
Heptane Maltene	1470 (1484)	536 (541)	2.743 (2.741)	1377 (1383)	583 (585)	2.362 (2.364)
Pentane Asphaltene	4764 (4717)	848 (844)	5.613 (5.586)	4858 (5011)	1039 (1040)	4.671 (4.815)
Heptane Asphaltene	4772 (4770)	538 (556)	8.857 (8.567)	5619 (5526)	1132 (1120)	4.962 (4.932)
Ion-Exchange Chromatography (IEC)**						
Pentane Eluate	852 [899]	407 [449]	2.095 [2.001]	910 [917]	435 [438]	2.092 [2.093]
Cyclohexane Eluate	1347 [1351]	461 [478]	2.923 [2.824]	1134 [1321]	440 [452]	3.029 [2.921]
Combined Pentane + Cyclohexane Eluate	1263 [1152]	470 [470]	2.688 [2.450]	1221 [1144]	439 [445]	2.780 [2.568]
Acid Subfraction I	1856 [1788]	575 [589]	3.226 [3.034]	1783 [1841]	599 [599]	2.974 [3.069]
Acid Subfraction II	1471 [1544]	479 [484]	3.067 [3.185]	1661 [1684]	498 [500]	3.332 [3.366]
Acid Subfraction III	3062 [3008]	566 [516]	5.402 [5.824]	3379 [3291]	721 [666]	4.680 [4.941]
Base Subfraction I	1650 [1748]	499 [551]	3.306 [3.169]	1566 [1735]	511 [555]	3.066 [3.124]
Base Subfraction II	1512 [1492]	505 [472]	2.991 [3.156]	1514 [1431]	494 [446]	3.061 [3.208]
Base Subfraction III	1762 [1873]	413 [507]	4.266 [3.689]	1720 [1831]	411 [530]	4.177 [3.454]

* MWD data of deasphaltened fractions from duplicate GPC runs are in parantheses.

** MWD data of ion-exchange fractions shown in brackets are from duplicate IEC experiments.

TABLE 10

MWD of Residual Pitch No. 2 and Its Various Maltene and Asphaltene, and Ion-Exchange Extract and Eluate Fractions

CANMET Residual Pitch No. 2	GPC System No. 1			GPC System No. 2		
	Mw	Mn	Mw/Mn	Mw	Mn	Mw/Mn
Whole Pitch	384 (398)	186 (169)	2.058 (2.351)	478 (461)	207 (206)	2.301 (2.274)
Deasphaltening*						
Pentane Maltene	345 (340)	214 (211)	1.610 (1.609)	370 (368)	215 (214)	1.716 (1.716)
Heptane Maltene	368 (367)	215 (217)	1.713 (1.693)	391 (392)	214 (215)	1.824 (1.820)
Pentane Asphaltene	422 (430)	188 (192)	2.244 (2.240)	456	223	2.042
Heptane Asphaltene	413 (394)	167 (147)	2.474 (2.675)	512	231	2.218
Ion-Exchange Chromatography (IEC)**						
Pentane Eluate	446 [365]	258 [242]	1.724 [1.509]	462 [384]	240 [228]	1.920 [1.686]
Cyclohexane Eluate	386 [332]	224 [212]	1.723 [1.565]	373 [321]	202 [192]	1.851 [1.671]
Combined Pentane + Cyclohexane Eluate	426 [367]	244 [235]	1.747 [1.564]	419 [356]	220 [212]	1.903 [1.682]
Acid Subfraction I	368 [316]	222 [198]	1.659 [1.594]	356 [304]	206 [187]	1.728 [1.624]
Acid Subfraction II	380 [398]	224 [243]	1.694 [1.637]	367 [396]	203 [225]	1.806 [1.759]
Acid Subfraction III	618 [574]	319 [326]	1.937 [1.763]	625 [592]	298 [309]	2.094 [1.912]
Base Subfraction I	386 [313]	212 [189]	1.822 [1.657]	383 [309]	199 [179]	1.917 [1.725]
Base Subfraction II	473 [309]	247 [181]	1.910 [1.710]	475 [306]	231 [168]	2.051 [1.818]
Base Subfraction III	445 [322]	221 [161]	2.011 [1.996]	457 [329]	214 [165]	2.136 [1.997]

* MWD data of deasphaltened fractions from duplicate GPC runs are in parantheses.

** MWD data of ion-exchange fractions shown in brackets are from duplicate IEC experiments.

TABLE 11

MWD of Residual Pitch No. 3 and Its Various Maltene and Asphaltene, and Ion-Exchange Extract and Eluate Fractions

CANMET Residual Pitch No. 3	GPC System No. 1			GPC System No. 2		
	Mw	Mn	Mw/Mn	Mw	Mn	Mw/Mn
Whole Pitch	674 (672)	214 (197)	3.149 (3.403)	917 (906)	326 (321)	2.811 (2.821)
Deasphaltening*						
Pentane Maltene	431 (435)	268 (270)	1.604 (1.609)	459 (457)	273 (272)	1.682 (1.678)
Heptane Maltene	457 (449)	275 (272)	1.664 (1.647)	484 (485)	279 (280)	1.734 (1.731)
Pentane Asphaltene	879 (883)	287 (290)	3.057 (3.041)	1032 (1085)	369 (374)	2.793 (2.899)
Heptane Asphaltene	791 (812)	229 (233)	3.446 (3.479)	1076 (1115)	370 (374)	2.906 (2.978)
Ion-Exchange Chromatography (IEC)**						
Pentane Eluate	433 [426]	274 [282]	1.578 [1.509]	420 [413]	246 [252]	1.705 [1.637]
Cyclohexane Eluate	413 [427]	234 [242]	1.761 [1.765]	404 [411]	212 [215]	1.904 [1.912]
Combined Pentane + Cyclohexane Eluate	425 [425]	254 [255]	1.683 [1.667]	413 [414]	228 [229]	1.814 [1.807]
Acid Subfraction I	562 [506]	317 [291]	1.772 [1.734]	562 [514]	293 [271]	1.918 [1.893]
Acid Subfraction II	524 [551]	285 [293]	1.836 [1.878]	530 [564]	262 [271]	2.025 [2.077]
Acid Subfraction III	566 [470]	239 [211]	2.363 [2.220]	601 [484]	233 [195]	2.575 [2.485]
Base Subfraction I	426 [455]	240 [252]	1.773 [1.808]	423 [451]	220 [229]	1.917 [1.970]
Base Subfraction II	521 [397]	286 [214]	1.821 [1.849]	521 [384]	264 [193]	1.973 [1.984]
Base Subfraction III	544 [417]	312 [206]	1.739 [2.025]	536 [428]	282 [190]	1.897 [2.245]

* MWD data of deasphaltened fractions from duplicate GPC runs are in parantheses.

** MWD data of ion-exchange fractions shown in brackets are from duplicate IEC experiments.

TABLE 12

MWD of Residual Pitch No. 4 and its Various Maltene and Asphaltene, and Ion-Exchange Extract and Eluate Fractions

CANMET Residual Pitch No. 4	GPC System No. 1			GPC System No. 2		
	Mw	Mn	Mw/Mn	Mw	Mn	Mw/Mn
Whole Pitch	466 (463)	223 (218)	2.087 (2.123)	580 (581)	251 (251)	2.309 (2.316)
Deasphaltening*						
Pentane Maltene	397 (401)	241 (243)	1.643 (1.651)	434 (427)	248 (246)	1.745 (1.736)
Heptane Maltene	404 (414)	238 (244)	1.694 (1.697)	427 (422)	240 (237)	1.779 (1.783)
Pentane Asphaltene	542 (561)	216 (225)	2.512 (2.492)	539	252	2.137
Heptane Asphaltene	608 (600)	195 (192)	3.111 (3.112)	696	288	2.417
Ion Exchange Chromatography (IEC)**						
Pentane Eluate	395 [417]	244 [259]	1.617 [1.607]	394 [417]	223 [239]	1.762 [1.743]
Cyclohexane Eluate	347 [382]	217 [219]	1.596 [1.743]	346 [390]	204 [205]	1.695 [1.901]
Combined Pentane and Cyclohexane Eluate	365 [387]	227 [230]	1.609 [1.681]	370 [389]	213 [213]	1.735 [1.826]
Acid Subfraction I	491 [433]	274 [246]	1.792 [1.757]	520 [449]	273 [240]	1.904 [1.874]
Acid Subfraction II	504 [437]	266 [259]	1.896 [1.686]	531 [463]	252 [248]	2.106 [1.863]
Acid Subfraction III	589 [538]	263 [282]	2.236 [1.903]	613 [560]	248 [268]	2.468 [2.083]
Base Subfraction I	414 [415]	229 [226]	1.807 [1.832]	433 [427]	223 [217]	1.937 [1.971]
Base Subfraction II	414 [347]	227 [205]	1.819 [1.694]	436 [350]	226 [194]	1.923 [1.802]
Base Subfraction III	490 [370]	273 [211]	1.797 [1.747]	517 [355]	264 [199]	1.956 [1.781]

* MWD data of deasphaltened fractions from duplicate GPC run are shown in parentheses.

** MWD data of ion exchange fractions shown in brackets are from duplicate IEC experiments.

TABLE 13

MWD of Residual Pitch No. 5 and its Various Maltene and Asphaltene, and Ion-Exchange Extract and Eluate Fractions

CANMET Residual Pitch No. 5	GPC System No. 1			GPC System No. 2		
	Mw	Mn	Mw/Mn	Mw	Mn	Mw/Mn
Whole Pitch	3304 (3216)	510 (532)	6.468 (6.038)	3188 (3213)	658 (657)	4.839 (4.884)
Deasphaltening*						
Pentane Maltene	1199 (1234)	483 (493)	2.481 (2.503)	1120 (1122)	519 (521)	2.156 (2.152)
Heptane Maltene	1597 (1572)	533 (527)	2.994 (2.982)	1497 (1512)	575 (584)	2.604 (2.589)
Pentane Asphaltene	5225 (5367)	805 (816)	6.492 (6.576)	5494 (5413)	1065 (1056)	5.158 (5.124)
Heptane Asphaltene	5297 (5597)	530 (558)	9.977 (10.030)	6416 (6476)	1149 (1159)	5.584 (5.585)
Ion Exchange Chromatography (IEC)**						
Pentane Eluate	1015 [948]	433 [433]	2.341 [2.188]	1008 [945]	408 [407]	2.467 [2.318]
Cyclohexane Eluate	1543 [1482]	509 [498]	3.031 [2.973]	1487 [1538]	490 [499]	3.036 [3.079]
Combined Pentane + Cyclohexane Eluate	1180 [1169]	373 [462]	3.160 [2.531]	1307 [1207]	456 [477]	2.866 [2.699]
Acid Subfraction I	1778 [2114]	558 [666]	3.182 [3.172]	1763 [1930]	561 [650]	3.142 [2.968]
Acid Subfraction II	1692 [3035]	429 [593]	3.941 [5.113]	1397 [2105]	395 [573]	3.537 [3.669]
Acid Subfraction III	5317 [6006]	751 [571]	7.074 [10.516]	2917 [3680]	706 [548]	4.130 [6.707]
Base Subfraction I	1771 [2091]	548 [604]	3.228 [3.462]	1566 [1708]	515 [555]	3.037 [3.075]
Base Subfraction II	1627 [1302]	564 [470]	2.882 [2.768]	1408 [1157]	519 [440]	2.174 [2.628]
Base Subfraction III	1540 [2255]	655 [498]	2.350 [4.520]	1328 [1816]	589 [467]	2.253 [3.884]

* MWD data of deasphaltened fractions from duplicate GPC run are shown in parentheses.

** MWD data of ion exchange fractions shown in brackets are from duplicate IEC experiments.

TABLE 14

MWD of Residual Pitch No. 6 and its Various Maltene and Asphaltene, and Ion-Exchange Extract and Eluate Fractions

CANMET Residual Pitch No. 6	GPC System No. 1			GPC System No. 2		
	Mw	Mn	Mw/Mn	Mw	Mn	Mw/Mn
Whole Pitch	429 (412)	192 (196)	2.234 (2.102)	527 (597)	231 (248)	2.279 (2.409)
Deasphaltening*						
Pentane Maltene	384 (383)	240 (240)	1.602 (1.594)	411 (413)	245 (245)	1.673 (1.681)
Heptane Maltene	387 (384)	237 (235)	1.629 (1.632)	355 (376)	209 (220)	1.692 (1.706)
Pentane Asphaltene	494 (482)	200 (205)	2.465 (2.348)	576	253	2.277
Heptane Asphaltene	486 (490)	176 (180)	2.759 (2.715)	635	269	2.357
Ion-Exchange Chromatography (IEC)**						
Pentane Eluate	415 [402]	251 [253]	1.653 [1.588]	367 [372]	215 [219]	1.707 [1.700]
Cyclohexane Eluate	343 [352]	212 [214]	1.617 [1.642]	320 [330]	188 [190]	1.704 [1.734]
Combined Pentane + Cyclohexane Eluate	380 [391]	232 [236]	1.633 [1.655]	347 [365]	202 [207]	1.721 [1.764]
Acid Subfraction I	450 [428]	289 [272]	1.553 [1.575]	428 [411]	259 [246]	1.649 [1.669]
Acid Subfraction II	458 [414]	267 [261]	1.713 [1.588]	452 [401]	240 [231]	1.880 [1.731]
Acid Subfraction III	649 [489]	278 [261]	2.335 [1.873]	679 [500]	260 [241]	2.611 [2.070]
Base Subfraction I	385 [413]	222 [236]	1.734 [1.751]	381 [395]	207 [215]	1.835 [1.839]
Base Subfraction II	502 [379]	267 [207]	1.878 [1.830]	493 [363]	248 [187]	1.980 [1.939]
Base Subfraction III	500 [637]	290 [268]	1.723 [2.371]	469 [634]	256 [246]	1.830 [2.580]

* MWD data of deasphaltened fractions from duplicate GPC run are shown in parentheses.

** MWD data of ion exchange fractions shown in brackets are from duplicate IEC experiments.

TABLE 15

MWD of Residual Pitch No. 7 and Its Various Maltene and Asphaltene, and Ion-Exchange Extract and Eluate Fractions

CANMET Residual Pitch No. 7	GPC System No. 1			GPC System No. 2		
	Mw	Mn	Mw/Mn	Mw	Mn	Mw/Mn
Whole Pitch	490 (475)	228 (211)	2.143 (2.242)	587 (589)	284 (281)	2.067 (2.096)
Deasphaltening*						
Pentane Maltene	392 (390)	258 (257)	1.157 (1.515)	429 (418)	268 (261)	1.596 (1.599)
Heptane Maltene	404 (399)	260 (259)	1.552 (1.539)	409	245	1.670
Pentane Asphaltene	642 (667)	231 (245)	2.773 (2.722)	772	318	2.423
Heptane Asphaltene	823 (838)	218 (225)	3.774 (3.724)	907	357	2.535
Ion Exchange Chromatography (IEC)**						
Pentane Eluate	404 [409]	270 [277]	1.496 [1.476]	379 [389]	236 [244]	1.604 [1.595]
Cyclohexane Eluate	412 [397]	247 [242]	1.669 [1.641]	390 [373]	219 [213]	1.781 [1.750]
Combined Pentane + Cyclohexane Eluate	402 [397]	253 [251]	1.592 [1.581]	392 [379]	228 [223]	1.715 [1.697]
Acid Subfraction I	487 [443]	306 [277]	1.589 [1.598]	477 [443]	279 [255]	1.709 [1.737]
Acid Subfraction II	418 [492]	257 [299]	1.627 [1.645]	401 [494]	228 [272]	1.759 [1.818]
Acid Subfraction III	535 [600]	248 [320]	2.152 [1.874]	548 [559]	226 [274]	2.418 [2.038]
Base Subfraction I	442 [445]	257 [260]	1.715 [1.708]	418 [422]	229 [231]	1.827 [1.828]
Base Subfraction II	489 [412]	276 [228]	1.771 [1.803]	478 [400]	252 [204]	1.894 [1.962]
Base Subfraction III	502 [444]	306 [233]	1.639 [1.906]	475 [429]	268 [204]	1.771 [2.105]

* MWD data of deasphaltened fractions from duplicate GPC runs are in parentheses.

** MWD data of ion-exchange fractions shown in brackets are from duplicate IEC experiments.

TABLE 16

MWD of Residual Pitch No. 8 and Its Various Maltene and Asphaltene, and Ion-Exchange Extract and Eluate Fractions

CANMET Residual Pitch No. 8	GPC System No. 1			GPC System No. 2		
	Mw	Mn	Mw/Mn	Mw	Mn	Mw/Mn
Whole Pitch	1362 (1315)	445 (439)	3.057 (2.995)	1484 (1508)	510 (510)	2.908 (2.956)
Deasphaltening*						
Pentane Maltene	884 (881)	429 (428)	2.058 (2.055)	886 (884)	460 (459)	1.924 (1.926)
Heptane Maltene	987 (955)	447 (438)	2.208 (2.180)	994 (1008)	477 (485)	2.083 (2.079)
Pentane Asphaltene	2382 (2343)	411 (407)	5.788 (5.755)	3116 (3038)	766 (753)	4.064 (4.034)
Heptane Asphaltene	2583 (2559)	379 (376)	6.805 (6.803)	3246 (3158)	708 (687)	4.582 (4.594)
Ion Exchange Chromatography (IEC)**						
Pentane Eluate	821 [820]	410 [413]	1.999 [1.983]	787 [797]	359 [362]	2.193 [2.200]
Cyclohexane Eluate	979 [964]	373 [373]	2.626 [2.581]	950 [960]	335 [340]	2.831 [2.822]
Combined Pentane + Cyclohexane Eluate	848 [887]	380 [385]	2.229 [2.303]	851 [894]	344 [349]	2.467 [2.562]
Acid Subfraction I	1347 [1271]	490 [473]	2.738 [2.683]	1399 [1302]	482 [457]	2.901 [2.847]
Acid Subfraction II	1356 [1086]	419 [401]	3.233 [2.705]	1397 [1152]	407 [390]	3.431 [2.952]
Acid Subfraction III	1226 [2514]	230 [553]	5.322 [4.546]	1327 [2325]	221 [612]	5.996 [3.797]
Base Subfraction I	1191 [1275]	419 [436]	2.845 [2.925]	1199 [1297]	391 [411]	3.061 [3.154]
Base Subfraction II	1269 [980]	432 [294]	2.933 [3.332]	1229 [1023]	408 [275]	3.014 [3.711]
Base Subfraction III	1191 [1447]	464 [354]	2.566 [4.086]	1095 [1505]	426 [344]	2.565 [4.377]

* MWD data of deasphaltened fractions from duplicate GPC runs are in parentheses.

** MWD data of ion-exchange fractions shown in brackets are from duplicate IEC experiments.

TABLE 17

MWD of Residual Pitch No. 9 and Its Various Maltene and Asphaltene, and Ion-Exchange Extract and Eluate Fractions

CANMET Residual Pitch No. 9	GPC System No. 1			GPC System No. 2		
	Mw	Mn	Mw/Mn	Mw	Mn	Mw/Mn
Whole Pitch	261 (263)	148 (148)	1.757 (1.757)	306 (314)	174 (177)	1.750 (1.771)
Deasphaltening*						
Pentane Maltene	239 (240)	176 (176)	1.359 (1.360)	256 (258)	173 (175)	1.475 (1.472)
Heptane Maltene	245 (246)	176 (177)	1.390 (1.391)	240 (240)	167 (166)	1.438 (1.439)
Pentane Asphaltene	290 (292)	149 (152)	1.942 (1.919)	314	187	1.683
Heptane Asphaltene	295 (301)	135 (144)	2.177 (2.090)	322	188	1.712
Ion Exchange Chromatography (IEC)**						
Pentane Eluate	243 [259]	181 [193]	1.345 [1.346]	226 [251]	163 [173]	1.389 [1.447]
Cyclohexane Eluate	226 [221]	166 [166]	1.363 [1.328]	207 [198]	150 [147]	1.382 [1.345]
Combined Pentane + Cyclohexane Eluate	237 [236]	174 [176]	1.361 [1.341]	219 [218]	156 [158]	1.400 [1.383]
Acid Subfraction I	281 [266]	194 [185]	1.447 [1.437]	271 [251]	182 [171]	1.487 [1.467]
Acid Subfraction II	303 [386]	211 [246]	1.439 [1.565]	300 [360]	192 [212]	1.557 [1.694]
Acid Subfraction III	386 [350]	205 [195]	1.881 [1.793]	385 [338]	189 [179]	2.022 [1.888]
Base Subfraction I	233 [224]	161 [162]	1.450 [1.386]	217 [208]	149 [148]	1.453 [1.405]
Base Subfraction II	302 [221]	193 [157]	1.562 [1.403]	292 [202]	183 [142]	1.597 [1.425]
Base Subfraction III	315 [216]	216 [153]	1.456 [1.407]	301 [202]	196 [141]	1.532 [1.438]

* MWD data of deasphaltened fractions from duplicate GPC runs are in parentheses.

** MWD data of ion-exchange fractions shown in brackets are from duplicate IEC experiments.

TABLE 18

MWD of Residual Pitch No. 10 and Its Various Maltene and Asphaltene, and Ion-Exchange Extract and Eluate Fractions

CANMET Residual Pitch No. 10	GPC System No. 1			GPC System No. 2		
	Mw	Mn	Mw/Mn	Mw	Mn	Mw/Mn
Whole Pitch	290 (267)	163 (148)	1.778 (1.799)	328 (310)	178 (171)	1.845 (1.815)
Deasphaltening*						
Pentane Maltene	255 (255)	182 (182)	1.399 (1.402)	272 (271)	182 (178)	1.496 (1.519)
Heptane Maltene	258 (259)	181 (182)	1.420 (1.422)	253 (254)	173 (173)	1.462 (1.463)
Pentane Asphaltene	298 (303)	147 (154)	2.015 (1.966)	324	185	1.754
Heptane Asphaltene	310 (319)	131 (137)	2.354 (2.326)	348	193	1.804
Ion-Exchange Chromatography (IEC)**						
Pentane Eluate	267 [276]	191 [200]	1.398 [1.381]	250 [262]	171 [179]	1.462 [1.460]
Cyclohexane Eluate	234 [224]	162 [162]	1.443 [1.380]	224 [207]	151 [147]	1.480 [1.411]
Combined Pentane + Cyclohexane Eluate	250 [253]	174 [180]	1.438 [1.401]	235 [236]	158 [162]	1.484 [1.456]
Acid Subfraction I	304 [288]	216 [196]	1.409 [1.466]	289 [274]	199 [182]	1.449 [1.505]
Acid Subfraction II	273 [302]	203 [216]	1.345 [1.400]	259 [286]	182 [191]	1.422 [1.496]
Acid Subfraction III	255 [429]	175 [242]	1.453 [1.771]	238 [431]	158 [220]	1.501 [1.953]
Base Subfraction I	265 [241]	173 [165]	1.534 [1.458]	246 [222]	160 [151]	1.538 [1.470]
Base Subfraction II	299 [216]	182 [152]	1.638 [1.418]	220 [287]	150 [174]	1.467 [1.644]
Base Subfraction III	331 [291]	218 [148]	1.515 [1.480]	197 [296]	139 [190]	1.420 [1.554]

* MWD data of deasphaltened fractions from duplicate GPC runs are in parantheses.

** MWD data of ion-exchange fractions shown in brackets are from duplicate IEC experiments.

TABLE 19

MWD of Residual Pitch No. 11 and Its Various Maltene and Asphaltene, and Ion-Exchange Extract and Eluate Fractions

CANMET Residual Pitch No. 11	GPC System No. 1			GPC System No. 2		
	Mw	Mn	Mw/Mn	Mw	Mn	Mw/Mn
Whole Pitch	1188 (1087)	418 (410)	2.839 (2.648)	1138 (1132)	464 (465)	2.450 (2.433)
Deasphaltening*						
Pentane Maltene	776 (793)	405 (409)	1.915 (1.935)	794 (782)	435 (432)	1.824 (1.807)
Heptane Maltene	844 (847)	408 (409)	2.066 (2.069)	845 (854)	435 (436)	1.942 (1.958)
Pentane Asphaltene	2122 (2157)	409 (418)	5.187 (5.157)	2446 (2472)	654 (654)	3.740 (3.779)
Heptane Asphaltene	2379 (2464)	385 (392)	6.177 (6.285)	2883 (2822)	598 (593)	4.816 (4.754)
Ion-Exchange Chromatography (IEC)**						
Pentane Eluate	685 [672]	381 [378]	1.797 [1.779]	666 [668]	331 [327]	2.012 [2.041]
Cyclohexane Eluate	880 [825]	401 [375]	2.196 [2.200]	879 [816]	368 [338]	2.382 [2.411]
Combined Pentane + Cyclohexane Eluate	773 [677]	386 [367]	2.003 [1.845]	775 [696]	350 [333]	2.210 [2.085]
Acid Subfraction I	1272 [1181]	493 [470]	2.576 [2.510]	1249 [1182]	474 [448]	2.632 [2.639]
Acid Subfraction II	1260 [1281]	414 [478]	3.040 [2.677]	1260 [1389]	393 [480]	3.206 [2.894]
Acid Subfraction III	1760 [1460]	378 [348]	4.656 [4.186]	2006 [1563]	410 [396]	4.887 [3.941]
Base Subfraction I	1120 [1113]	433 [438]	2.584 [2.536]	1038 [1001]	385 [383]	2.694 [2.607]
Base Subfraction II	1342 [1065]	535 [398]	2.509 [2.671]	1152 [1015]	462 [360]	2.493 [2.818]
Base Subfraction III	604 [1092]	340 [333]	1.776 [3.271]	555 [1048]	300 [303]	1.851 [3.458]

* MWD data of deasphaltened fractions from duplicate GPC runs are in parantheses.

** MWD data of ion-exchange fractions shown in brackets are from duplicate IEC experiments.

TABLE 20

MWD of Residual Pitch No. 12 and Its Various Maltene and Asphaltene, and Ion-Exchange Extract and Eluate Fractions

CANMET Residual Pitch No. 12	GPC System No. 1			GPC System No. 2		
	Mw	Mn	Mw/Mn	Mw	Mn	Mw/Mn
Whole Pitch	380 (347)	184 (196)	2.066 (1.818)	413 (357)	218 (218)	1.889 (1.889)
Deasphaltening*						
Pentane Maltene	351 (344)	235 (232)	1.495 (1.480)	355 (357)	228 (228)	1.558 (1.564)
Heptane Maltene	341 (343)	225 (227)	1.512 (1.511)	342	214	1.598
Pentane Asphaltene	361 (374)	144 (152)	2.506 (2.456)	413	220	1.873
Heptane Asphaltene	378 (382)	159 (166)	2.368 (2.294)	449	229	1.957
Ion-Exchange Chromatography (IEC)**						
Pentane Eluate	369 [328]	245 [214]	1.502 [1.531]	343 [345]	212 [216]	1.616 [1.597]
Cyclohexane Eluate	328 [346]	214 [219]	1.531 [1.579]	321 [327]	190 [195]	1.691 [1.674]
Combined Pentane + Cyclohexane Eluate	345 [352]	226 [228]	1.522 [1.543]	316 [338]	197 [203]	1.605 [1.658]
Acid Subfraction I	396 [411]	276 [297]	1.430 [1.382]	375 [385]	247 [261]	1.517 [1.473]
Acid Subfraction II	403 [345]	261 [234]	1.541 [1.472]	395 [340]	234 [212]	1.687 [1.598]
Acid Subfraction III	293 [414]	186 [247]	1.574 [1.678]	297 [427]	171 [228]	1.732 [1.870]
Base Subfraction I	373 [346]	230 [216]	1.616 [1.597]	374 [340]	217 [200]	1.716 [1.696]
Base Subfraction II	274 [457]	175 [279]	1.567 [1.635]	310 [468]	170 [260]	1.821 [1.799]
Base Subfraction III	404 [322]	262 [184]	1.538 [1.745]	404 [320]	240 [172]	1.683 [1.858]

* MWD data of deasphaltened fractions from duplicate GPC runs are in parantheses.

** MWD data of ion-exchange fractions shown in brackets are from duplicate IEC experiments.

TABLE 21

Elemental Analysis (Wt. %) of Twelve Whole Pitch Samples

Whole Pitch Sample No.	% C	% H	H/C Atomic Ratio	% N	% S	% O*
1	83.47	9.88	1.420	0.00	6.61	0.04
2	59.22	6.26	1.268	1.45	4.14	28.93
3	67.49	6.90	1.226	1.23	6.71	17.67
4	67.29	7.19	1.282	1.36	4.24	19.92
5	82.39	10.35	1.507	0.00	7.20	0.06
6	84.51	9.16	1.300	1.90	4.37	0.06
7	86.44	7.66	1.060	1.34	4.51	0.05
8	84.62	10.60	1.503	0.00	4.73	0.05
9	85.51	8.11	1.138	1.95	4.40	0.03
10	74.72	6.69	1.074	1.30	4.44	12.85
11	85.85	11.47	1.603	0.00	2.59	0.09
12	71.08	8.02	1.158	2.63	2.01	16.26

* by difference

TABLE 22

Elemental Analysis (Wt. %) of Benzene Solubles of Twelve Residual Pitch Samples (C, H, N, S, O*)

Benzene Soluble Sample No.	% C	% H	H/C Atomic Ratio	% N	% S	% O*
1	83.62	9.01	1.292	0.00	7.42	-
2	69.54	6.96	1.201	1.18	4.35	17.97
3	74.26	7.24	1.169	1.34	6.75	10.41
4	75.80	7.48	1.184	1.39	5.52	9.81
5	83.65	9.91	1.421	0.00	6.39	0.05
6	83.61	9.12	1.308	2.90	4.37	0.00
7	86.54	7.62	1.050	1.41	4.42	0.01
8	84.69	10.58	1.499	0.00	4.71	0.02
9	83.57	9.20	1.320	2.01	5.18	0.04
10	70.80	6.64	1.125	1.37	4.74	16.45
11	85.36	11.59	1.629	0.00	2.96	0.09
12	80.61	8.13	1.210	1.27	2.37	7.62

* by difference

TABLE 23

Elemental Analysis (Wt. %) of Twelve Pentane-Maltene Samples

Pentane-Maltene Sample No.	% C	% H	H/C Atomic Ratio	% N	% S	% O*
1	82.41	10.15	1.477	0.00	7.48	-
2	87.29	8.37	1.150	0.00	4.29	0.05
3	85.37	8.71	1.224	0.00	5.94	-
4	86.55	8.84	1.225	0.00	4.65	-
5	82.41	11.55	1.680	0.00	6.02	0.02
6	84.11	9.87	1.408	1.33	4.67	0.02
7	87.11	8.66	1.192	0.00	4.14	0.09
8	82.96	12.05	1.743	0.00	4.89	0.10
9	83.77	10.16	1.455	1.53	4.51	0.03
10	85.82	9.06	1.266	0.00	4.35	0.77
11	84.52	12.36	1.754	1.16	1.92	0.04
12	87.40	9.69	1.330	0.00	2.91	0.00

* by difference

TABLE 24

Elemental Analysis (Wt. %) of Twelve Pentane-Asphaltene Samples

Pentane-Asphaltene Sample No.	% C	% H	H/C Atomic Ratio	% N	% S	% O*
1	73.75	7.98	1.298	2.13	8.29	7.85
2	51.91	5.38	1.243	1.52	4.92	36.27
3	52.50	5.72	1.307	1.46	7.02	33.30
4	48.99	5.43	1.330	1.46	4.84	39.28
5	71.93	8.06	1.344	1.30	8.02	10.69
6	77.06	7.40	1.152	2.08	4.59	8.87
7	87.49	5.97	0.81	2.01	4.50	0.03
8	66.80	7.26	1.304	1.10	6.46	18.38
9	86.37	7.00	0.972	1.87	4.77	-
10	50.91	5.15	1.213	1.62	4.66	37.66
11	85.33	8.86	1.245	1.74	4.09	-
12	57.15	5.59	1.173	1.54	2.93	32.79

* by difference

TABLE 25

Elemental Analysis (Wt. %) of Twelve Heptane-Maltene Samples

Heptane-Maltene Sample No.	% C	% H	H/C Atomic Ratio	% N	% S	% O*
1	82.93	11.04	1.597	0.00	6.01	0.02
2	83.00	8.46	1.223	1.20	4.44	2.90
3	85.65	8.77	1.228	0.00	5.61	-
4	87.09	8.91	1.227	0.00	4.02	-
5	82.68	10.89	1.580	0.00	6.52	-
6	84.42	10.02	1.424	1.47	4.10	-
7	85.85	8.33	1.164	1.18	4.56	0.08
8	84.76	10.81	1.530	0.00	4.24	0.19
9	84.62	9.48	1.344	1.03	4.80	0.07
10	85.79	8.36	1.169	1.08	4.64	0.16
11	84.84	12.13	1.715	0.77	2.30	-
12	87.54	8.66	1.187	1.10	2.76	-

* by difference

TABLE 26

Elemental Analysis (Wt. %) of Twelve Heptane-Asphaltene Samples

Heptane-Asphaltene Sample No.	% C	% H	H/C Atomic Ratio	% N	% S	% O*
1	68.87	7.58	1.320	1.30	6.91	15.34
2	58.44	5.75	1.18	1.49	4.98	29.34
3	53.00	5.63	1.274	1.44	7.14	32.79
4	50.17	5.35	1.279	1.34	4.67	38.47
5	69.83	7.59	1.304	1.39	7.79	13.40
6	68.51	7.33	1.283	1.68	4.91	17.57
7	87.26	6.05	0.83	2.06	4.68	-
8	62.99	7.03	1.339	1.12	6.39	22.47
9	85.85	7.78	1.08	1.51	4.85	0.01
10	49.17	5.07	1.237	1.56	3.89	40.31
11	86.25	8.43	1.172	1.43	3.99	-
12	62.53	6.26	1.201	1.49	2.52	27.20

* by difference

TABLE 27

Ion-Exchange Chromatographic Results of Pentane-Maltenes of Twelve Residual Pitch Samples

Eluents	Sample No. 1 (%)	Sample No. 2 (%)	Sample No. 3 (%)	Sample No. 4 (%)	Sample No. 5 (%)	Sample No. 6 (%)	Sample No. 7 (%)	Sample No. 8 (%)	Sample No. 9 (%)	Sample No. 10 (%)	Sample No. 11 (%)	Sample No. 12 (%)
Pentane Eluate	74.62 (77.36)*	69.91 (68.14)	78.45 (65.95)	65.99 (72.99)	77.24 (79.20)	73.09 (73.46)	66.81 (73.55)	86.44 (85.54)	73.29 (52.04)	81.91 (69.20)	83.97 (83.13)	76.99 (76.19)
Cyclohexane Eluate	7.65 (8.12)	3.34 (2.74)	2.74 (7.34)	4.08 (3.31)	2.26 (6.50)	3.93 (5.47)	2.07 (6.65)	2.53 (3.24)	10.51 (13.34)	5.36 (11.46)	3.34 (3.05)	5.30 (5.42)
Benzene (A-1)	10.45 (8.83)	16.81 (15.93)	4.97 (10.12)	12.20 (8.43)	1.77 (6.95)	4.30 (6.99)	4.25 (10.10)	2.67 (4.94)	8.12 (17.13)	4.32 (10.49)	2.50 (6.60)	4.39 (8.74)
60% Benzene: 40% MeOH (A-2)	1.29 (0.83)	1.96 (1.09)	1.41 (1.28)	2.96 (3.02)	1.16 (1.40)	1.70 (1.19)	1.66 (1.18)	0.84 (0.81)	2.11 (3.18)	1.68 (1.35)	0.79 (0.52)	1.31 (1.47)
80% Benzene: 20% HOAC (A-3)	0.01 (0.014)	0.25 (1.81)	0.52 (0.036)	0.30 (1.33)	1.93 (0.20)	0.35 (0.07)	0.48 (0.21)	0.45 (0.0083)	0.42 (0.30)	0.96 (0.13)	0.39 (0.015)	0.67 (0.06)
Benzene (C-1)	7.99 (9.03)	9.80 (8.40)	5.91 (7.31)	11.20 (5.69	3.85 (7.12)	5.44 (10.77)	5.09 (8.52)	3.70 (7.03)	5.31 (11.69)	4.97 (9.44)	2.99 (6.81)	8.14 (9.56)
60% Benzene: 40% MeOH (C-2)	1.79 (2.46)	2.44 (2.43)	1.18 (1.56)	2.67 (1.22)	1.20 (1.43)	1.19 (1.66)	1.26 (0.91)	0.74 (0.86)	0.47 (0.92)	0.73 (0.76)	0.91 (0.78)	1.13 (1.89)
55% Benzene: 37% MeOH: 8% IPA (C-3)	3.18 (1.77)	0.23 (3.76)	9.69 (0.07)	2.30 (6.25)	9.04 (0.44)	9.77 (1.69)	8.56 (0.25)	5.38 (0.075)	1.19 (0.20)	4.64 (0.25)	5.60 (0.13)	7.96 (1.02)
TOTAL	106.89 (108.41)	104.74 (104.30)	104.87 (93.67)	101.30 (102.24)	98.45 (103.24)	99.77 (101.30)	90.18 (101.37)	102.75 (102.50)	101.42 (98.80)	104.57 (103.08)	100.49 (101.04)	105.89 (104.35)

* Results in parantheses are from duplicate experiments

TABLE 28

Compound Type Distribution (%) in Pentane Deasphaltened Maltenes of Twelve Residual Pitch Samples After Ion-Exchange Chromatography

Eluents		1	2	3	4	5	6	7	8	9	10	11	12
Pentane (Saturates)		11.63	18.12	10.63	12.52	16.24	10.11	11.37	20.60	8.91	14.34	31.46	25.43
5% Benzene in Pentane (Mono-Aromatics)		7.99	9.61	6.13	6.15	10.82	6.61	8.17	11.45	5.05	7.74	14.54	8.15
15% Benzene in Pentane (Di-Aromatics)		10.61	13.68	12.46	10.59	14.68	11.01	10.09	13.94	6.58	10.48	10.77	12.18
Benzene (Polyaromatics)		26.40	28.02	32.17	33.04	24.89	36.36	31.35	23.55	34.67	42.68	17.01	33.55
60% MeOH: 20% Benzene: 20% Et.Ether)		24.01	22.64	29.14	21.14	22.12	19.86	32.79	19.73	27.48	20.81	17.48	14.27
Methanol)	Polar Polyaromatics	2.16	0.65	0.70	0.59	1.27	0.45	0.54	0.36	1.92	0.81	2.76	0.46
Pyridine)		5.71	0.44	0.48	0.21	3.51	0.40	0.57	1.41	0.86	0.40	0.86	0.39
Benzene)		0.40	0.15	0.36	0.10	0.18	0.13	0.21	0.07	0.39	0.04	0.16	0.13
TOTAL		88.91	93.30	92.07	84.35	93.77	84.93	95.09	91.11	85.86	97.30	95.04	94.56

TABLE 29

Per Cent by Weight Fraction Distribution in Residual Pitch Samples

(Deasphaltening with n-Pentane)

Fractions	#1	#2	#3	#4	#5	#6	#7	#8	#9	#10	#11	#12
Benzene Insoluble*	3.94	28.31	7.48	5.12	0.91	2.91	2.36	0.62	4.84	5.93	7.23	8.68
Maltene	66.73	33.97	46.44	58.25	66.61	37.49	56.33	82.20	25.85	43.71	78.94	48.59
Asphaltene*	27.97	37.70	46.00	36.24	29.07	48.14	35.20	13.90	67.26	45.28	10.71	39.02
Pentane Eluate	49.79	23.75	36.43	38.44	51.44	27.40	37.63	71.05	18.95	35.80	66.29	37.41
Cyclohexane Eluate	5.11	1.13	1.27	2.38	1.51	1.47	1.17	2.08	2.72	2.34	2.64	2.58
Anion Eluate, A-1*	6.97	5.71	2.31	7.11	1.18	1.61	2.39	2.19	2.09	1.89	1.97	2.13
A-2*	0.86	0.67	0.65	1.72	0.77	0.63	0.94	0.69	0.55	0.73	0.62	0.64
A-3*	0.00	0.08	0.24	0.17	1.28	0.13	0.27	0.37	0.11	0.42	0.31	0.33
Cation Eluate, C-1*	5.33	3.32	2.74	6.52	2.56	2.04	2.87	3.04	1.37	2.17	2.36	3.96
C-2*	1.19	0.83	0.55	1.55	0.79	0.45	0.71	0.61	0.12	0.32	0.72	0.55
C-3*	2.12	0.07	4.50	1.34	6.02	3.66	4.82	4.42	0.31	2.03	4.42	3.87
Saturates*	6.38	4.51	4.00	5.11	8.60	2.92	4.41	15.06	1.93	5.47	21.69	10.17
Monoaromatics*	4.39	1.99	2.31	2.51	5.73	1.91	3.17	8.37	1.09	2.95	10.02	3.26
Diaromatics*	5.82	3.40	4.70	4.32	7.77	3.18	3.92	10.19	1.43	3.99	7.42	4.87
Polyaromatics*	14.49	6.97	11.07	13.32	13.18	10.50	12.16	17.22	7.51	16.28	11.73	13.42
Polar Polyaromatics*	17.50	5.90	11.43	8.95	14.24	5.98	13.37	16.75	6.56	8.55	14.54	6.05
% Total (Fractions marked with *)	96.96	99.46	97.98	93.98	92.10	84.06	86.68	93.43	95.17	96.01	93.74	96.95

TABLE 30

Elemental Analysis (Wt. %) of Ion-Exchange Eluates for Samples 1, 2 and 3

Eluate	Sample No. 1						Sample No. 2						Sample No. 3					
	% C	% H	H/C Atomic Ratio	% N	% S	% O*	% C	% H	H/C Atomic Ratio	% N	% S	% O*	% C	% H	H/C Atomic Ratio	% N	% S	% O*
Combined Pentane and Cyclohexane	84.32	10.55	1.501	0.00	5.19	-	85.45	11.90	1.671	0.00	2.65	0.00	83.59	8.78	1.260	0.00	6.13	1.50
A-1	83.39	8.81	1.267	1.25	6.45	0.10	84.88	7.14	1.009	2.21	2.91	2.86	75.16	7.03	1.122	1.71	5.79	10.31
A-2	72.33	7.96	1.320	2.41	4.16	13.14	78.29	6.44	0.987	3.95	1.76	9.56	71.84	6.69	1.117	3.01	5.27	13.19
A-3	74.06	7.96	1.29	2.43	3.83	11.72	64.91	7.63	1.41	5.44	0.84	21.18	69.39	6.17	1.067	1.57	2.03	20.84
C-1	83.51	9.20	1.321	1.58	5.66	0.05	87.40	7.85	1.077	1.63	3.18	-	82.53	6.79	0.987	1.72	7.23	1.73
C-2	80.04	9.96	1.493	2.79	3.49	3.72	81.62	9.33	1.371	2.69	1.51	4.85	83.81	7.87	1.126	2.57	5.82	-
C-3	51.64	10.73	2.490	10.52	1.16	25.95	58.50	6.89	1.41	2.04	0.35	32.22	84.66	8.29	1.175	3.12	4.03	-

* by difference

TABLE 31

Elemental Analysis (Wt. %) of Ion-Exchange Eluates for Samples 4, 5 and 6

Eluate	Sample No. 4						Sample No. 5						Sample No. 6					
	% C	% H	H/C Atomic Ratio	% N	% S	% O*	% C	% H	H/C Atomic Ratio	% N	% S	% O*	% C	% H	H/C Atomic Ratio	% N	% S	% O*
Combined Pentane and Cyclohexane Eluate	85.55	9.63	1.350	0.00	4.85	-	83.59	10.71	1.537	0.00	5.55	0.15	85.78	9.01	1.260	0.00	3.47	1.74
A-1	78.56	6.84	1.044	2.52	4.53	7.55	73.49	9.34	1.525	1.32	6.00	9.85	86.27	7.44	1.034	3.02	3.43	-
A-2	78.46	6.92	1.058	2.53	4.09	8.00	77.06	9.55	1.487	1.22	7.02	5.15	84.95	6.91	0.976	4.36	2.04	1.74
A-3	65.38	6.45	1.183	0.92	4.05	23.20	73.89	9.60	1.559	0.00	5.27	11.24	67.86	6.78	1.19	1.83	0.21	23.32
C-1	80.47	7.90	1.178	1.48	4.92	5.23	75.55	9.15	1.453	1.38	7.47	6.45	86.32	7.33	1.018	2.17	3.77	0.41
C-2	78.28	7.53	1.154	1.50	6.89	5.80	76.76	9.21	1.439	1.57	5.61	6.85	84.37	7.87	1.119	3.00	3.22	1.54
C-3	77.98	7.55	1.161	2.62	4.36	7.49	79.10	9.96	1.510	2.13	4.58	4.23	85.56	8.66	1.214	3.41	2.40	-

* by difference

TABLE 32

Elemental Analysis (Wt. %) of Ion-Exchange Eluates for Samples 7, 8 and 9

Eluate	Sample No. 7						Sample No. 8						Sample No. 9					
	% C	% H	H/C Atomic Ratio	% N	% S	% O*	% C	% H	H/C Atomic Ratio	% N	% S	% O*	% C	% H	H/C Atomic Ratio	% N	% S	% O*
Combined Pentane and Cyclohexane	86.50	9.61	1.333	0.76	3.17	-	85.67	11.43	1.601	0.00	3.02	-	87.48	8.35	1.145	0.00	4.18	-
A-1	87.47	7.00	0.96	3.44	2.95	-	84.71	8.19	1.160	1.91	4.26	0.93	87.34	5.94	0.816	2.38	3.55	0.79
A-2	87.64	6.68	0.914	3.65	1.96	0.07	82.99	8.47	1.224	2.26	3.63	2.65	84.95	5.85	0.826	3.67	2.46	3.07
A-3	67.36	5.75	1.024	2.48	0.41	24.0	65.44	7.82	1.433	3.99	1.01	21.74	71.95	6.08	1.014	2.90	1.70	17.37
C-1	87.77	6.68	0.913	2.37	3.20	-	85.23	8.91	1.254	1.13	4.73	0.00	87.29	6.16	0.846	1.67	4.11	0.77
C-2	86.22	7.39	1.028	3.10	3.31	-	84.34	9.46	1.345	2.02	4.28	-	83.37	7.00	1.007	2.44	5.79	1.40
C-3	86.07	8.02	1.118	3.46	2.61	-	84.79	9.67	1.368	2.32	3.18	0.04	85.95	7.50	1.047	3.29	3.29	-

* by difference

TABLE 33

Elemental Analysis (Wt. %) of Ion-Exchange Eluates for Samples 10, 11 and 12

Eluate	Sample No. 10						Sample No. 11						Sample No. 12					
	% C	% H	H/C Atomic Ratio	% N	% S	% O*	% C	% H	H/C Atomic Ratio	% N	% S	% O	% C	% H	H/C Atomic Ratio	% N	% S	% O*
Combined Pentane and Cyclohexane	86.84	9.70	1.340	0.00	3.41	0.05	86.07	12.52	1.745	0.00	1.09	0.32	87.49	9.62	1.319	0.00	1.18	1.71
A-1	86.20	6.72	0.935	3.04	3.04	1.00	85.39	8.86	1.245	1.88	2.07	1.80	86.21	7.20	1.002	2.94	1.15	2.50
A-2	86.13	5.88	0.819	3.95	2.31	1.73	84.39	8.65	1.230	1.98	2.01	2.97	84.75	7.00	0.991	4.03	0.98	3.24
A-3	62.53	6.60	1.270	3.31	1.20	26.36	67.91	7.64	1.350	3.29	0.81	20.35	64.12	6.18	1.160	2.37	0.18	27.15
C-1	86.12	6.72	0.936	1.56	4.23	1.37	86.07	8.87	1.236	1.25	2.64	1.17	86.40	7.99	1.109	1.95	1.75	1.91
C-2	83.59	6.69	0.96	2.08	4.85	2.79	85.12	9.53	1.343	1.84	1.96	1.55	85.16	8.60	1.211	2.85	1.65	1.74
C-3	84.51	7.59	1.077	3.24	2.67	1.99	84.30	9.35	2.038	4.13	1.03	1.19	86.54	8.63	1.196	3.18	1.11	0.54

* by difference

TABLE 34

Elemental Analysis (Wt. %) of Compound Type Fractions
of Residual Pitch Samples (C,H,N,S,O)

Sample No.	Saturates						Mono-Aromatics						Di-Aromatics						Polyaromatics					Polar Polyaromatics						
	% C	% H	H/C Atomic Ratio	% N	% S	% O	% C	% H	H/C Atomic Ratio	% N	% S	% O	% C	% H	H/C Atomic Ratio	% N	% S	% D	% C	% H	H/C Atomic Ratio	% N	% S	% O	% C	% H	H/C Atomic Ratio	% N	% S	% D
1	86.65	12.96	1.79	0.00	0.12	0.27	86.05	11.65	1.63	0.00	2.28	0.02	84.45	10.87	1.55	0.00	4.68	0.00	83.97	9.18	1.31	0.00	6.73	0.12	84.00	9.48	1.36	0.00	6.46	0.06
2	85.77	14.27	1.99	0.00	0.00	0.00	86.28	11.99	1.67	0.00	1.76	0.02	86.30	10.37	1.44	0.00	3.36	0.00	87.35	8.27	1.14	0.00	4.36	0.02	86.06	9.09	1.27	1.05	3.88	0.00
3	86.42	13.38	1.86	0.00	0.25	0.00	85.64	12.10	1.69	0.00	2.28	0.00	84.88	10.54	1.49	0.00	4.30	0.28	85.92	7.85	1.09	0.00	6.27	-	85.75	8.83	1.24	0.67	4.63	0.12
4	86.44	13.48	1.87	0.00	0.00	0.08	85.61	11.97	1.68	0.00	2.44	-	85.95	10.04	1.40	0.00	3.81	0.20	86.60	7.38	1.02	0.00	5.27	0.75	83.11	10.14	1.46	0.00	6.51	0.24
5	85.36	13.60	1.91	0.00	0.95	0.09	84.83	11.74	1.66	0.00	3.55	-	83.03	11.26	1.63	0.00	5.43	0.28	82.22	9.43	1.38	0.00	6.51	1.84	85.86	8.42	1.17	0.94	4.33	0.45
6	86.51	13.48	1.87	0.00	0.00	0.01	85.91	11.98	1.67	0.00	2.11	0.00	85.89	10.19	1.42	0.00	3.90	0.02	85.86	8.58	1.19	0.00	5.33	0.23	85.06	9.20	1.30	0.64	5.09	0.01
7	85.99	13.97	1.95	0.00	0.00	0.04	86.02	12.28	1.71	0.00	1.55	0.15	86.29	10.53	1.46	0.00	3.12	0.06	86.18	9.12	1.26	0.00	4.17	0.53	85.98	9.82	1.37	0.00	3.87	0.33
8	86.16	13.79	1.92	0.00	0.00	0.05	85.22	12.53	1.76	0.00	2.42	-	85.07	11.57	1.63	0.00	3.69	-	85.62	9.39	1.32	0.00	5.00	-	84.90	9.44	1.33	0.00	5.42	0.24
9	86.22	13.78	1.92	0.00	0.00	0.00	86.77	12.72	1.76	0.00	0.33	0.18	86.29	10.66	1.48	0.00	3.15	-	86.45	7.30	1.01	0.00	6.34	-	87.23	7.04	0.97	0.00	5.50	0.23
10	86.77	13.24	1.83	0.00	0.00	0.00	86.15	12.60	1.76	0.00	1.39	0.00	86.39	10.24	1.42	0.00	3.34	0.03	86.96	8.05	1.11	0.00	4.80	0.19	88.01	7.39	1.01	0.00	4.58	0.02
11	86.85	13.22	1.83	0.00	0.00	0.00	88.07	11.84	1.61	0.00	0.00	0.09	86.79	11.50	1.59	0.00	1.59	0.12	86.81	10.54	1.46	0.00	2.60	0.05	86.56	10.72	1.49	0.00	2.20	0.52
12	86.82	13.04	1.80	0.00	0.00	0.14	87.51	11.80	1.62	0.00	0.62	0.07	89.03	9.25	1.25	0.00	1.69	0.03	89.91	8.02	1.07	0.00	2.05	0.02	89.81	8.17	1.09	0.00	2.00	0.00

* by difference

TABLE 35

Nitrogen Content (wt. %) of the Fractions in Residual Pitch Samples (Deasphaltening with n-Pentane)

Fractions	#1	#2	#3	#4	#5	#6	#7	#8	#9	#10	#11	#12
Whole Pitch	0.00	1.45	1.23	1.36	0.00	1.90	1.34	0.00	1.95	1.30	0.00	2.63
Benzene Solubles	0.00	1.18	1.34	1.39	0.00	2.90	1.41	0.00	2.01	1.37	0.00	1.27
Asphaltene	2.13	1.52	1.46	1.46	1.30	2.08	2.01	1.10	1.87	1.62	1.74	1.54
Maltene	0.00	0.00	0.00	0.00	0.00	1.33	0.00	0.00	1.53	0.00	1.16	0.00
Combined Pentane & Cyclohexane Eluate	0.00	0.00	0.00	0.00	0.00	0.00	0.76	0.00	0.00	0.00	0.00	0.00
Anion Eluate, A-1	1.25	2.21	1.71	2.52	1.32	3.02	3.44	1.91	2.38	3.04	1.88	2.94
A-2	2.41	3.95	3.01	2.53	1.22	4.36	3.65	2.26	3.67	3.95	1.98	4.03
A-3	2.43	5.44	1.57	0.92	0.00	1.83	2.48	3.99	2.90	3.31	3.29	2.37
Cation Eluate, C-1	1.58	1.63	1.72	1.48	1.38	2.17	2.37	1.13	1.67	1.56	1.25	1.95
C-2	2.79	2.69	2.57	1.50	1.57	3.00	3.10	2.02	2.44	2.08	1.84	2.85
C-3	10.52	2.04	3.12	2.62	2.13	3.41	3.46	2.32	3.29	3.24	4.13	3.18
Saturates	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Mono-aromatics	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Di-aromatics	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Polyaromatics	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Polar Polyaromatics	0.00	1.05	0.67	0.00	0.94	0.64	0.00	0.00	0.00	0.00	0.00	0.00

TABLE 36

Amounts of Nitrogen (grams) in the Fractions from 100 grams of Residual Pitch Samples (Deasphaltening with n-Pentane)

Fractions	#1	#2	#3	#4	#5	#6	#7	#8	#9	#10	#11	#12
Whole Pitch	0.00	1.45	1.23	1.36	0.00	1.90	1.34	0.00	1.95	1.30	0.00	2.63
Benzene Solubles	0.00	0.845	1.24	1.31	0.00	2.48	1.29	0.00	1.87	1.22	0.00	1.11
Asphaltene	0.595	0.573	0.671	0.529	0.377	1.00	0.756	0.782	0.354	0.580	1.15	0.576
Maltene	0.00	0.00	0.00	0.00	0.00	0.485	0.00	0.00	0.395	0.00	0.916	0.00
Combined Pentane & Cyclohexane Eluate	0.00	0.00	0.00	0.00	0.00	0.00	0.295	0.00	0.00	0.00	0.00	0.00
Anion Eluate, A-1	0.087	0.126	0.039	0.179	0.015	0.049	0.082	0.042	0.050	0.057	0.037	0.062
A-2	0.020	0.026	0.019	0.043	0.009	0.027	0.034	0.016	0.020	0.029	0.012	0.026
A-3	0.00	0.004	0.003	0.001	0.00	0.002	0.006	0.014	0.003	0.014	0.01	0.008
Cation Eluate, C-1	0.084	0.054	0.047	0.096	0.035	0.044	0.068	0.034	0.023	0.034	0.029	0.077
C-2	0.033	0.022	0.014	0.023	0.012	0.014	0.022	0.012	0.003	0.007	0.013	0.016
C-3	0.223	0.001	0.140	0.035	0.128	0.125	0.167	0.103	0.010	0.066	0.183	0.123
Saturates	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Mono-aromatics	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Di-aromatics	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Polyaromatics	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Polar Polyaromatics	0.00	0.061	0.076	0.00	0.133	0.038	0.00	0.00	0.00	0.00	0.00	0.00

TABLE 37

Sulfur Content (wt. %) of the Fractions in Residual Pitch Samples (Deasphalting with n-Pentane)

Fractions		#1	#2	#3	#4	#5	#6	#7	#8	#9	#10	#11	#12
Whole Pitch		6.61	4.14	6.71	4.24	7.20	4.37	4.51	4.73	4.40	4.44	2.59	2.01
Benzene Solubles		7.42	4.35	6.75	5.52	6.39	4.37	4.42	4.71	5.18	4.74	2.96	2.37
Asphaltene		8.29	4.92	7.02	4.84	8.02	4.59	4.50	6.46	4.77	4.66	4.09	2.93
Maltene		7.48	4.29	5.94	4.65	6.02	4.67	4.14	4.89	4.51	4.35	1.92	2.91
Combined Pentane & Cyclohexane Eluate		5.19	2.65	6.13	4.85	5.55	3.47	3.17	3.02	4.18	3.41	1.09	1.18
Anion Eluate,	A-1	6.45	2.91	5.79	4.53	6.00	3.43	2.95	4.26	3.55	3.04	2.07	1.15
	A-2	4.16	1.76	5.27	4.09	7.02	2.04	1.96	3.63	2.46	2.31	2.01	0.98
	A-3	3.83	0.84	2.03	4.05	5.27	0.21	0.41	1.01	1.70	1.20	0.81	0.18
Cation Eluate,	C-1	5.66	3.18	7.23	4.92	7.47	3.77	3.20	4.73	4.11	4.23	2.64	1.75
	C-2	3.49	1.51	5.82	6.89	5.61	3.22	3.31	4.28	5.79	4.85	1.96	1.65
	C-3	1.16	0.35	4.03	4.36	4.58	2.40	2.61	3.18	3.29	2.67	1.03	1.11
Saturates		0.12	0.00	0.25	0.00	0.95	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Mono-aromatics		2.28	1.76	2.28	2.44	3.55	2.11	1.55	2.42	0.33	1.39	0.00	0.62
Di-aromatics		4.68	3.36	4.30	3.81	5.43	3.90	3.12	3.69	3.15	3.34	1.59	1.69
Polyaromatics		6.73	4.36	6.27	5.27	6.51	5.33	4.17	5.00	6.34	4.80	2.60	2.05
Polar Polyaromatics		6.46	3.88	4.63	6.51	4.33	5.09	3.87	5.42	5.50	4.58	2.20	2.00

TABLE 38

Amounts of Sulfur (grams) in the Fractions from 100 grams of Residual Pitch Samples (Deasphalting with n-Pentane)

Fractions	#1	#2	#3	#4	#5	#6	#7	#8	#9	#10	#11	#12
Whole Pitch	6.61	4.14	6.71	4.24	7.20	4.37	4.51	4.73	4.40	4.44	2.59	2.01
Benzene Solubles	7.03	3.12	6.24	5.21	6.11	3.74	4.05	4.53	4.82	4.22	2.65	2.08
Asphaltene	2.32	1.85	3.23	1.75	2.33	2.21	1.59	0.90	3.21	2.11	0.44	1.14
Maltene	4.99	1.46	2.75	2.71	4.01	1.75	2.33	4.02	1.16	1.90	1.52	1.41
Combined Pentane & Cyclohexane Eluate	2.85	0.66	2.31	2.00	2.94	1.00	1.23	2.21	0.91	1.30	0.75	0.47
Anion Eluate, A-1	0.45	0.17	0.13	0.32	0.07	0.06	0.07	0.09	0.07	0.06	0.04	0.02
A-2	0.036	0.012	0.034	0.070	0.054	0.013	0.018	0.025	0.013	0.017	0.012	0.006
A-3	0.00	0.001	0.005	0.007	0.067	0.00	0.001	0.003	0.002	0.005	0.003	0.00
Cation Eluate, C-1	0.30	0.11	0.20	0.32	0.19	0.08	0.09	0.14	0.05	0.09	0.06	0.07
C-2	0.041	0.013	0.032	0.107	0.044	0.014	0.023	0.026	0.007	0.016	0.014	0.009
C-3	0.025	0.00	0.181	0.058	0.276	0.088	0.126	0.141	0.010	0.054	0.046	0.043
Saturates	0.007	0.00	0.00	0.00	0.081	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Mono-aromatics	0.100	0.035	0.052	0.061	0.203	0.040	0.076	0.202	0.003	0.041	0.00	0.02
Di-aromatics	0.273	0.114	0.202	0.164	0.421	0.124	0.122	0.376	0.045	0.133	0.118	0.082
Polyaromatics	0.975	0.303	0.694	0.701	0.858	0.559	0.507	0.861	0.476	0.781	0.297	0.275
Polar Polyaromatics	1.130	0.228	0.529	0.582	0.616	0.304	0.517	0.907	0.361	0.392	0.319	0.121

TABLE 39

Comparison of Average Molecular Weights in Maltenes and Ion-Exchange Eluates of Twelve Residual Pitch Samples

Decreasing MW

Sample No.	Whole Pitch	Pentane Maltene	Pentane Eluate	Cyclohexane Eluate	Combined Eluate	A-1	A-2	A-3	C-1	C-2	C-3
5	3304* 510** 6.47***	1199 483 2.48	1015 433 2.34	1543 509 3.03	1180 373 3.16	1778 558 3.18	1692 429 3.94	5317 751 10.52	1771 548 3.23	1627 564 2.89	1540 655 2.35
1	2563 470 5.45	1202 488 2.46	852 407 2.09	1347 461 2.92	1263 470 2.69	1856 575 3.22	1471 479 3.06	3062 566 5.40	1650 499 3.31	1512 505 2.99	1762 413 4.27
8	1362 445 3.06	884 429 2.06	821 410 1.99	979 373 2.61	848 380 2.23	1347 490 2.74	1356 419 3.23	1226 230 5.32	1191 419 2.85	1269 432 2.93	1191 464 2.57
11	1188 418 2.84	776 405 1.92	685 381 1.79	880 401 2.19	773 386 2.00	1272 493 2.58	1260 414 3.04	1760 378 4.66	1120 433 2.58	1342 535 2.51	694 340 1.78
3	674 214 3.15	431 268 1.61	433 274 1.58	413 234 1.76	425 254 1.67	562 317 1.77	524 285 1.84	566 239 2.36	426 240 1.77	521 286 1.82	544 312 1.74
7	490 228 2.14	392 258 1.16	404 270 1.49	412 247 1.67	402 253 1.59	487 306 1.59	418 257 1.65	535 248 2.15	442 257 1.72	489 276 1.77	502 306 1.64
4	466 223 2.09	397 241 1.64	395 244 1.62	347 217 1.59	365 227 1.61	491 274 1.79	504 266 1.89	589 263 2.23	414 229 1.81	414 227 1.82	490 273 1.80
6	429 192 2.23	384 240 1.60	415 251 1.65	343 212 1.62	380 232 1.63	450 289 1.55	458 267 1.71	649 278 2.33	385 222 1.73	502 267 1.88	500 290 1.72
2	384 186 2.06	345 214 1.61	446 258 1.72	386 224 1.72	426 244 1.74	368 222 1.66	380 224 1.69	618 319 1.93	386 212 1.82	473 247 1.91	445 221 2.01
12	380 184 2.07	351 235 1.49	369 245 1.50	328 214 1.53	345 226 1.52	396 276 1.43	403 261 1.54	293 186 1.57	373 230 1.62	274 175 1.57	404 262 1.54
10	290 163 1.78	255 182 1.40	267 191 1.39	234 162 1.44	250 174 1.44	304 216 1.41	273 203 1.35	255 175 1.45	265 173 1.53	299 182 1.64	331 218 1.52
9	261 148 1.76	239 176 1.36	243 181 1.34	226 166 1.36	237 174 1.36	281 194 1.45	303 211 1.44	386 205 1.88	233 161 1.45	302 193 1.56	315 216 1.46

* Mw　　** Mn　　*** Mw/Mn

TABLE 40

IR Spectral Analysis of Model Compounds in CH_2Cl_2 and THF
(Concentration, Band Position, Absorbance and Functional Groups)

Compound Type	Concentration in CH_2Cl_2 [mmole/L]	Strongest Absorption Bands							
		3800 - 3200 cm^{-1}			1900 - 1450 cm^{-1}				
		Hydrogen Stretching			C = O Stretching			Ring Stretching	
		Groups cm^{-1}	Absorbance A	A/mmole/L	Groups cm^{-1}	Absorbance A	A/mmole/L	Type	cm^{-1}
Pyrrolic		N-H							
Carbazole	33.8	3470	0.263	0.008				Pyrrole	1490
2-Methylindole	47.5	3470	0.423	0.009				Pyrrole	1555
Amide		$(QCO)NH_2$			$(QCO)NH_2$				
Benzamide	10.6	3530	0.049	0.005	1685	0.375	0.035	Benzene	1590
		3410	0.066	0.006					
	(19.5)*				(1685)	(0.997)	(0.051)		
	31.3	3530	0.167	0.005					
		3410	0.227	0.007	1685				
Carboxylic Acid		(CO)OH			(CO)OH				
Benzoic Acid	15.1	3500			1735	0.229	0.015	Benzene	1605
					1695	0.274	0.018		
	(13.8)				(1720)	(0.490)	(0.036)		
Salicylic Acid	30.9	3480			1690	0.592	0.019	Benzene	1485
Phenylacetic Acid	28.1	3490			1665	0.430	0.014		
Phenylacetic Acid	28.1	3490			1740	0.184	0.006	Benzene	1495
					1710	0.500	0.018		
Cyclohexane Carboxylic Acid	37.4	3500			1740	0.337	0.009	Saturated	
					1705	0.761	0.020		
Cyclohexyl Acetic Acid	44.1	3500			1750	0.328	0.007	Saturated	
					1735	0.221	0.005		
					1750	0.937	0.021		
Phenols		(Q)OH free							
2,6-Di-tert butyl phenol	26.7	3640						Benzene	1600
2.4-Di-methyl phenol	38.9	3600						Benzene	1505
2,6-Di-methyl phenol	31.7	3610						Benzene	1475
3,5-Di-methyl phenol	28.3	3590						Benzene	1595
Naphthol	29.7	3580						Benzene	1595
1-Hydroxy-isoquinoline	17.8	3400						Pyridine	1660
	37.6								
8-Hydroxy quinoline	24.3	3420						Pyridine	1510
Other N-Hetero Aromatics									
Acridine	31.7							Pyridine	1520
Phenanthridine	32.7							Pyridine	1620
5,6-Benzoquinoline	34.0							Pyridine	1495

* Values in parenthesis from analysis in THF

TABLE 41

IR Analysis of Ion-Exchange Eluate Fractions of #1 Residual Pitch Pentane-Maltene in CH_2Cl_2

Fraction	Concentration mg/g Solvent	Pyrrolic Compounds, 3470 cm^{-1}					Carboxylic Acids 1695 cm^{-1}, 1735 cm^{-1}					Aromatic Ring 1605 cm^{-1}			
			Expressed as Carbazole					Expressed as Benzoic Acid							
		Absorbance A	mg/g Solvent (from Calibration Curve)	mmole* /g Fraction	mmole /g Maltene	mmole /g Residual Pitch	Absorbance A	mg/g Solvent (from Calibration Curve)	mmole* /g Fraction (Average of Two Values)	mmole /g Maltene	mmole /g Residual Pitch	Absorbance A	A/g Fraction	A/g Maltene	A/g Residual Pitch
Pentane Eluate	71.24	-	-	-	-	-	ND	ND	ND	ND	ND	0.12	1.73	0.09	0.06
Cyclohexane Eluate	41.53	0.035	0.50	0.07	0.006	0.004	ND	ND	ND	ND	ND	0.13	3.08	0.24	0.16
Anion Eluate, A-1	10.02	0.037	0.52	0.31	0.03	0.02	ND	ND	ND	ND	ND	0.06	5.99	0.63	0.42
A-2	9.58	0.038	0.54	0.34	0.004	0.002	ND	ND	ND	ND	ND	0.26	27.35	0.35	0.24
A-3	3.82	-	-	-	-	-	0.231 (1695 cm^{-1}) 0.205 (1735 cm^{-1})	1.14 1.13	2.43	0.002	0.001	0.04	10.99	0.09	0.06
Cation Eluate, C-1	9.57	0.017	0.24	0.15	0.01	0.007	ND	ND	ND	ND	ND	0.05	5.12	0.41	0.27
C-2	6.69	-	-	-	-	-	ND	ND	ND	ND	ND	0.04	4.48	0.08	0.05
C-3	5.09	-	-	-	-	-	ND	ND	ND	ND	ND	0.03	6.88	0.22	0.15

ND = Not determined

\- = None detected

* = Method of calculation: MW of Carbazole 167.20

MW of Benzoic Acid 122.12

$$\text{mmole Carbazole (Benzoic Acid)} \Big/ \text{g Fraction} = \frac{1000 \times \text{mg Carbazole (Benzoic Acid)} \big/ \text{g } CH_2Cl_2}{1000 \times \text{MW}} \times \frac{1000}{\text{mg Fraction} \big/ \text{g } CH_2Cl_2}$$

TABLE 42

IR Analysis of Ion-Exchange Eluate Fractions of #2 Residual Pitch Pentane-Maltene in CH_2Cl_2

Fraction	Concentration mg/g Solvent	Pyrrolic Compounds, 3470 cm^{-1}					Carboxylic Acids 1695 cm^{-1}, 1735 cm^{-1}					Aromatic Ring 1605 cm^{-1}			
			Expressed as Carbazole					Expressed as Benzoic Acid							
		Absorbance A	mg/g Solvent (from Calibration Curve)	mmole* /g Fraction	mmole /g Maltene	mmole /g Residual Pitch	Absorbance A	mg/g Solvent (from Calibration Curve)	mmole* /g Fraction (Average of Two Values)	mmole /g Maltene	mmole /g Residual Pitch	Absorbance A	A/g Fraction	A/g Maltene	A/g Residual Pitch
Pentane Eluate	66.95	0.03	0.42	0.04	0.03	0.01	ND	ND	NO	ND	ND	0.15	2.24	1.56	0.53
Cyclohexane Eluate	62.46	0.09	1.32	0.13	0.004	0.001	ND	ND	NO	ND	ND	0.26	4.16	0.14	0.05
Anion Eluate, A-1	9.08	0.07	0.95	0.63	0.11	0.04	NO	NO	NO	NO	ND	0.04	4.41	0.74	0.25
A-2	9.93	0.14	2.05	1.24	0.02	0.01	ND	ND	ND	NO	NO	0.10	9.97	0.19	0.06
A-3	1.22	0.01	0.11	0.54	0.001	0.0004	- (1695 cm^{-1}) - (1735 cm^{-1})	- -	- -	- -	- -	0.14	11.47	0.03	0.01
Cation Eluate, C-1	8.96	0.03	0.38	0.25	0.02	0.01	NO	NO	NO	ND	ND	0.06	6.36	0.62	0.21
C-2	8.75	-	-	-	-	-	NO	NO	NO	ND	NO	0.10	11.31	0.28	0.09
C-3	4.71	-	-	-	-	-	ND	NO	ND	NO	ND	0.06	12.74	0.03	0.01

Footnotes: See Table 41

TABLE 43

IR Analysis of Ion-Exchange Eluate Fractions of #3 Residual Pitch Pentane-Maltene in CH_2Cl_2

Fraction	Concentration mg/g Solvent	Pyrrolic Compounds, 3470 cm^{-1}					Carboxylic Acids 1695 cm^{-1}, 1735 cm^{-1}					Aromatic Ring 1605 cm^{-1}			
			Expressed as Carbazole					Expressed as Benzoic Acid							
		Absorbance A	mg/g Solvent (from Calibration Curve	mmole*/g Fraction	mmole/g Maltene	mmole/g Residual Pitch	Absorbance A	mg/g Solvent (from Calibration Curve)	mmole*/g Fraction (Average of Two Values)	mmole/g Maltene	mmole/g Residual Pitch	Absorbance A	A g Fraction	A g Maltene	A g Residual Pitch
Pentane Eluate	81.49	0.06	0.85	0.06	0.05	0.02	ND	ND	ND	ND	ND	0.22	2.72	2.13	0.99
Cyclohexane Eluate	89.99	0.20	2.88	0.19	0.005	0.002	ND	ND	ND	ND	ND	0.36	4.00	0.11	0.05
Anion Eluate, A-1	8.10	0.07	0.95	0.70	0.03	0.02	ND	ND	ND	ND	ND	0.05	6.17	0.31	0.14
A-2	9.57	0.11	1.63	1.02	0.01	0.007	ND	ND	ND	ND	ND	0.05	5.54	0.08	0.04
A-3	3.57	-	-	-	-	-	0.35 (1695 cm^{-1}) 0.26 (1735 cm^{-1})	1.52 1.51	3.47	0.02	0.01	0.08	22.97	0.12	0.06
Cation Eluate, C-1	7.29	0.03	0.47	0.39	0.02	0.01	ND		ND	ND	ND	0.04	6.04	0.36	0.17
C-2	7.65	0.02	0.33	0.26	0.003	0.001	ND		ND	ND	ND	0.05	6.27	0.07	0.03
C-3	6.77	0.01	0.16	0.14	0.01	0.006	ND		ND	ND	ND	0.07	10.34	1.00	0.46

Footnotes: See Table 41

TABLE 44

IR Analysis of Ion-Exchange Eluate Fractions of #4 Residual Pitch Pentane-Maltene in CH_2Cl_2

Fraction	Concentration mg/g Solvent	Pyrrolic Compounds, 3470 cm^{-1}					Carboxylic Acids 1695 cm^{-1}, 1735 cm^{-1}					Aromatic Ring 1605 cm^{-1}			
		Absorbance A	Expressed as Carbazole				Absorbance A	Expressed as Benzoic Acid				Absorbance A	A g Fraction	A g Maltene	A g Residual Pitch
			mg/g Solvent (from Calibration Curve)	mmole*/g Fraction	mmole/g Maltene	mmole/g Residual Pitch		mg/g Solvent (from Calibration Curve)	mmole*/g Fraction (Average of Two Values)	mmole/g Maltene	mmole/g Residual Pitch				
Pentane Eluate	39.97	0.03	0.46	0.07	0.04	0.04	ND	ND	ND	ND	ND	0.13	1.73	1.13	0.66
Cyclohexane Eluate	60.29	0.14	2.04	0.20	0.008	0.005	ND	ND	ND	ND	ND	4.31	0.17	0.17	0.10
Anion Eluate, A-1	6.16	0.04	0.63	0.61	0.07	0.04	ND	ND	ND	ND	ND	0.05	7.30	0.61	0.36
A-2	4.69	0.06	0.86	1.10	0.03	0.02	ND	ND	ND	ND	ND	0.04	9.30	0.09	0.05
A-3	6.04	-	-	-	-	-	0.44 (1695 cm^{-1}) 0.32 (1735 cm^{-1})	1.82 2.14	2.68	0.008	0.004	0.08	13.74	0.18	0.10
Cation Eluate, C-1	5.85	0.04	0.56	0.57	0.06	0.04	ND	ND	ND	ND	ND	0.06	10.08	0.57	0.33
C-2	6.59	0.02	0.29	0.25	0.007	0.004	ND	ND	ND	ND	ND	0.02	3.49	0.04	0.02
C-3	7.12	-	-	-	-	-	ND	ND	ND	ND	ND	0.06	8.71	0.54	0.31

Footnotes: See Table 41

TABLE 45

IR Analysis of Ion-Exchange Eluate Fractions of #5 Residual Pitch Pentane-Maltene in CH_2Cl_2

Fraction	Concentration mg/g Solvent	Pyrrolic Compounds, 3470 cm^{-1}					Carboxylic Acids 1694 cm^{-1}, 1735 cm^{-1}					Aromatic Ring 1605 cm^{-1}			
		Absorbance A	Expressed as Carbazole				Absorbance A	Expressed as Benzoic Acid				Absorbance A	A/g Fraction	A/g Maltene	A/g Residual Pitch
			mg/g Solvent (from Calibration Curve)	mmole*/g Fraction	mmole/g Maltene	mmole/g Residual Pitch		mg/g Solvent (from Calibration Curve)	mmole*/g Fraction (Average of Two Values)	mmole/g Maltene	mmole/g Residual Pitch				
Pentane Eluate	66.47	0.03	0.40	0.04	0.03	0.02	ND	ND	ND	ND	ND	0.07	1.08	0.84	0.56
Cyclohexane Eluate	85.93	0.10	1.50	0.10	0.002	0.002	ND	ND	ND	ND	ND	0.21	2.44	0.05	0.03
Anion Eluate, A-1	8.02	0.02	0.30	0.22	0.004	0.003	ND	ND	ND	ND	ND	0.04	4.86	0.09	0.06
A-2	7.79	0.01	0.14	0.11	0.001	0.001	ND	ND	ND	ND	ND	0.03	3.59	0.04	0.03
A-3	10.03	-	-	-	-	-	0.37 (1695 cm^{-1}) 0.30 (1735 cm^{-1})	1.61 1.91	1.76	0.03	0.02	0.06	6.08	0.12	0.08
Cation Eluate, C-1	11.24	0.02	0.28	0.15	0.006	0.004	ND	ND	ND	ND	ND	0.04	3.11	0.12	0.08
C-2	8.44	0.01	0.05	0.04	0.0004	0.0002	ND	ND	ND	ND	ND	0.03	3.44	0.04	0.03
C-3	9.23	-	-	-	-	-	ND	ND	ND	ND	ND	0.05	4.88	0.44	0.29

Footnotes: See Table 41

TABLE 46

IR Analysis of Ion-Exchange Eluate Fractions or #6 Residual Pitch Pentane-Maltene in CH_2Cl_2

Fraction	Concentration mg/g Solvent	Pyrrolic Compounds, 3470 cm^{-1}					Carboxylic Acids 1695 cm^{-1}, 1735 cm^{-1}					Aromatic Ring 1605 cm^{-1}			
			Expressed as Carbazole					Expressed as Benzoic Acid							
		Absorbance A	mg/g Solvent (from Calibration Curve)	mmole* /g Fraction	mmole /g Maltene	mmole /g Residual Pitch	Absorbance A	mg/g Solvent (from Calibration Curve)	mmole* /g Fraction (Average of Two Values)	mmole /g Maltene	mmole /g Residual Pitch	Absorbance A	A/g Fraction	A/g Maltene	A/g Residual Pitch
Pentane Eluate	52.29	0.05	0.70	0.08	0.06	0.02	NO	NO	ND	ND	ND	0.19	3.71	2.71	1.02
Cyclohexane Eluate	43.17	0.13	1.89	0.26	0.01	0.004	ND	ND	ND	ND	ND	0.23	5.33	0.21	0.08
Anion Eluate, A-1	9.48	0.11	1.60	1.01	0.04	0.02	ND	ND	ND	ND	ND	0.07	7.38	0.32	0.12
A-2	8.84	0.14	2.08	1.41	0.02	0.01	ND	ND	ND	ND	ND	0.10	11.31	0.19	0.07
A-3	5.14	-	-	-	-	-	0.24 (1695 cm^{-1}) - (1735 cm^{-1})	1.17 1.27	1.94	0.007	0.003	0.08	14.98	0.05	0.02
Cation Eluate, C-1	8.22	0.05	0.65	0.48	0.03	0.01	ND	ND	ND	ND	ND	0.06	7.18	0.39	0.15
C-2	8.87	0.03	0.35	0.24	0.003	0.001	ND	ND	ND	ND	ND	0.07	7.78	0.09	0.03
C-3	6.13	0.01	0.11	0.11	0.01	0.004	ND	ND	ND	ND	ND	0.06	10.44	1.02	0.38

Footnotes: See Table 41

TABLE 47

IR Analysis of Ion-Exchange Eluate Fractions
or #7 Residual Pitch Pentane-Maltene in CH_2Cl_2

		Pyrrolic Compounds, 3470 cm^{-1}					Carboxylic Acids 1695 cm^{-1}, 1735 cm^{-1}					Aromatic Ring 1605 cm^{-1}			
			Expressed as Carbazole					Expressed as Benzoic Acid							
	Concentration mg/g Solvent	Absorbance A	mg/g Solvent (from Calibration Curve)	mmole* /g Fraction	mmole /g Maltene	mmole /g Residual Pitch	Absorbance A	mg/g Solvent (from Calibration Curve)	mmole* /g Fraction (Average of Two Values)	mmole /g Maltene	mmole /g Residual Pitch	Absorbance A	A/g Fraction	A/g Maltene	A/g Residual Pitch
Pentane Eluate	81.71	0.08	1.13	0.08	0.06	0.03	ND	ND	ND	ND	ND	0.25	3.08	2.06	1.16
Cyclohexane Eluate	47.78	0.17	2.41	0.30	0.006	0.004	ND	ND	ND	ND	ND	0.24	4.99	0.10	0.06
Anion Eluate, A-1	8.69	0.11	1.51	1.04	0.04	0.02	ND	ND	ND	ND	ND	0.06	6.90	0.29	0.16
A-2	8.06	0.13	1.89	1.40	0.02	0.01	ND	ND	ND	ND	ND	0.05	6.70	0.11	0.06
A-3	3.52	-	-	-	-	-	0.43 (1695 cm^{-1}) 0.28 (1735 cm^{-1})	1.79 1.69	4.04	0.02	0.01	0.08	23.58	0.11	0.06
Cation Eluate, C-1	9.91	0.06	0.87	0.53	0.03	0.02	ND	ND	ND	ND	ND	0.06	6.36	0.33	0.19
C-2	9.39	0.04	0.61	0.37	0.005	0.003	ND	ND	ND	ND	ND	0.06	6.44	0.08	0.04
C-3	10.08	0.02	0.21	0.12	0.01	0.006	ND	ND	ND	ND	ND	0.09	8.83	0.76	0.43

Footnotes: See Table 41

TABLE 48

IR Analysis of Ion-Exchange Eluate Fractions of #8 Residual Pitch Pentane-Maltene in CH_2Cl_2

Fraction	Concentration mg/g Solvent	Pyrrolic Compounds, 3470 cm^{-1}					Carboxylic Acids 1695 cm^{-1}, 1735 cm^{-1}					Aromatic Ring 1605 cm^{-1}			
		Absorbance A	Expressed as Carbazole				Absorbance A	Expressed as Benzoic Acid				Absorbance A	A/g Fraction	A/g Maltene	A/g Residual Pitch
			mg/g Solvent (from Calibration Curve)	mmole* /g Fraction	mmole /g Maltene	mmole /g Residual Pitch		mg/g Solvent (from Calibration Curve)	mmole* /g Fraction (Average of Two Values)	mmole /g Maltene	mmole /g Residual Pitch				
Pentane Eluate	85.06	0.01	0.18	0.01	0.01	0.01	ND	ND	ND	ND	ND	0.11	1.29	1.12	0.92
Cyclohexane Eluate	65.12	0.09	1.26	0.12	0.003	0.002	ND	ND	ND	ND	ND	0.20	3.04	0.08	0.07
Anion Eluate, A-1	9.41	0.03	0.48	0.31	0.008	0.007	ND	ND	ND	ND	ND	0.13	13.60	0.36	0.30
A-2	12.00	0.04	0.59	0.29	0.003	0.002	ND	ND	ND	ND	ND	0.10	8.25	0.07	0.06
A-3	4.73	-	-	-	-	-	0.02 (1695 cm^{-1}) 0.046 (1735 cm^{-1})	0.20 0.21	0.35	0.002	0.002	0.25	52.85	0.24	0.20
Cation Eluate, C-1	10.59	0.02	0.23	0.13	0.005	0.004	ND	ND	ND	ND	ND	0.05	4.62	0.17	0.14
C-2	8.50	0.01	0.09	0.05	0.0004	0.0003	ND	ND	ND	ND	ND	0.03	4.00	0.03	0.02
C-3	8.00	-	-	-	-	-	ND	ND	ND	ND	ND	0.06	7.83	0.42	0.34

Footnotes: See Table 41

TABLE 49

IR Analysis of Ion-Exchange Eluate Fractions of #9 Residual Pitch Pentane-Maltene in CH_2Cl_2

Fraction	Concentration mg/g Solvent	Pyrrolic Compounds, 3470 cm^{-1}					Carboxylic Acids 1695 cm^{-1}, 1735 cm^{-1}					Aromatic Ring 1605 cm^{-1}			
			Expressed as Carbazole					Expressed as Benzoic Acid							
		Absorbance A	mg/g Solvent (from Calibration Curve)	mmole*/g Fraction	mmole/g Maltene	mmole/g Residual Pitch	Absorbance A	mg/g Solvent (from Calibration Curve)	mmole*/g Fraction (Average of Two Values)	mmole/g Maltene	mmole/g Residual Pitch	Absorbance A	A/g Fraction	A/g Maltene	A/g Residual Pitch
Pentane Eluate	63.05	0.03	0.44	0.04	0.03	0.008	NO	NO	NO	NO	NO	0.23	3.68	2.70	0.70
Cyclohexane Eluate	80.15	0.10	1.38	0.10	0.01	0.003	ND	ND	NO	NO	NO	0.38	4.70	0.49	0.13
Anion Eluate, A-1	10.39	0.09	1.22	0.70	0.06	0.01	NO	NO	NO	NO	ND	0.07	6.93	0.56	0.14
A-2	9.74	0.16	2.33	1.43	0.03	0.008	ND	ND	NO	NO	ND	0.09	9.14	0.19	0.05
A-3	10.30	0.04	0.51	0.30	0.001	0.0003	0.33 (1695 cm^{-1}) 0.22 (1735 cm^{-1})	1.46 1.22	1.07	0.005	0.001	0.15	14.08	0.06	0.02
Cation Eluate, C-1	9.67	0.03	0.43	0.27	0.01	0.004	NO	ND	NO	NO	NO	0.06	6.00	0.32	0.08
C-2	9.37	0.02	0.31	0.20	0.001	0.0002	ND	ND	ND	ND	ND	0.05	4.80	0.02	0.005
C-3	12.73	0.01	0.13	0.06	0.001	0.0002	ND	ND	ND	ND	ND	0.12	9.19	0.11	0.03

Footnotes: See Table 41

TABLE 50

IR Analysis of Ion-Exchange Eluate Fractions of #10 Residual Pitch Pentane-Maltene in CH_2Cl_2

Fraction	Concentration mg/g Solvent	Pyrrolic Compounds, 3470 cm^{-1}					Carboxylic Acids 1694 cm^{-1}, 1735 cm^{-1}					Aromatic Ring 1605 cm^{-1}			
		Absorbance A	Expressed as Carbazole				Absorbance A	Expressed as Benzoic Acid				Absorbance A	A/g Fraction	A/g Maltene	A/g Residual Pitch
			mg/g Solvent (from Calibration Curve)	mmole* /g Fraction	mmole /g Maltene	mmole /g Residual Pitch		mg/g Solvent (from Calibration Curve)	mmole* /g Fraction (Average of Two Values)	mmole /g Maltene	mmole /g Residual Pitch				
Pentane Eluate	71.87	0.03	0.47	0.04	0.03	0.01	NO	NO	ND	NO	NO	0.21	2.91	2.38	1.04
Cyclohexane Eluate	65.71	0.13	1.83	0.17	0.01	0.004	NO	NO	NO	NO	NO	0.28	4.32	0.23	0.10
Anion Eluate, A-1	10.07	0.11	1.54	0.71	0.04	0.02	NO	NO	NO	NO	NO	0.07	7.35	0.32	0.14
A-2	10.33	0.18	2.62	1.52	0.02	0.01	NO	NO	NO	NO	NO	0.07	6.58	0.11	0.05
A-3	11.86	0.05	0.69	0.35	0.003	0.001	0.18 (1695 cm^{-1}) 0.13 (1735 cm^{-1})	0.97 0.77	0.60	0.006	0.003	0.27	22.51	9.22	0.10
Cation Eluate, C-1	17.80	0.03	0.38	0.29	0.01	0.006	NO	ND	NO	NO	NO	0.05	6.54	0.32	0.14
C-2	10.72	0.03	0.44	0.24	0.002	0.001	NO	NO	NO	NO	NO	0.07	6.72	0.05	0.02
C-3	10.05	0.01	0.14	0.08	0.004	0.002	NO	NO	NO	NO	NO	0.09	9.45	0.44	0.19

Footnotes: See Table 41

TABLE 51

IR Analysis of Ion-Exchange Eluate Fractions of #11 Residual Pitch Pentane-Maltene in CH_2Cl_2

Fraction	Concentration mg/g Solvent	Pyrrolic Compounds, 3470 cm^{-1}					Carboxylic Acids 1694 cm^{-1}, 1735 cm^{-1}					Aromatic Ring 1605 cm^{-1}			
			Expressed as Carbazole					Expressed as Benzoic Acid							
		Absorbance A	mg/g Solvent (from Calibration Curve)	mmole* /g Fraction	mmole /g Maltene	mmole /g Residual Pitch	Absorbance A	mg/g Solvent (from Calibration Curve)	mmole* /g Fraction (Average of Two Values)	mmole /g Maltene	mmole /g Residual Pitch	Absorbance A	A/g Fraction	A/g Maltene	A/g Residual Pitch
Pentane Eluate	84.15	0.03	0.48	0.03	0.03	0.02	ND	ND	ND	ND	ND	0.16	1.88	1.58	1.25
Cyclohexane Eluate	70.69	0.14	0.20	0.02	0.001	0.0004	ND	ND	ND	ND	ND	0.21	3.01	0.11	0.09
Anion Eluate, A-1	9.41	0.04	0.57	0.36	0.01	0.007	ND	ND	ND	ND	ND	0.05	5.63	0.14	0.11
A-2	11.53	0.05	0.70	0.36	0.003	0.002	ND	ND	ND	ND	ND	0.08	7.03	0.06	0.05
A-3	4.95	-	-	-	-	-	0.04 (1695 cm^{-1}) 0.06 (1735 cm^{-1})	0.29 0.27	0.47	0.002	0.002	0.18	35.35	0.14	0.11
Cation Eluate, C-1	9.24	0.02	0.30	0.19	0.006	0.005	ND	ND	ND	ND	ND	0.07	7.90	0.23	0.18
C-2	8.19	0.01	0.11	0.08	0.001	0.0005	ND	ND	ND	ND	ND	0.08	9.65	0.09	0.07
C-3	9.09	-	-	-	-	-	ND	ND	ND	ND	ND	0.12	12.76	0.71	0.56

Footnotes: See Table 41

TABLE 52

IR Analysis of Ion-Exchange Eluate Fractions of #12 Residual Pitch Pentane-Maltene in CH_2Cl_2

Fraction	Concentration mg/g Solvent	Pyrrolic Compounds, 3470 cm^{-1}					Carboxylic Acids 1695 cm^{-1}, 1735 cm^{-1}					Aromatic Ring 1605 cm^{-1}			
			Expressed as Carbazole					Expressed as Benzoic Acid							
		Absorbance A	mg/g Solvent (from Calibration Curve)	mmole* /g Fraction	mmole /g Maltene	mmole /g Residual Pitch	Absorbance A	mg/g Solvent (from Calibration Curve)	mmole* /g Fraction (Average of Two Values)	mmole /g Maltene	mmole /g Residual Pitch	Absorbance A	A/g Fraction	A/g Maltene	A/g Residual Pitch
Pentane Eluate	85.04	0.07	0.93	0.07	0.05	0.02	ND	ND	ND	ND	ND	0.26	3.10	2.39	1.16
Cyclohexane Eluate	68.85	0.20	2.85	0.26	0.01	0.007	NO	ND	ND	ND	ND	0.32	4.88	0.26	0.13
Anion Eluate, A-1	11.34	0.14	2.08	1.10	0.05	0.02	NO	ND	ND	ND	ND	0.08	7.05	0.31	0.15
A-2	9.32	0.15	2.13	1.37	0.02	0.009	ND	ND	ND	ND	ND	0.08	8.69	0.11	0.05
A-3	6.09	-	-	-	-	-	0.44 (1695 cm^{-1}) 0.27 (1735 cm^{-1})	1.81 1.62	2.30	0.01	0.005	0.10	16.91	0.11	0.05
Cation Eluate, C-1	9.49	0.05	0.69	0.44	0.03	0.02	ND	ND	ND	ND	ND	0.04	4.42	0.36	0.17
C-2	8.19	0.02	0.25	0.18	0.002	0.001	ND	ND	ND	ND	ND	0.04	4.88	0.06	0.03
C-3	9.40	0.01	0.16	0.10	0.008	0.004	ND	ND	ND	ND	ND	0.07	7.45	0.59	0.29

Footnotes: See Table 41

TABLE 53

Millimoles of Pyrrolic Compounds (expressed as Carbazole) in 100 g of Residual Pitch Samples (Deasphaltene with n-Pentane)

Fractions	#1	#2	#3	#4	#5	#6	#7	#8	#9	#10	#11	#12
Pentane Eluate	-	0.90	2.26	2.47	1.85	2.19	3.12	1.05	0.80	1.39	2.24	2.43
Cyclohexane Eluate	0.37	0.14	0.24	0.48	0.16	0.38	0.35	0.24	0.28	0.39	0.04	0.67
Anion Eluate, A-1	2.16	3.57	1.62	4.34	0.27	1.63	2.49	0.67	1.47	1.73	0.72	2.34
A-2	0.29	0.82	0.67	1.89	0.08	0.89	1.31	0.21	0.78	1.12	0.22	0.87
A-3	-	0.04	-	-	-	-	-	-	0.03	0.14	-	-
Cation Eluate, C-1	0.80	0.845	1.06	3.73	0.38	0.96	1.50	0.39	0.36	0.63	0.46	1.72
C-2	-	-	0.14	0.38	0.02	0.11	0.26	0.03	0.02	0.08	0.05	0.10
C-3	-	-	0.64	-	-	0.39	0.59	-	0.02	0.17	-	0.39
Total	3.61	6.33	6.62	13.29	2.76	6.55	9.64	2.47	3.77	5.66	3.75	8.52

TABLE 54

Porphyrin Content in Benzene Solubles of of Residual Pitch Samples

Sample No.	Sample Weight (g)	Chloroform Extract Total Volume (mL)	Dilution	Absorbance at 400-410 cm	Porphyrin Concentration mg/mL	Porphyrin Concentration mg/g of Sample	Porphyrin % weight
1	10.0745	25	1:125	0.475	0.052	16.13	1.613
2	7.0086	25	1:25	0.03	0.004	0.36	0.036
3	9.8531	25	1:100	0.710	0.078	19.79	1.979
4	9.4699	25	1:25	0.220	0.027	1.78	0.178
5	11.0005	25	1:100	0.510	0.056	12.72	1.272
6	9.3409	25	1:50	0.290	0.029	3.88	0.388
7	10.3708	25	1:33.33	0.140	0.017	1.36	0.136
8	9.8410	25	1:25	0.540	0.060	3.81	0.381
9	7.6275	25	1:25	ND*	ND	ND	ND
10	7.7159	25	1:25	ND	ND	ND	ND
11	7.9908	25	1:25	0.360	0.038	2.97	0.297
12	8.7748	25	1:25	ND	ND	ND	ND

* ND = none detected

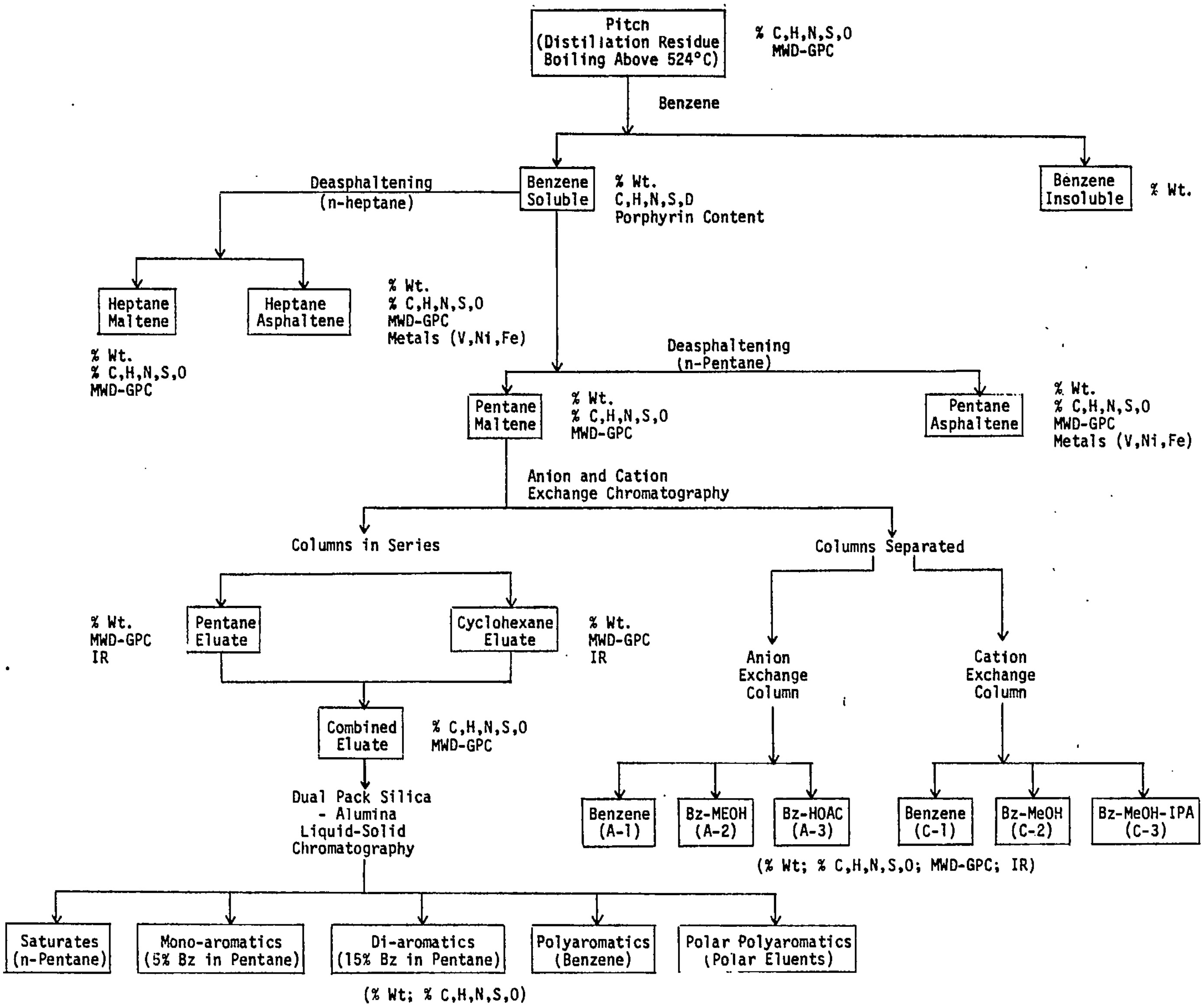
TABLE 55

Metal Content in Pentane- and Heptane-Asphaltenes

(μg/g, ppm)

Sample No.	Pentane-Asphaltene					Heptane-Asphaltene				
	Fe	Ni	V	V/Ni Ratio	% S	Fe	Ni	V	V/Ni Ratio	% S
1	1311	309	997	3.23	8.29	1476	296	1068	3.61	6.91
2	17	271	304	1.12	4.92	14	208	197	0.95	4.98
3	243	462	1493	3.23	7.02	190	444	1595	3.59	7.14
4	89	325	485	1.49	4.84	84	339	476	1.41	4.67
5	79	272	895	3.29	8.02	87	287	877	3.05	7.79
6	36	286	334	1.17	4.59	35	282	309	1.09	4.91
7	405	276	526	1.90	4.50	448	300	547	1.82	4.68
8	119	106	572	5.39	6.46	149	120	589	4.91	6.39
9	∿ 3	49	93	1.89	4.77	∿ 3	56	118	2.11	4.85
10	∿ 5	70	106	1.51	4.66	3	79	105	1.33	3.89
11	72	151	249	1.65	4.09	85	183	316	1.73	3.99
12	164	68	50	0.74	2.93	166	68	48	0.71	2.52

FIGURES



Fractionation and Analytical Scheme for Characterization of Residual Pitches

Figure 1

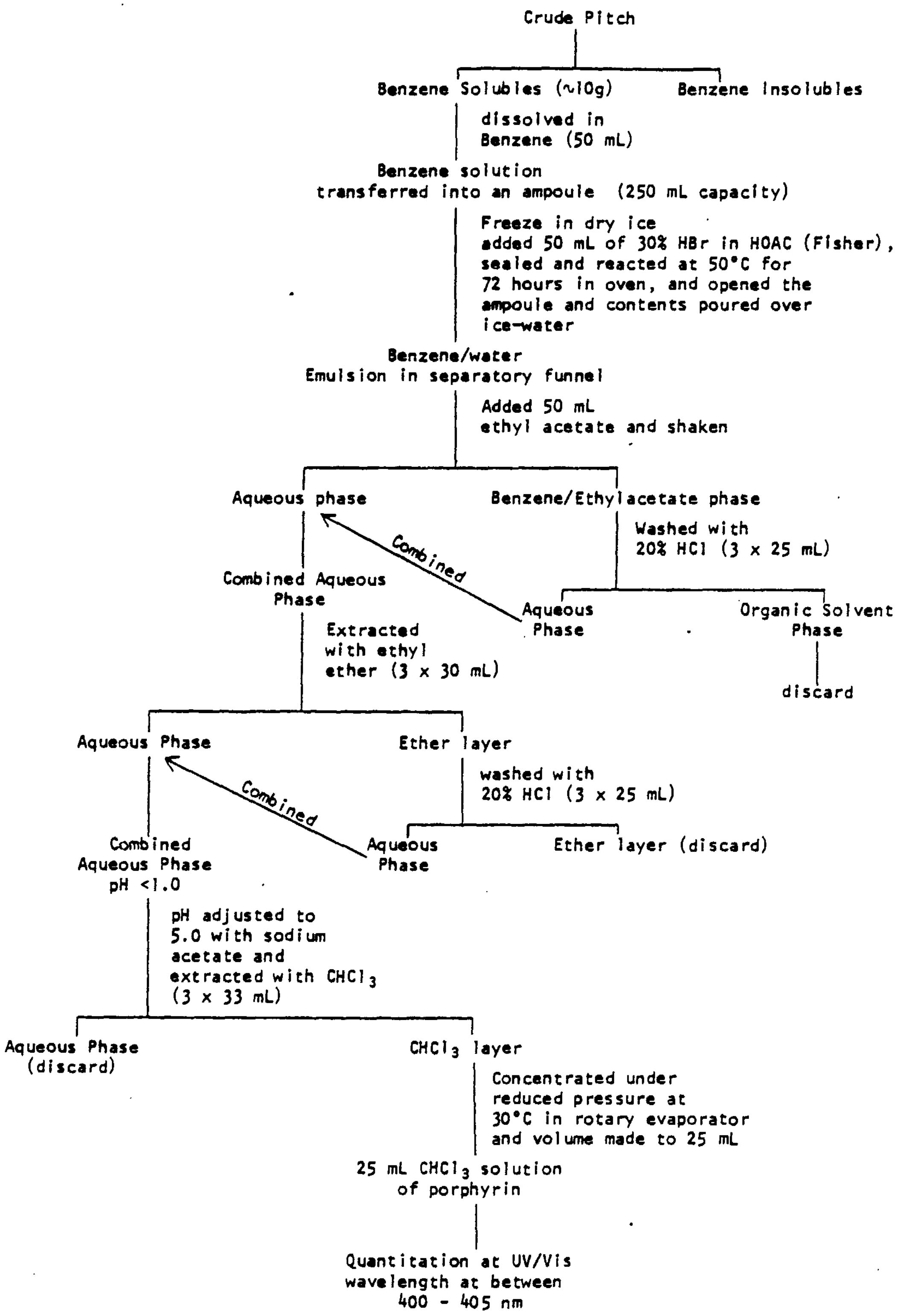


Figure 2 Flow chart showing method of isolation of porphyrin in pitch samples

Figure 3

Standard Calibration Curve #1 for Molecular Size Characterization of Pitch Samples #1, 5, 8 and 11 and their Fractions in GPC System #1

(See Table 3 for GPC Conditions and Table 4
for Molecular Weight/Retention Time Data)

```
RUN

Sum Errors Sqrd= 0.0060569          Coeff of Deter= 0.9029467
Fit:Y=A+B*X+C*X↑2+D*X↑3 A= 27.220027B=-3.8008813C= 0.1985471D= -.003568

GPC Cal Ret Time vs. log MW
```

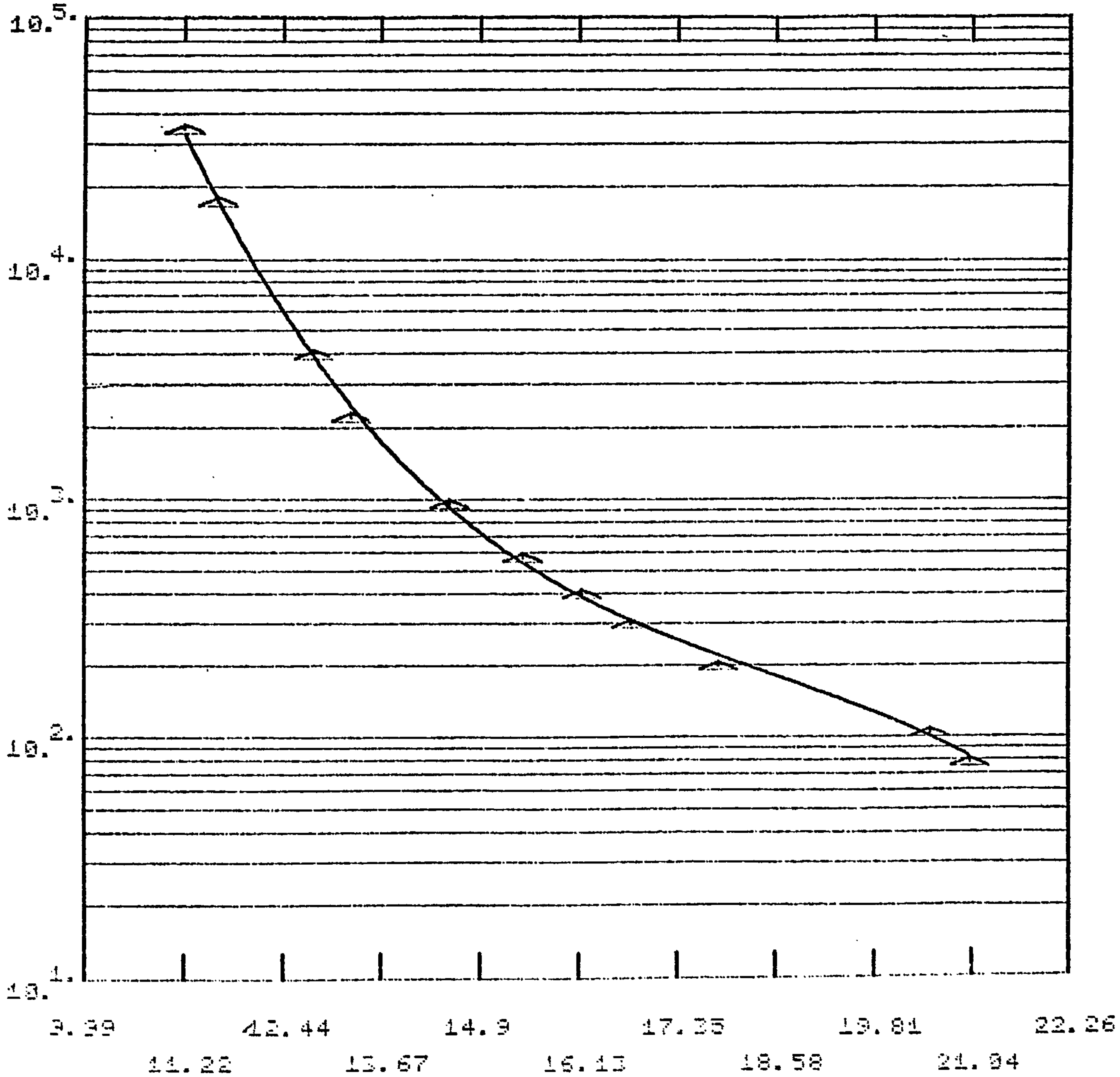


Figure 4

Standard Calibration Curve #2 for Molecular Size Characterization of Pitch Samples #2, 3, 4, 6, 7, 9, 10, 12 and their Fractions in GPC System #1

(See Table 3 for GPC Conditions and Table 5
for Molecular Weight/Retention Time Data)

```
Sum Errors Sqrd= 0.0024508              Coeff of Deter= 0.9612749
Fit:V=A+B*X+C*X↑2+D*X↑3.A= 17.291272B=-2.0320041C= 0.0947962D= -.001565

GPC Cal Ret Time vs. log MW
```

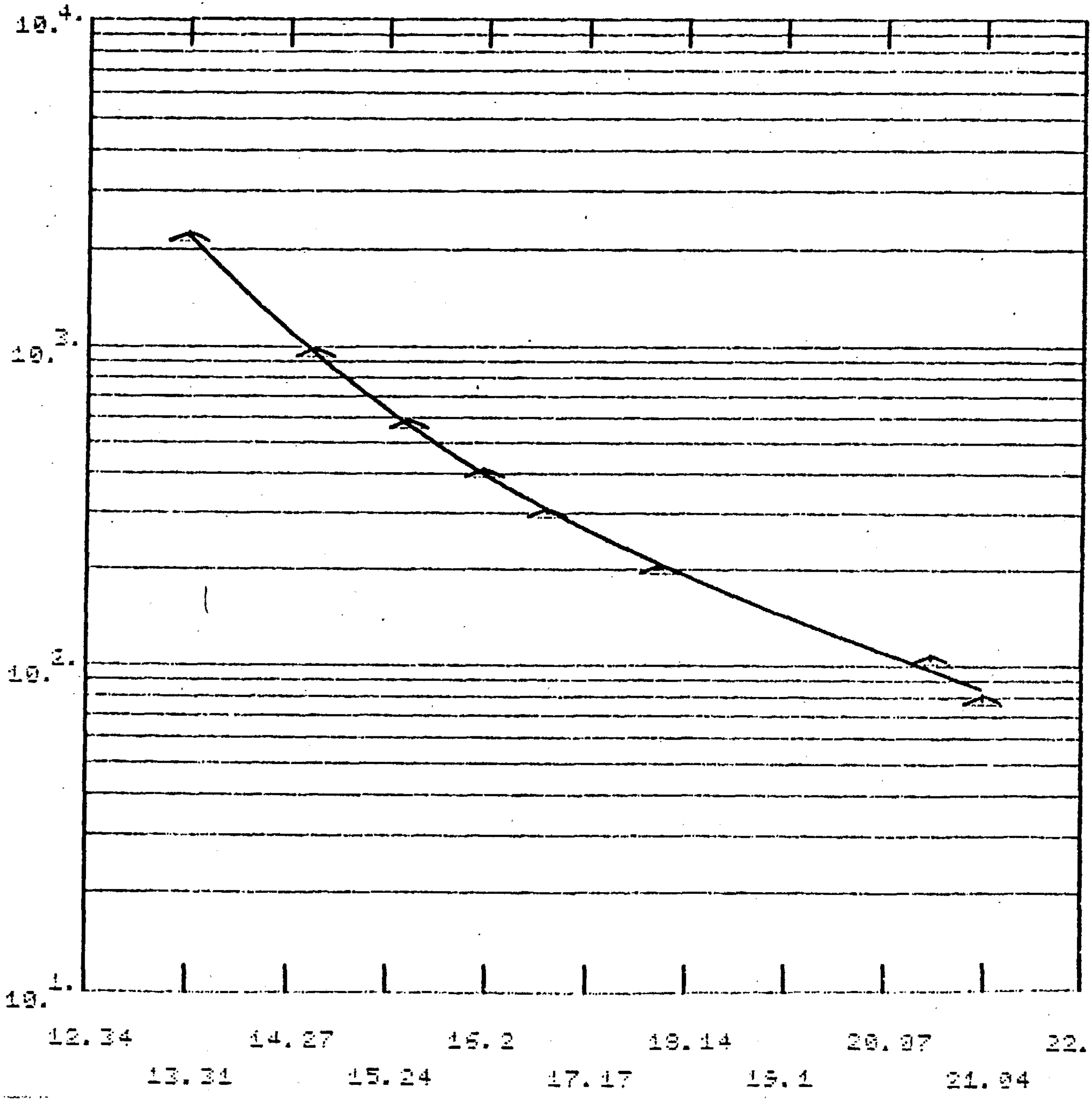


Figure 5

Standard Calibration Curve #3 for Molecular Size Characterization of All Pitch Samples and their Fractions in GPC System #2

(See Table 3 for GPC Conditions and Table 6 for Molecular Weight/Retention Time Data)

```
Sum Errors Sqrd= 0.0231282              Coeff of Deter= 0.9498371
Fit:Y=A+B*X+C*X↑2+D*X↑3 A= 16.405324B=-1.7177578C= 0.072941 D= -.001122
GPC Cal Ret Time vs. log MW
```

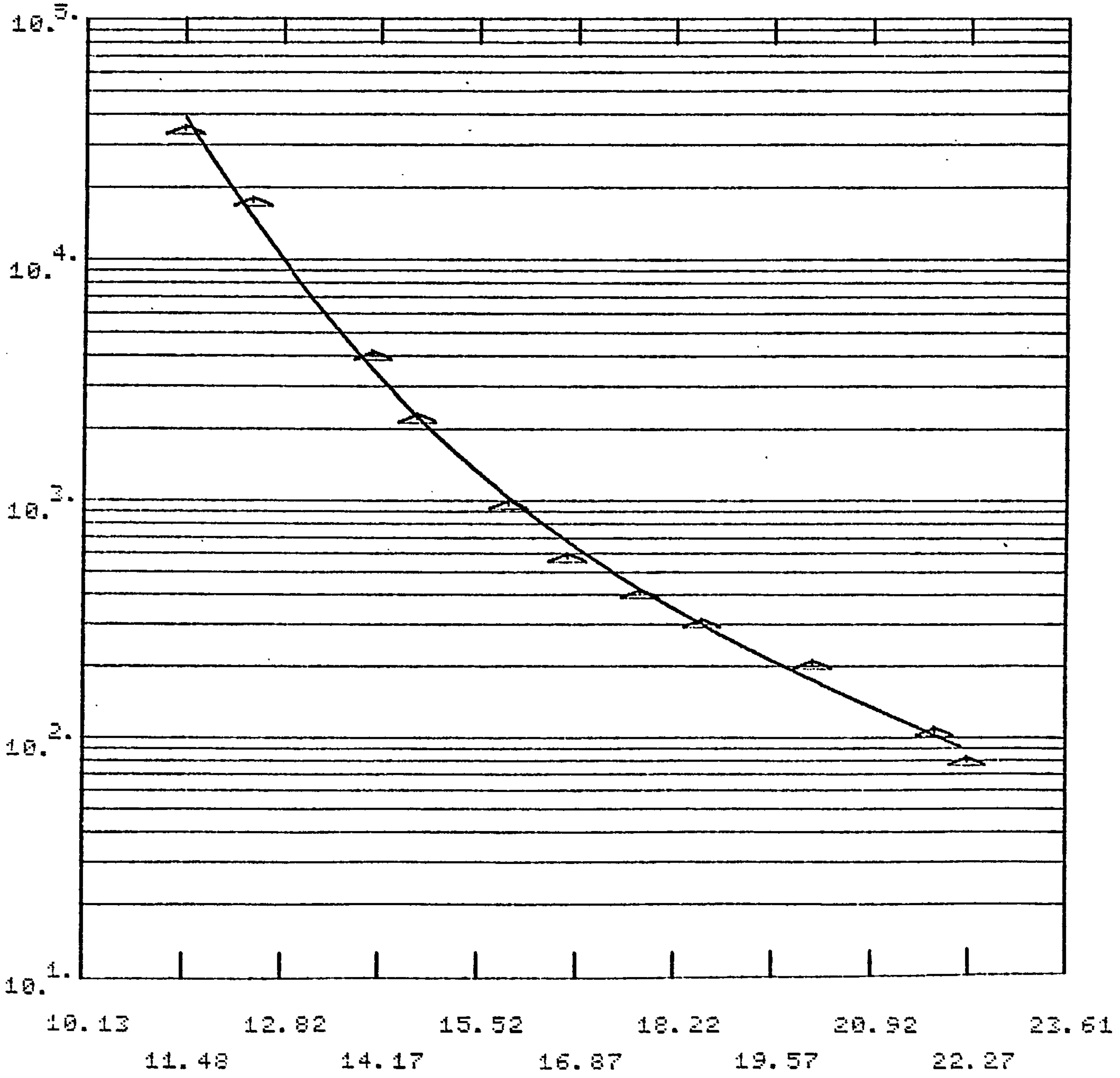
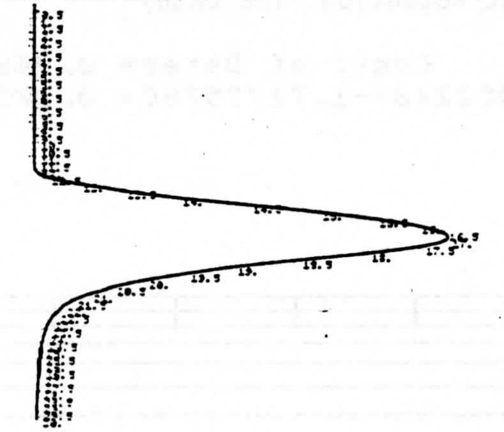


Figure 6 GPC Profiles, MWD Data and MWD-Normalized and Cumulative Curves of Pitch #4 in GPC System #1

CANMET PITCH SAMPLE NO. 4 — WHOLE PITCH

GPC SYSTEM NO. 1

INJECT TIME 15 12:44:41



CANMET RESIDUAL PITCHES 15 12:44:41

[illegible]ILE 1 METHOD 5. RUN 1 INDEX 1

SAMPLE
Cal Fit= 3.
Wt Avg MW (Mw)= 466. No. Avg MW (Mn)= 223.
Z Avg MW= 1033. Z+1 Avg MW= 2036.
Mw/Mn= 2.0871451 Area Max Scale= 9279.

PT	AREA	MW/SLICE	%AREA	CUM%
10.	0.	76745.16	0.	0.
10.1	0.	66826.020	0.	0.
10.2	0.	58315.345	0.	0.
10.3	0.	50999.589	0.	0.
10.4	0.	44696.58	0.	0.
10.5	0.	39255.524	0.	0.
10.6	0.	34549.090	0.	0.
10.7	0.	30470.02	0.	0.
10.8	0.	26927.71	0.	0.
10.9	0.	23945.994	0.	0.
11.	0.	21150.618	0.	0.
11.1	0.	18811.77	0.	0.
11.2	0.	16758.114	0.	0.
11.3	0.	14957.683	0.	0.
11.4	0.	13376.376	0.	0.
11.5	0.	11984.95	0.	0.
11.6	0.	10758.461	0.	0.
11.7	0.	9679.4204	0.	0.
11.8	0.	8717.4009	0.	0.
11.9	9.	7868.4851	0.002	0.002
12.	24.	7114.9722	0.005	0.007
12.1	48.	6445.8132	0.011	0.018
12.2	80.	5840.3531	0.018	0.036
12.3	132.	5316.8996	0.029	0.065
12.4	199.	4848.5289	0.044	0.109
12.5	294.	4414.9385	0.063	0.173
12.6	392.	4033.4465	0.087	0.26
12.7	523.	3690.3735	0.117	0.377
12.8	675.	3383.0494	0.151	0.527
12.9	848.	3105.7680	0.189	0.716
13.	1031.	2855.7007	0.23	0.946
13.1	1225.	2629.864	0.273	1.22
13.2	1424.	2425.5927	0.318	1.537
13.3	1625.	2240.5680	0.362	1.899
13.4	1828.	2072.7412	0.408	2.307
13.5	2037.	1920.2993	0.454	2.761
13.6	2258.	1781.6418	0.504	3.265
13.7	2495.	1655.3509	0.556	3.821
13.8	2747.	1540.1698	0.613	4.434
13.9	3017.	1434.9824	0.673	5.106
14.	3306.	1338.7966	0.737	5.844
14.1	3607.	1250.7291	0.804	6.648
14.2	3921.	1169.9928	0.874	7.522
14.3	4243.	1095.885	0.946	8.468
14.4	4569.	1027.7778	1.019	9.487
14.5	4895.	965.10949	1.092	10.579
14.6	5219.	907.37661	1.164	11.743
14.7	5534.	854.12755	1.234	12.977
14.8	5841.	804.95769	1.302	14.279
14.9	6141.	759.50166	1.369	15.648
15.	6430.	717.4316	1.434	17.082
15.1	6703.	678.45179	1.495	18.577
15.2	6965.	642.29932	1.553	20.13
15.3	7212.	608.72124	1.608	21.738
15.4	7448.	577.91159	1.661	23.399
15.5	7673.	548.46891	1.711	25.11
15.6	7884.	521.41449	1.758	26.868
15.7	8082.	496.18599	1.802	28.67
15.8	8268.	472.62605	1.844	30.514
15.9	8440.	450.63067	1.882	32.396
16.	8602.	430.04788	1.918	34.314
16.1	8749.	410.77655	1.951	36.265
16.2	8881.	392.71529	1.98	38.245
16.3	8997.	375.77157	2.006	40.252
16.4	9096.	359.86003	2.028	42.28
16.5	9174.	344.90577	2.046	44.326
16.6	9233.	330.83552	2.059	46.385
16.7	9268.	317.58519	2.067	48.451
16.8	9279.	305.09911	2.069	50.52
16.9	9261.	293.31067	2.065	52.585
17.	9217.	282.18161	2.055	54.641
17.1	9140.	271.66166	2.038	56.679
17.2	9036.	261.70026	2.015	58.694
17.3	8902.	252.28214	1.985	60.679
17.4	8737.	243.3471	1.948	62.627
17.5	8544.	234.86977	1.905	64.532
17.6	8327.	226.81923	1.857	66.389
17.7	8088.	219.16696	1.804	68.193
17.8	7834.	211.88652	1.747	69.94
17.9	7566.	204.95346	1.687	71.627
18.	7281.	198.34508	1.624	73.25
18.1	6983.	192.04032	1.557	74.807
18.2	6678.	186.01968	1.489	76.297
18.3	6361.	180.265	1.418	77.715
18.4	6043.	174.75945	1.348	79.062
18.5	5726.	169.40731	1.277	80.339
18.6	5415.	164.43398	1.207	81.547
18.7	5112.	159.58587	1.14	82.687
18.8	4826.	154.93032	1.076	83.763
18.9	4554.	150.45551	1.015	84.778
19.	4307.	146.15043	0.96	85.739
19.1	4086.	142.00478	0.911	86.65
19.2	3882.	138.00902	0.866	87.516
19.3	3676.	134.15411	0.82	88.335
19.4	3460.	130.43173	0.772	89.107
19.5	3253.	126.83403	0.725	89.832
19.6	3056.	123.35376	0.681	90.514
19.7	2870.	119.98403	0.64	91.154
19.8	2685.	116.7185	0.599	91.752
19.9	2509.	113.55118	0.559	92.312
20.	2337.	110.47653	0.521	92.833
20.1	2179.	107.40932	0.485	93.318
20.2	2024.	104.50471	0.451	93.769
20.3	1884.	101.75816	0.42	94.189
20.4	1753.	99.005441	0.391	94.58
20.5	1643.	96.32262	0.366	94.947
20.6	1555.	93.706015	0.347	95.293
20.7	1464.	91.152223	0.326	95.62
20.8	1353.	88.658073	0.302	95.922
20.9	1234.	86.22062	0.275	96.197
21.	1127.	83.837118	0.251	96.448
21.1	1036.	81.505052	0.231	96.679
21.2	957.	79.222109	0.213	96.892
21.3	886.	76.986129	0.198	97.09
21.4	820.	74.795143	0.183	97.273
21.5	764.	72.64734	0.17	97.443
21.6	706.	70.541003	0.157	97.601
21.7	654.	68.474861	0.146	97.746
21.8	609.	66.447218	0.136	97.882
21.9	575.	64.457222	0.128	98.01
22.	543.	62.503476	0.121	98.132
22.1	516.	60.585102	0.115	98.247
22.2	484.	58.701231	0.108	98.355
22.3	450.	56.851091	0.1	98.455
22.4	415.	55.034041	0.093	98.547
22.5	383.	53.249479	0.085	98.633
22.6	356.	51.496351	0.079	98.712
22.7	335.	49.776031	0.075	98.787
22.8	313.	48.086412	0.07	98.857
22.9	293.	46.427823	0.065	98.922
23.	277.	44.800091	0.062	98.984
23.1	262.	43.203066	0.058	99.042
23.2	246.	41.636663	0.055	99.097
23.3	234.	40.100052	0.052	99.149
23.4	221.	38.595642	0.049	99.199
23.5	210.	37.121066	0.047	99.245
23.6	199.	35.6772	0.044	99.29
23.7	189.	34.26414	0.042	99.332
23.8	179.	32.882004	0.04	99.372
23.9	170.	31.520916	0.038	99.41
24.	158.	30.211038	0.035	99.445
24.1	149.	28.922496	0.033	99.478
24.2	145.	27.665445	0.032	99.511
24.3	136.	26.44003	0.03	99.541
24.4	129.	25.246384	0.029	99.57
24.5	124.	24.084638	0.028	99.597
24.6	121.	22.954087	0.027	99.624
24.7	115.	21.857225	0.026	99.65
24.8	109.	20.791714	0.024	99.674
24.9	102.	19.758393	0.023	99.697
25.	100.	18.757266	0.022	99.719
25.1	94.	17.788306	0.021	99.74
25.2	90.	16.851463	0.02	99.76
25.3	88.	15.946633	0.02	99.78
25.4	84.	15.073607	0.019	99.799
25.5	81.	14.232446	0.018	99.817
25.6	74.	13.422701	0.017	99.833
25.7	71.	12.644192	0.016	99.849
25.8	68.	11.896624	0.015	99.864
25.9	66.	11.179656	0.015	99.879
26.	64.	10.492907	0.014	99.893
26.1	61.	9.8359951	0.014	99.907
26.2	57.	9.2083334	0.013	99.92
26.3	54.	8.6095423	0.012	99.932
26.4	54.	8.0390403	0.012	99.944
26.5	47.	7.4962486	0.01	99.954
26.6	46.	6.9805583	0.01	99.964
26.7	43.	6.4913213	0.01	99.974
26.8	42.	6.0278672	0.009	99.983
26.9	39.	5.5894915	0.009	99.992
27.	36.	5.175469	0.008	100.
Totals	448453.	209132356		

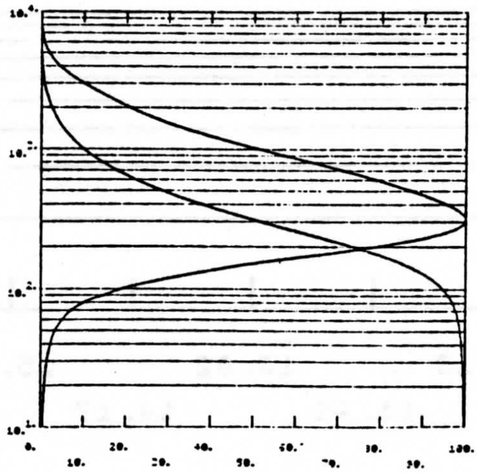
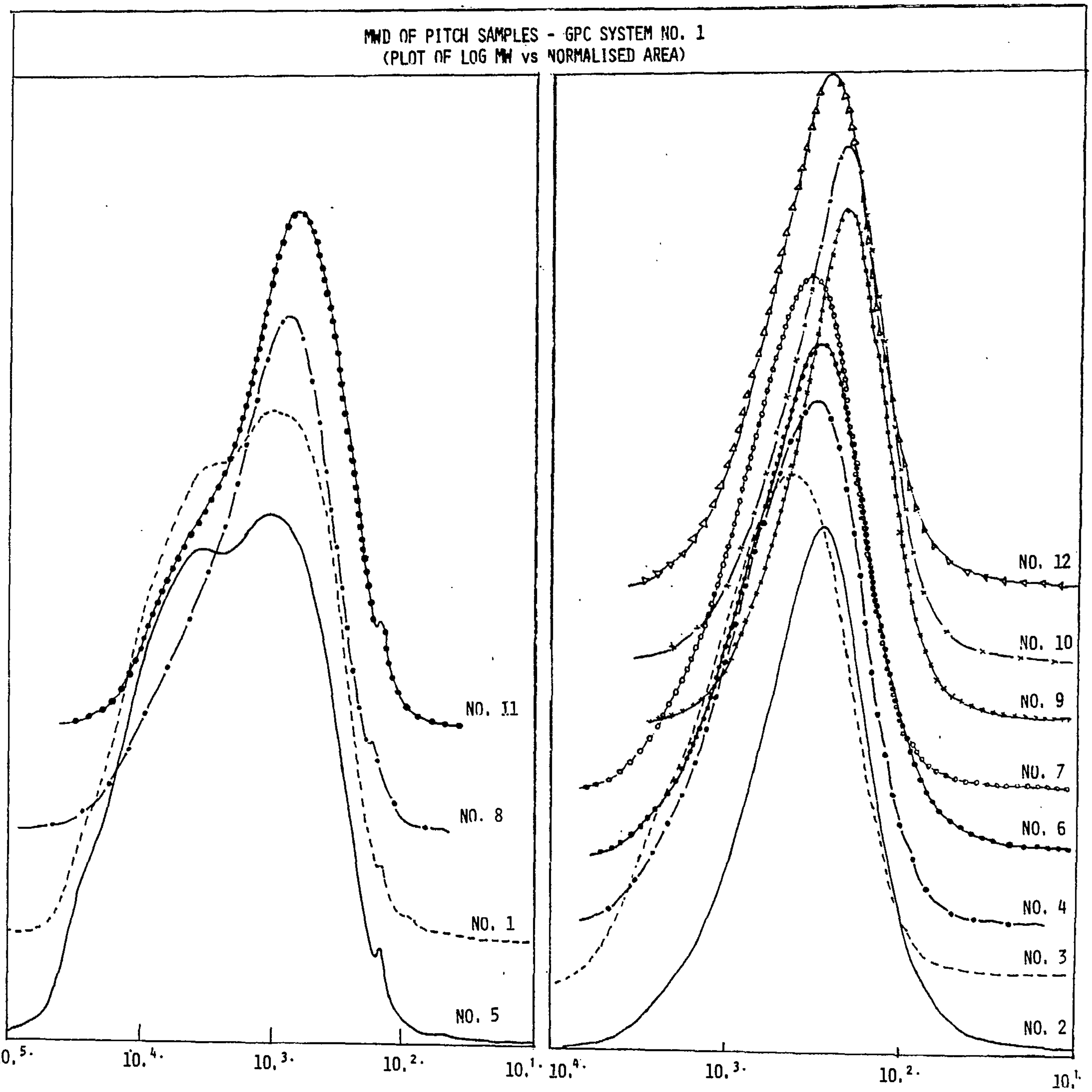


Figure 7 MWD-Normalized Curves of Twelve Pitch Samples in GPC System #1



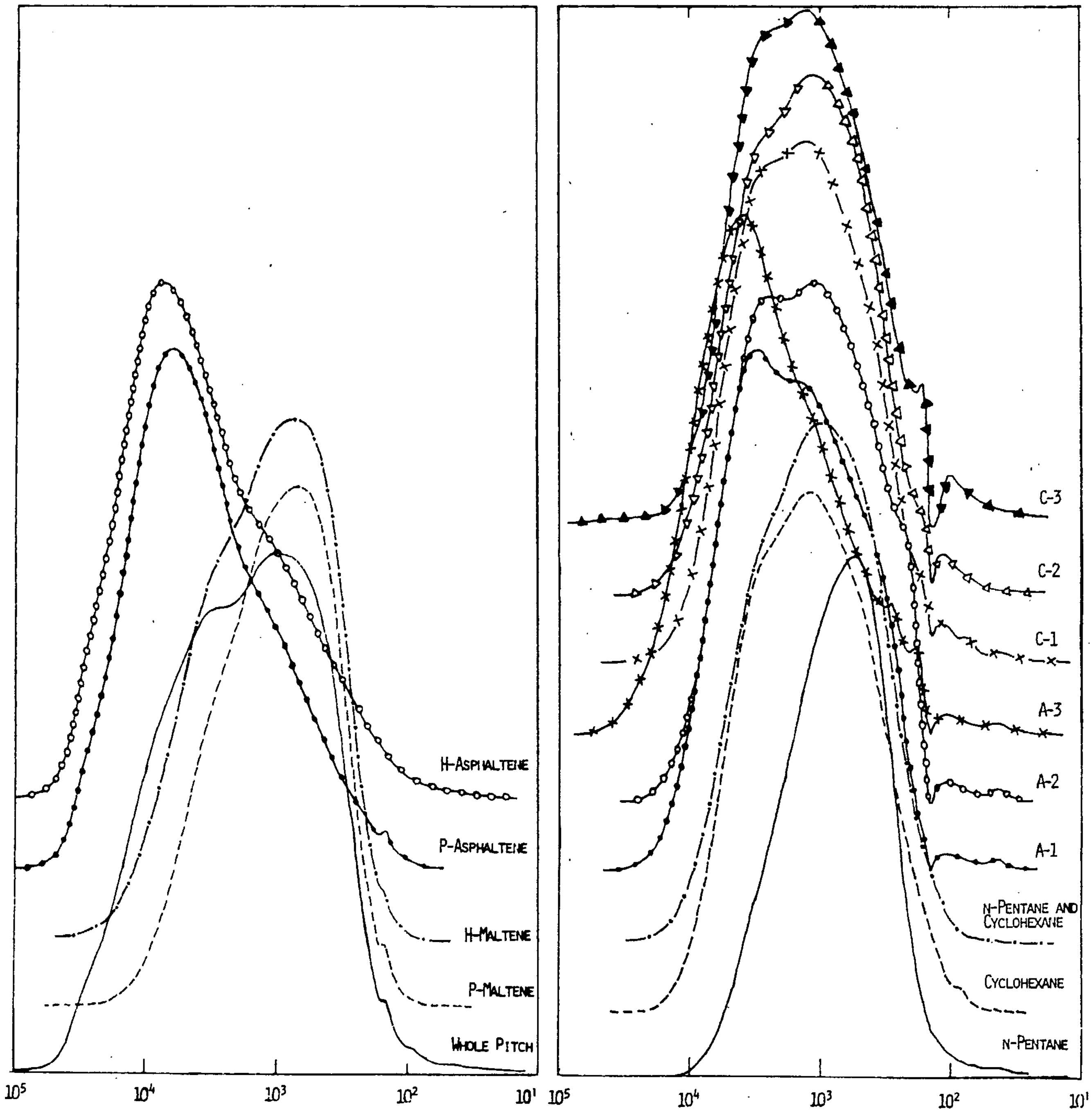
MWD DATA	NO. 1	NO. 2	NO. 3	NO. 4	NO. 5	NO. 6	NO. 7	NO. 8	NO. 9	NO. 10	NO. 11	NO. 12
M_W	2563	384	674	466	3304	429	490	1362	261	290	1188	380
M_N	470	186	214	223	510	192	228	445	148	163	418	184
M_W/M_N	5.45	2.06	3.15	2.09	6.45	2.23	2.14	3.06	1.76	1.79	2.84	2.07

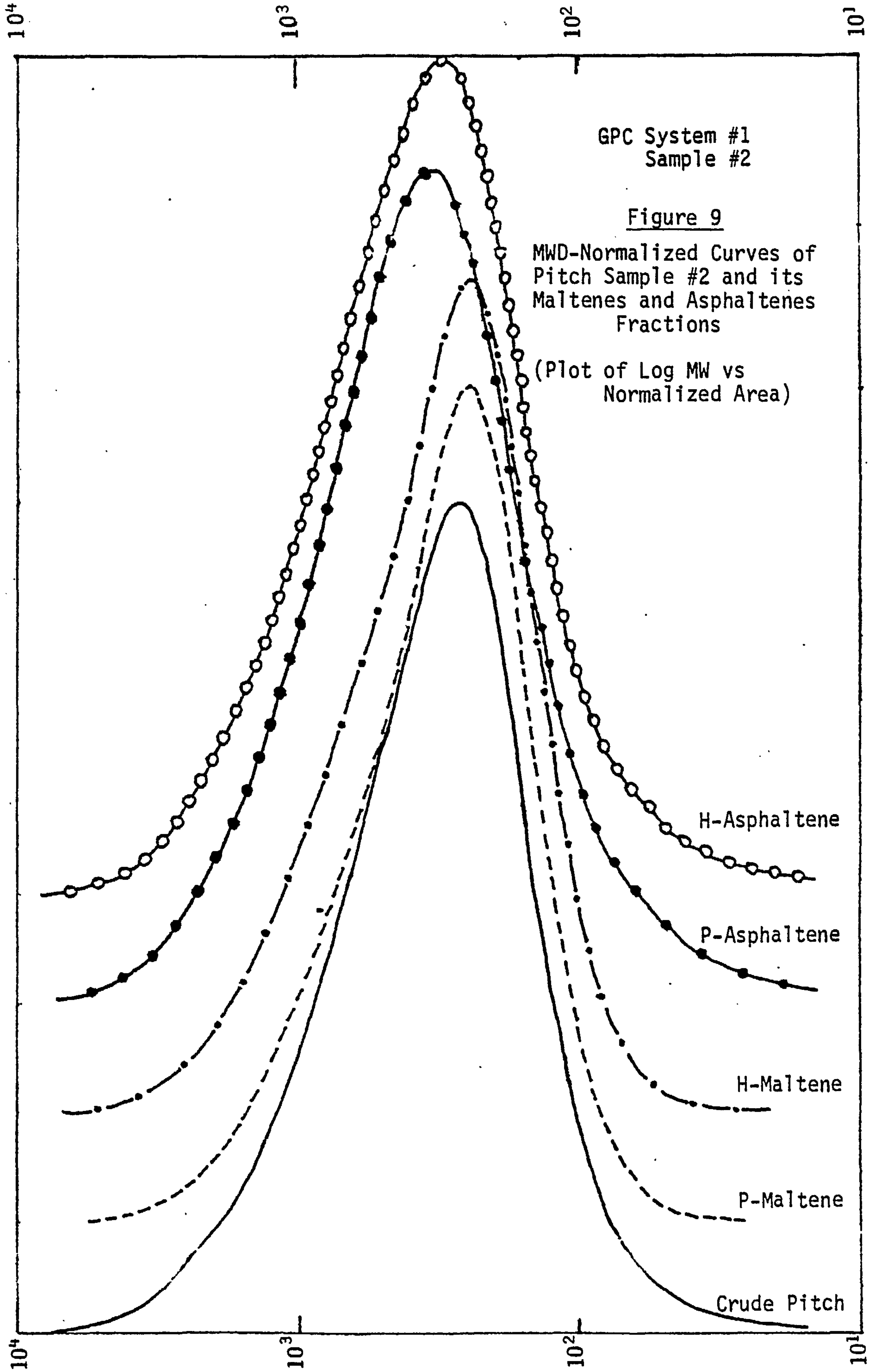
Figure 8

MWD of Residual Pitch Sample No. 1 and Its Various Maltene and Asphaltene, and Ion-Exchange Extract and Eluate Fractions

GPC System No. 1

(Plot of Log MW vs Normalized Area)



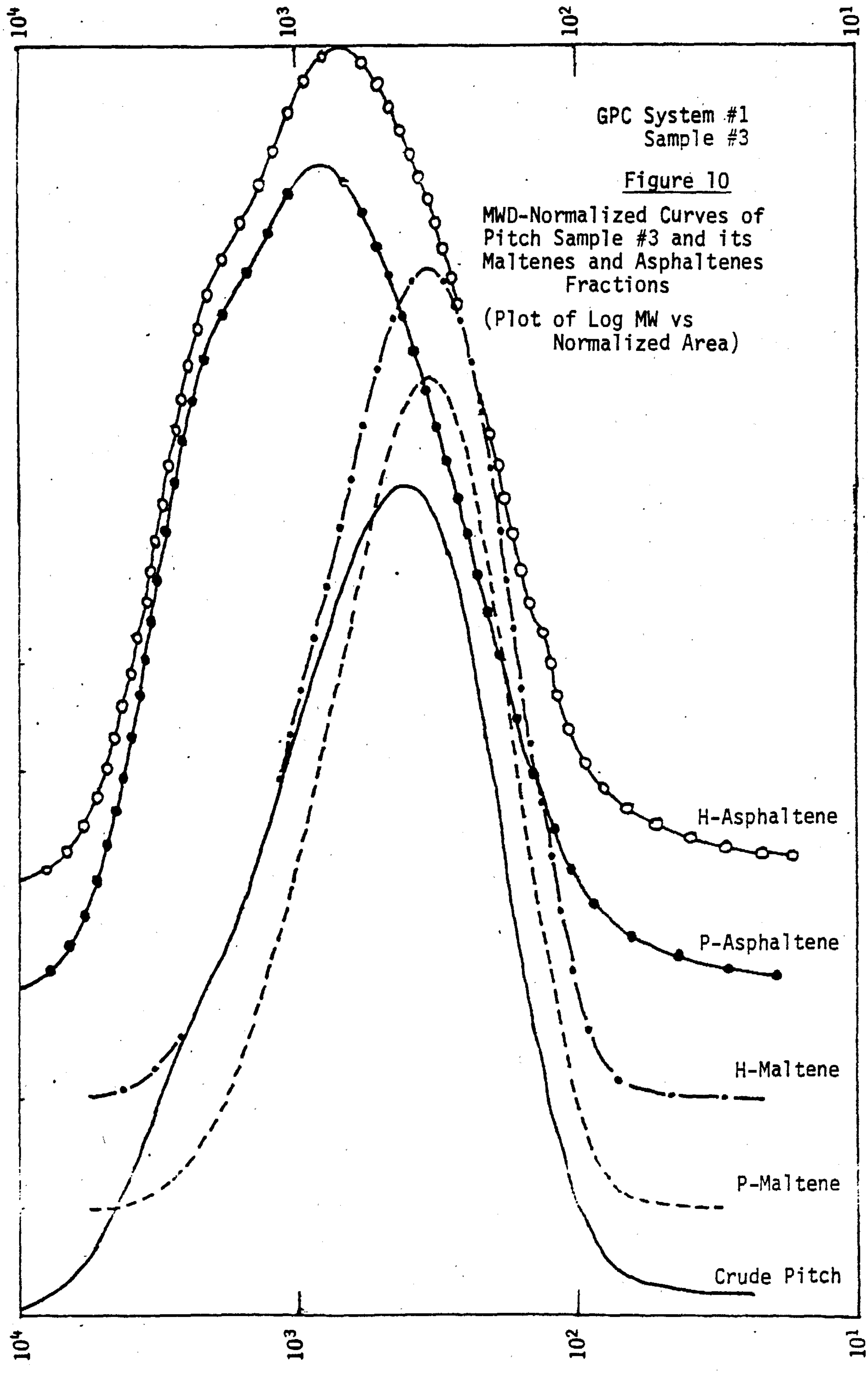


GPC System #1
Sample #2

Figure 9

MWD-Normalized Curves of Pitch Sample #2 and its Maltenes and Asphaltenes Fractions

(Plot of Log MW vs Normalized Area)



GPC System #1
Sample #3

Figure 10

MWD-Normalized Curves of Pitch Sample #3 and its Maltenes and Asphaltenes Fractions

(Plot of Log MW vs Normalized Area)

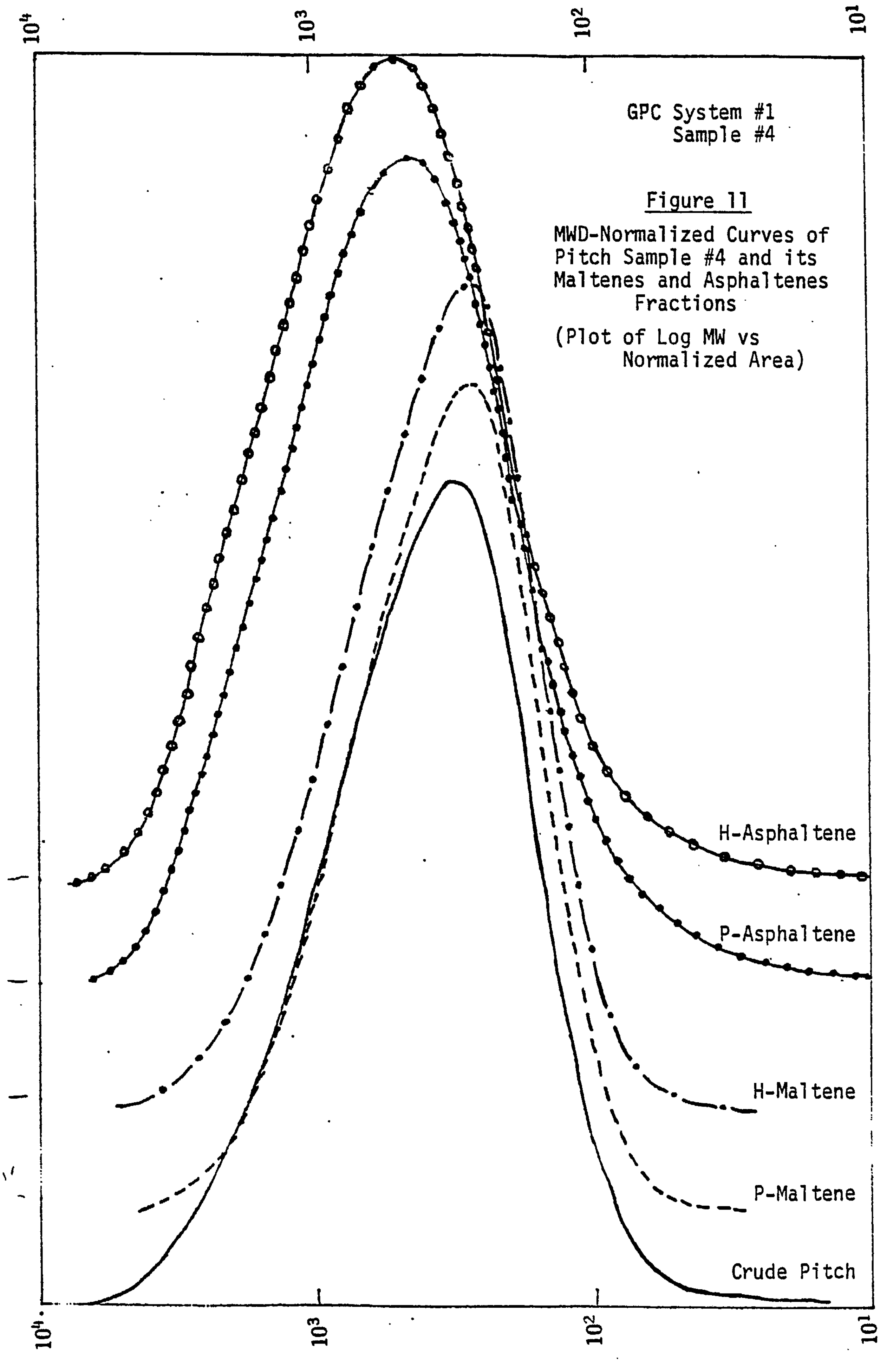
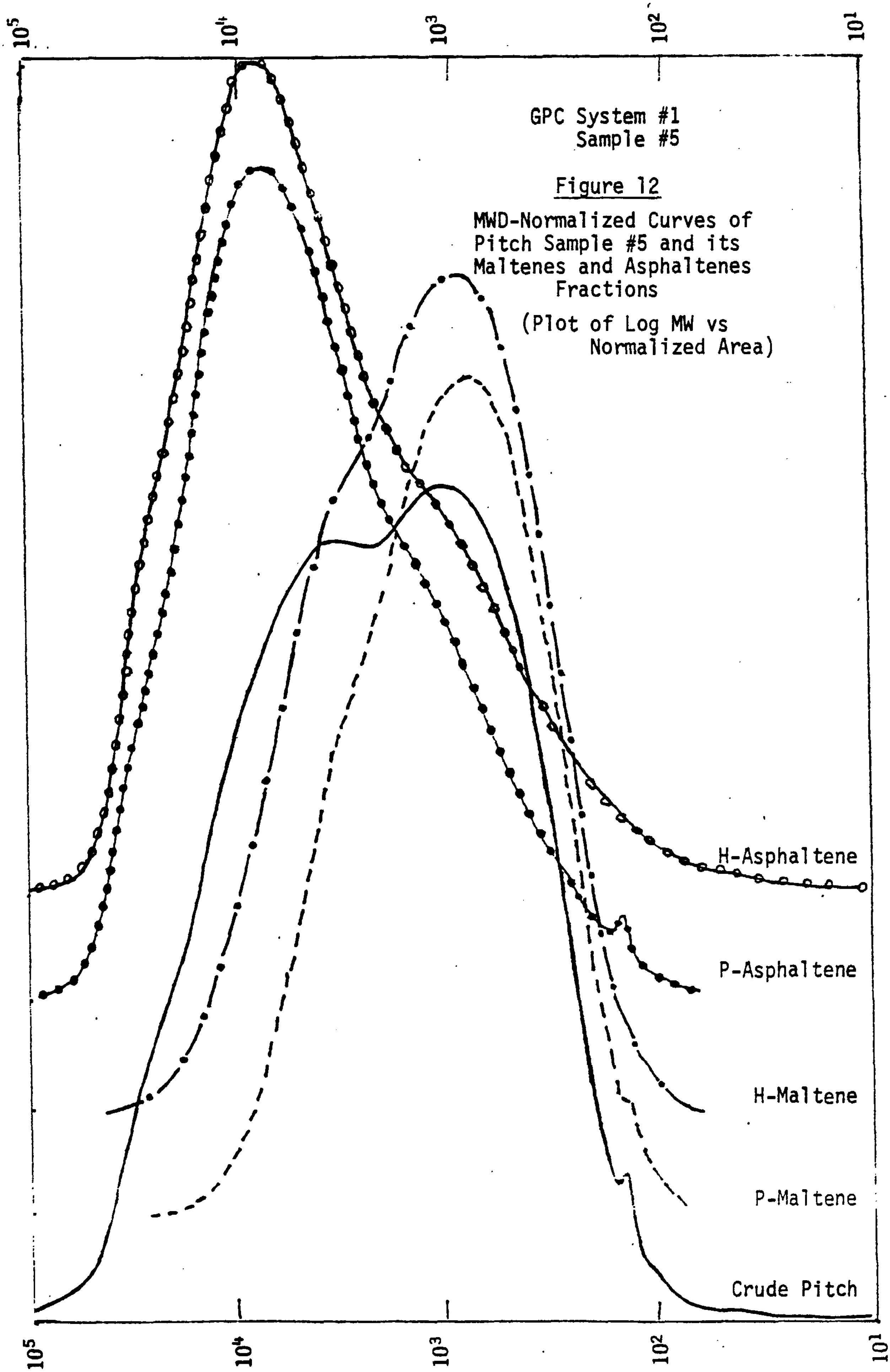


Figure 11

MWD-Normalized Curves of Pitch Sample #4 and its Maltenes and Asphaltenes Fractions

(Plot of Log MW vs Normalized Area)

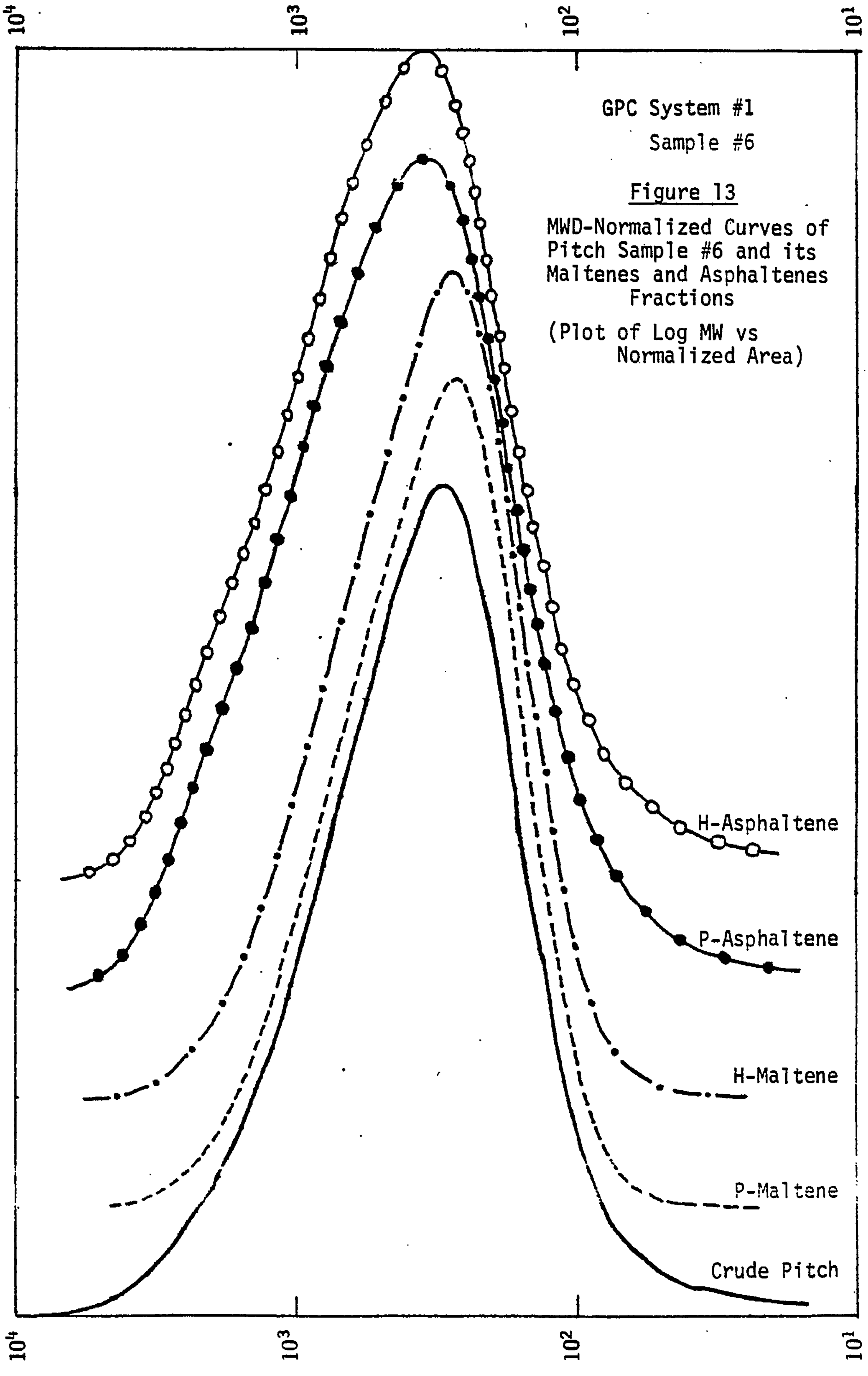


GPC System #1
Sample #5

Figure 12

MWD-Normalized Curves of Pitch Sample #5 and its Maltenes and Asphaltenes Fractions

(Plot of Log MW vs Normalized Area)



GPC System #1
Sample #6

Figure 13

MWD-Normalized Curves of Pitch Sample #6 and its Maltenes and Asphaltenes Fractions

(Plot of Log MW vs Normalized Area)

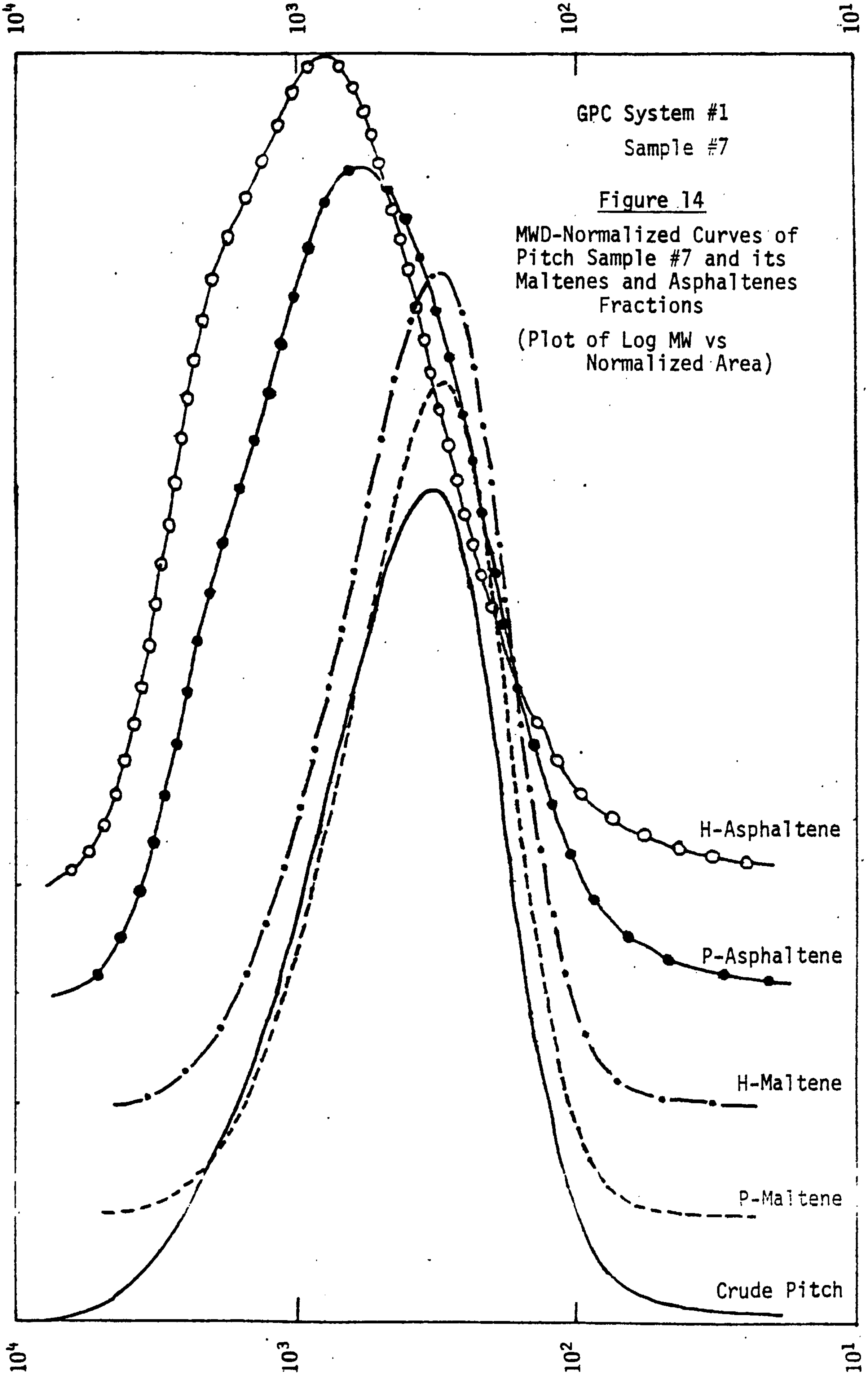
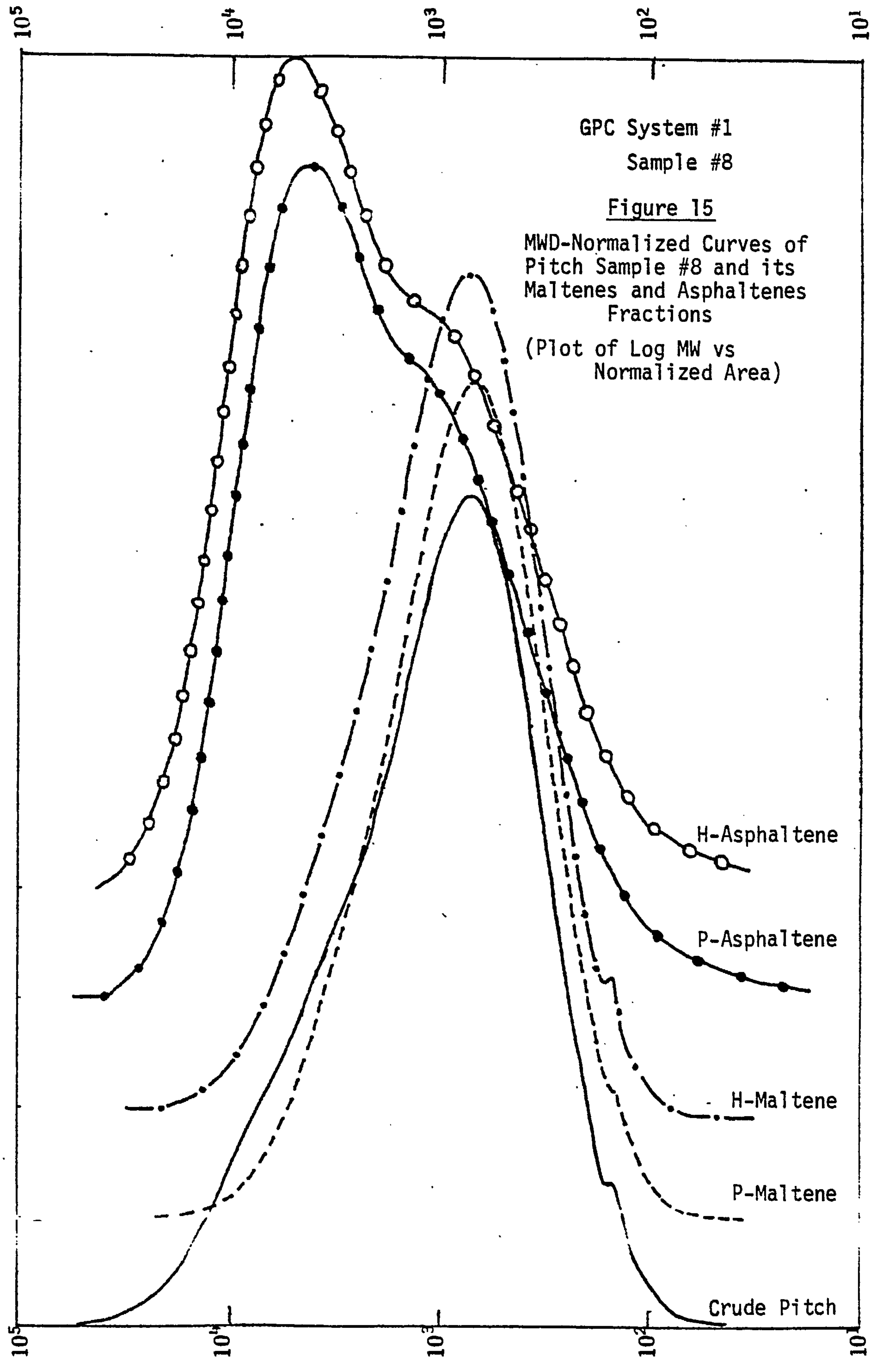


Figure 14

MWD-Normalized Curves of Pitch Sample #7 and its Maltenes and Asphaltenes Fractions

(Plot of Log MW vs Normalized Area)



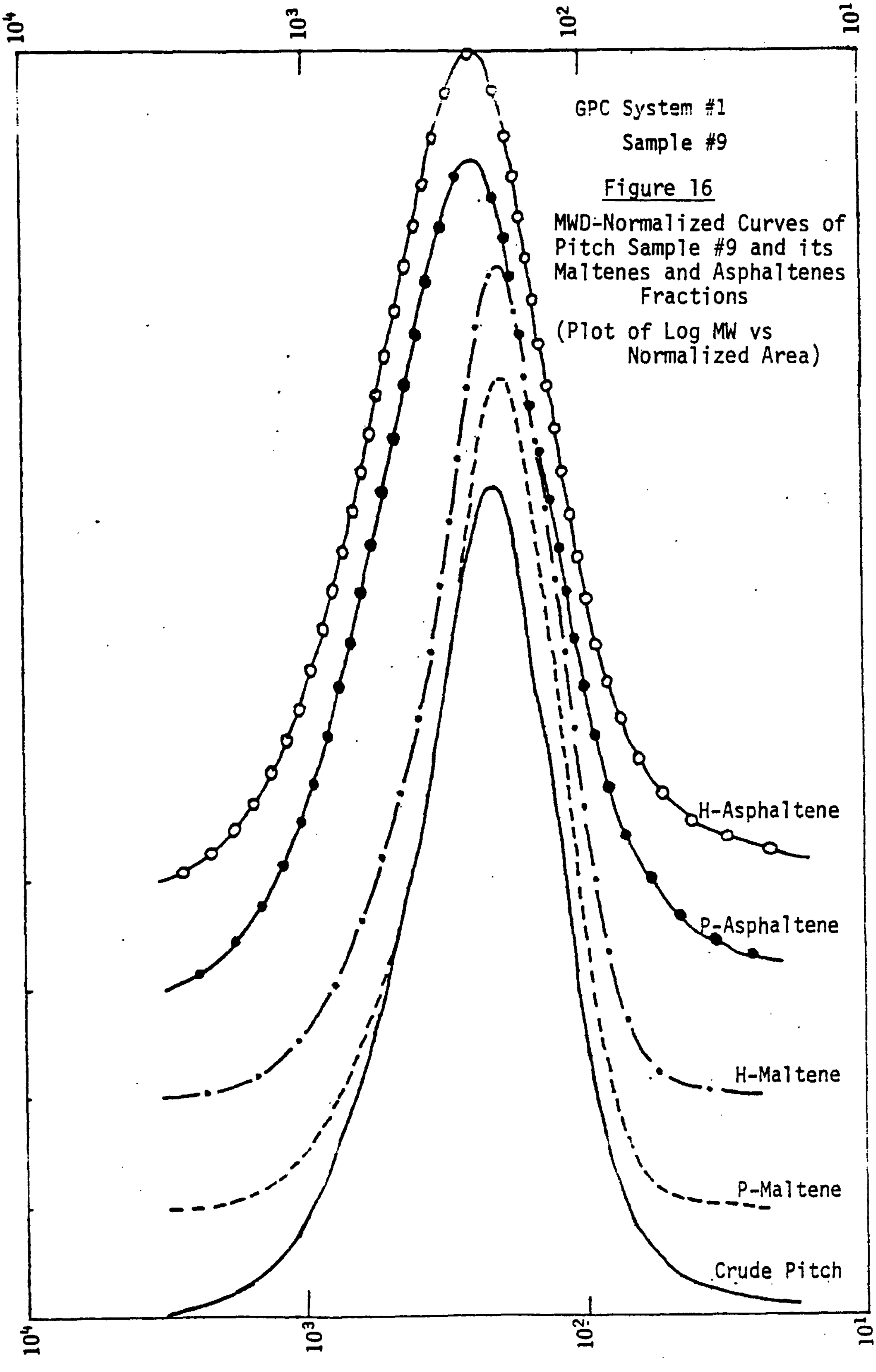
GPC System #1

Sample #8

Figure 15

MWD-Normalized Curves of Pitch Sample #8 and its Maltenes and Asphaltenes Fractions

(Plot of Log MW vs Normalized Area)



GPC System #1

Sample #9

Figure 16

MWD-Normalized Curves of Pitch Sample #9 and its Maltenes and Asphaltenes Fractions

(Plot of Log MW vs Normalized Area)

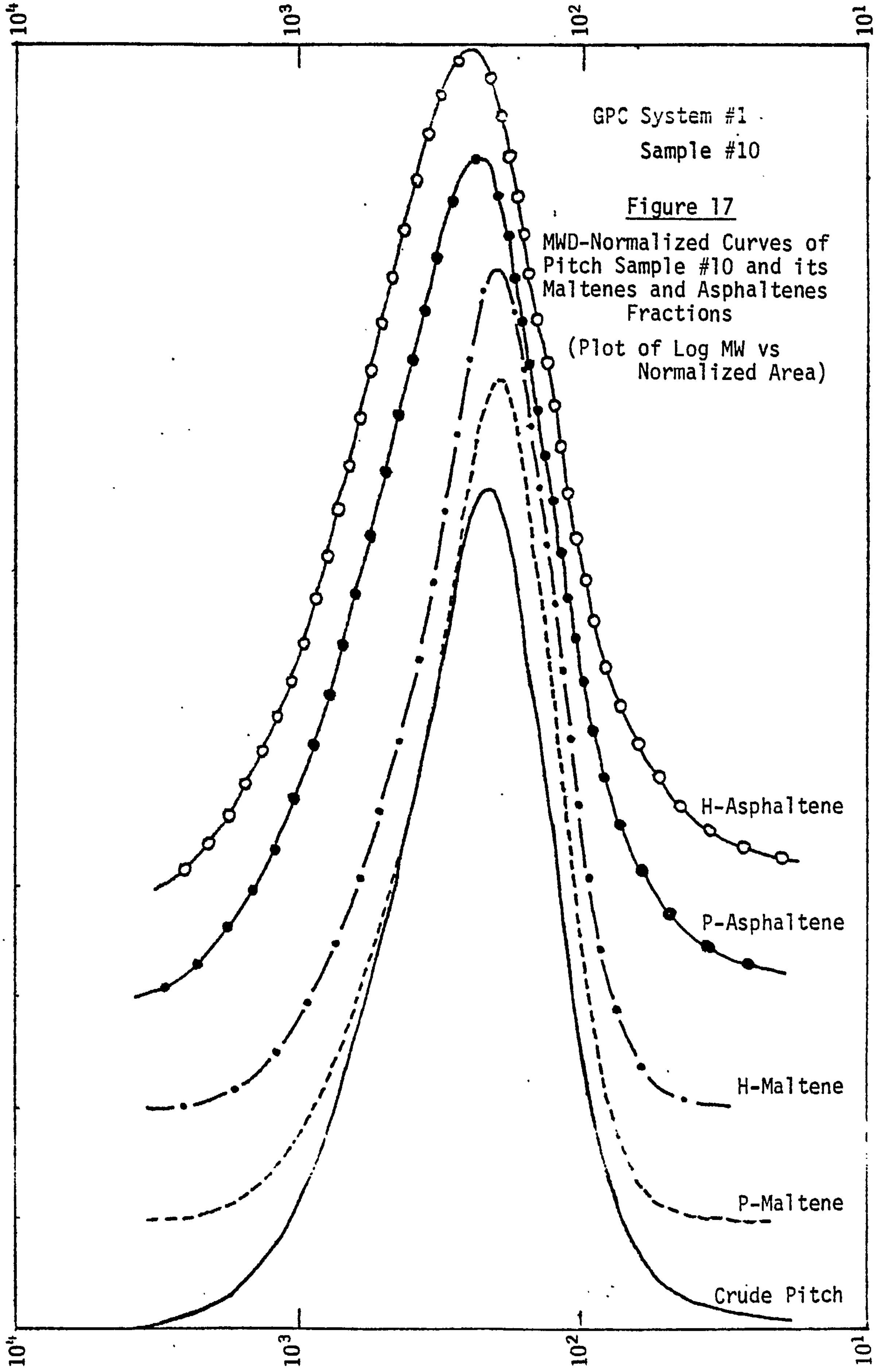
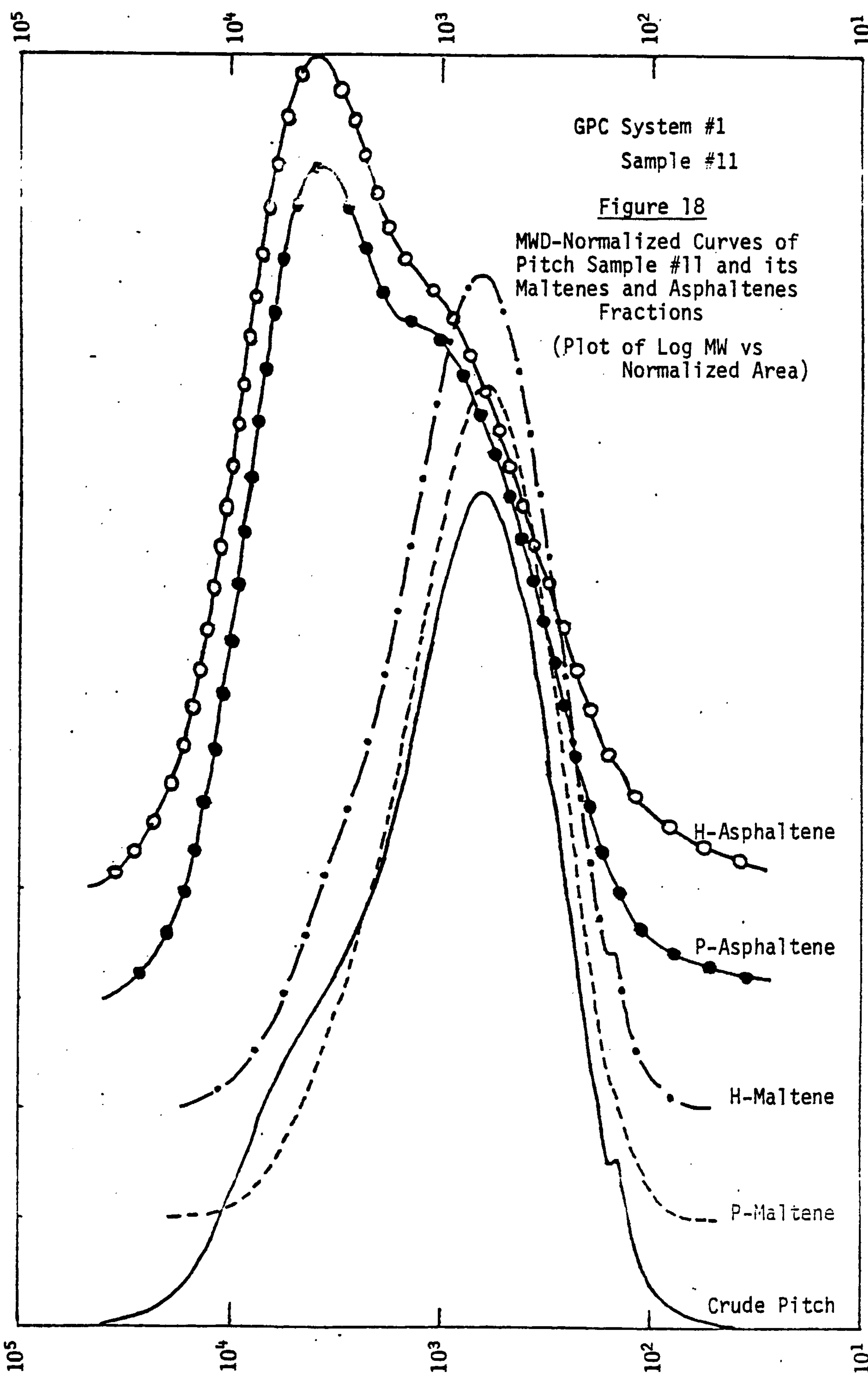


Figure 17

MWD-Normalized Curves of Pitch Sample #10 and its Maltenes and Asphaltenes Fractions

(Plot of Log MW vs Normalized Area)



GPC System #1

Sample #11

Figure 18

MWD-Normalized Curves of Pitch Sample #11 and its Maltenes and Asphaltenes Fractions

(Plot of Log MW vs Normalized Area)

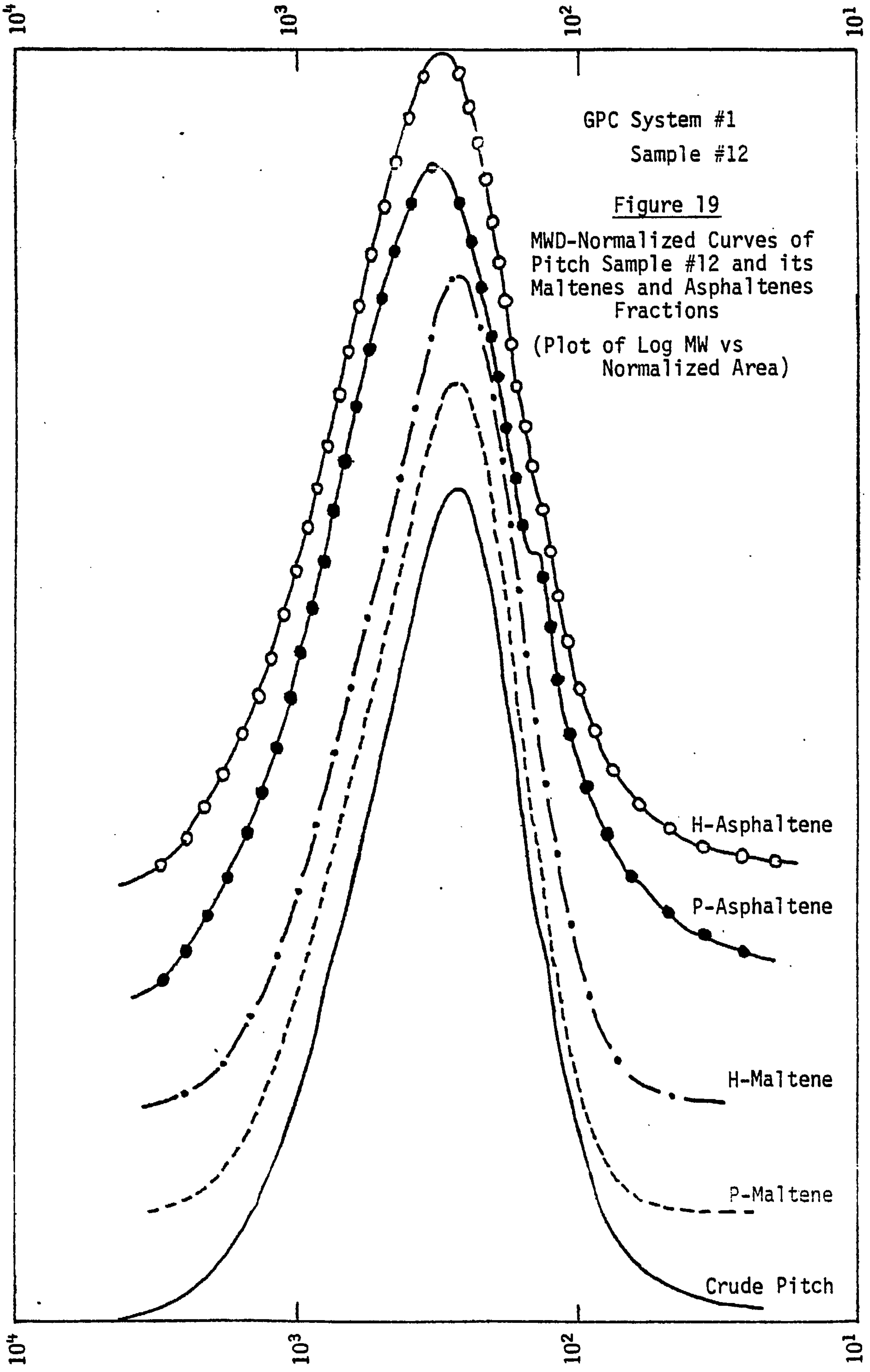


Figure 19

MWD-Normalized Curves of Pitch Sample #12 and its Maltenes and Asphaltenes Fractions

(Plot of Log MW vs Normalized Area)

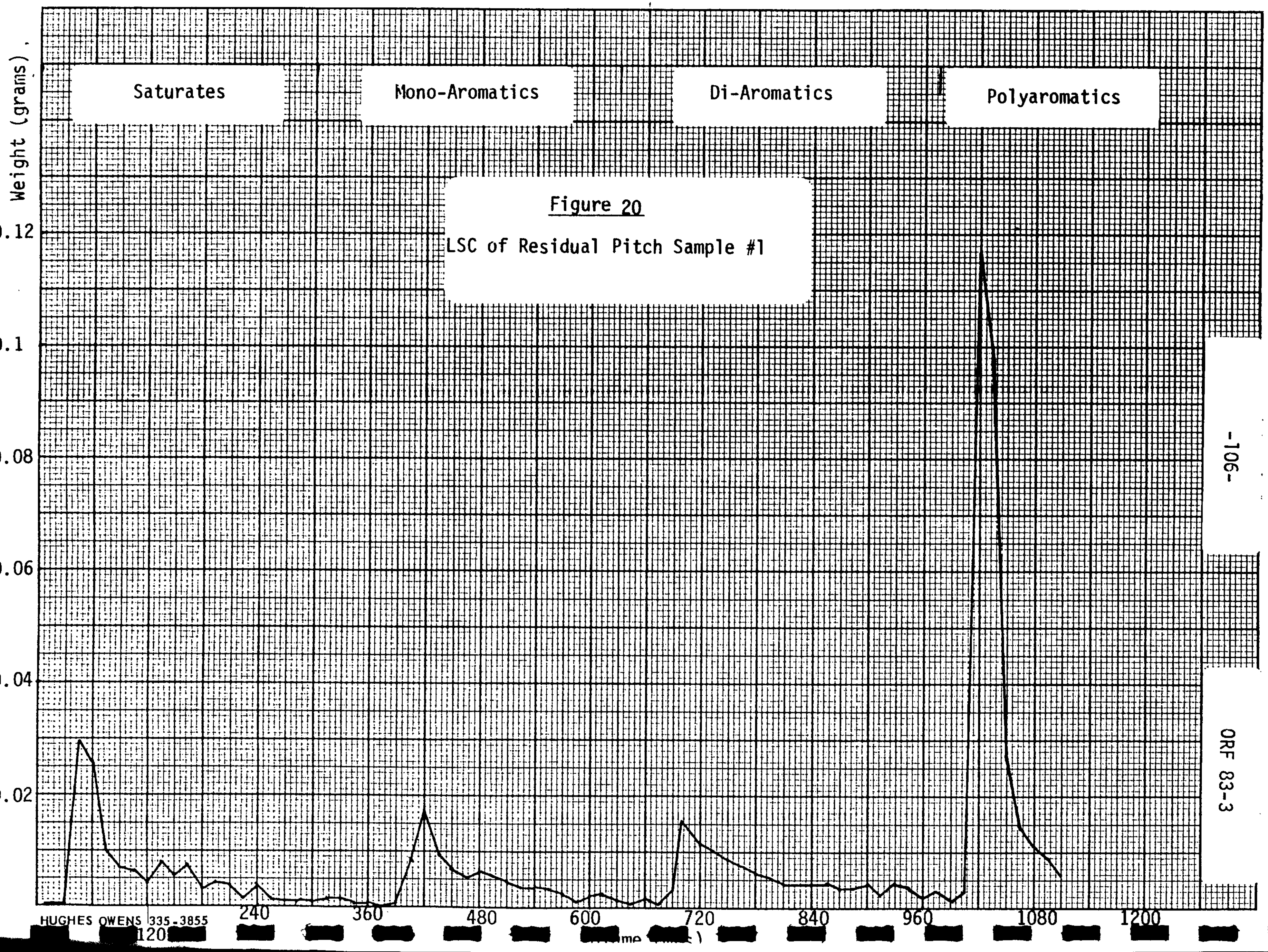


Figure 20

LSC of Residual Pitch Sample #1

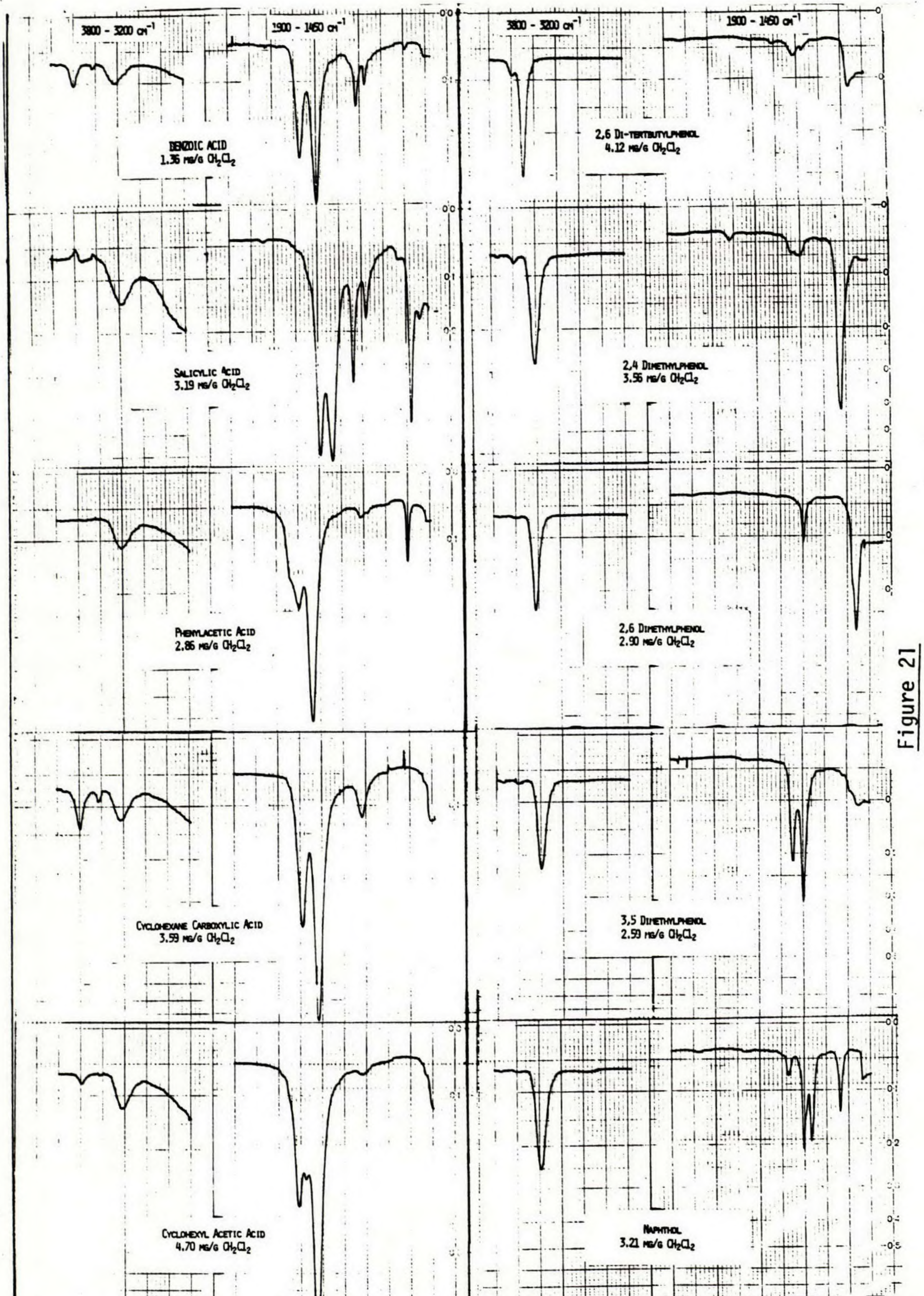
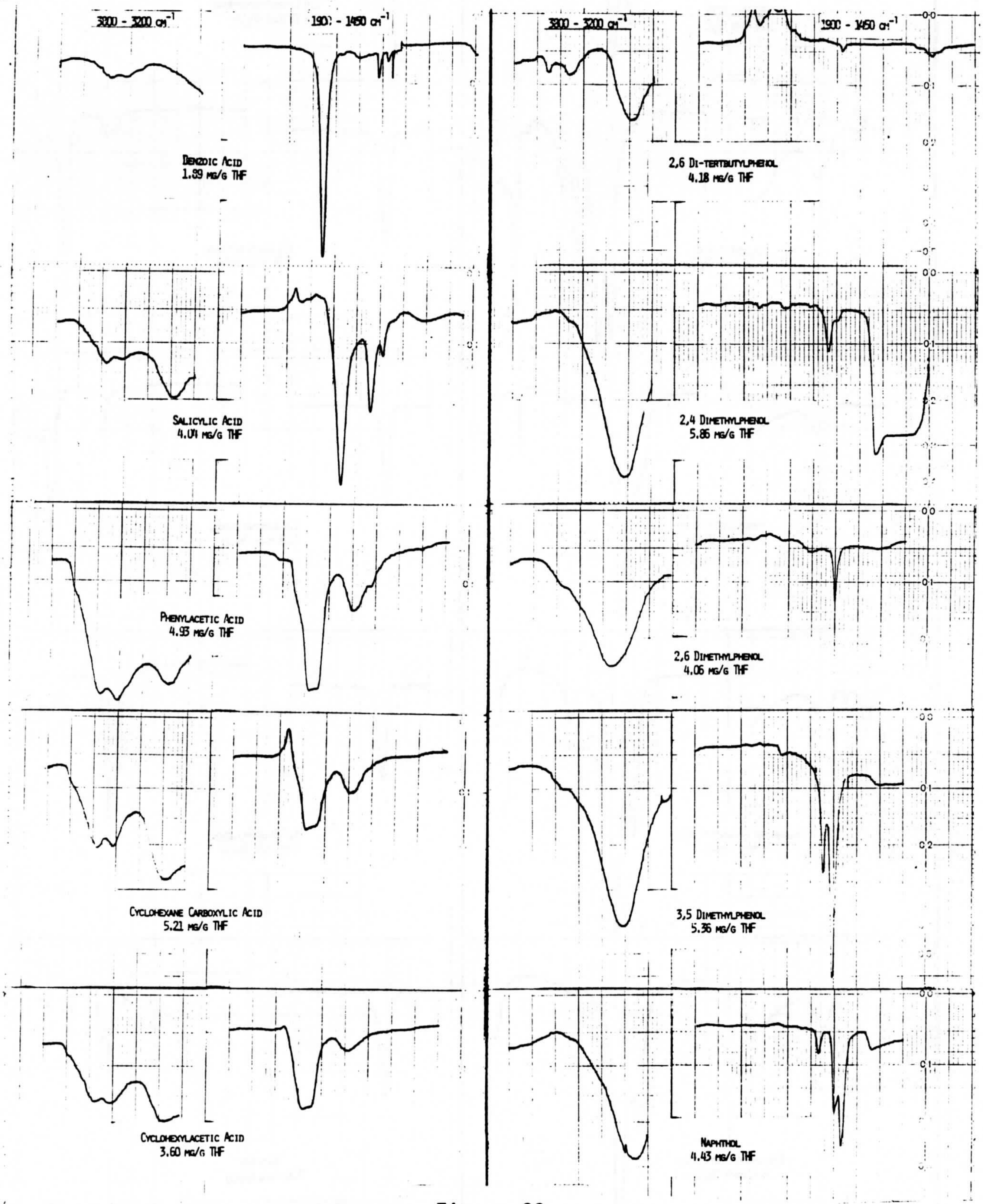


Figure 21

Infra-red Spectra of Model Compounds - Carboxylic Acids and Phenols in CH_2Cl_2



<u>Figure 22</u>

Infra-red Spectra of Model Compounds - Carboxylic Acids and Phenols in THF

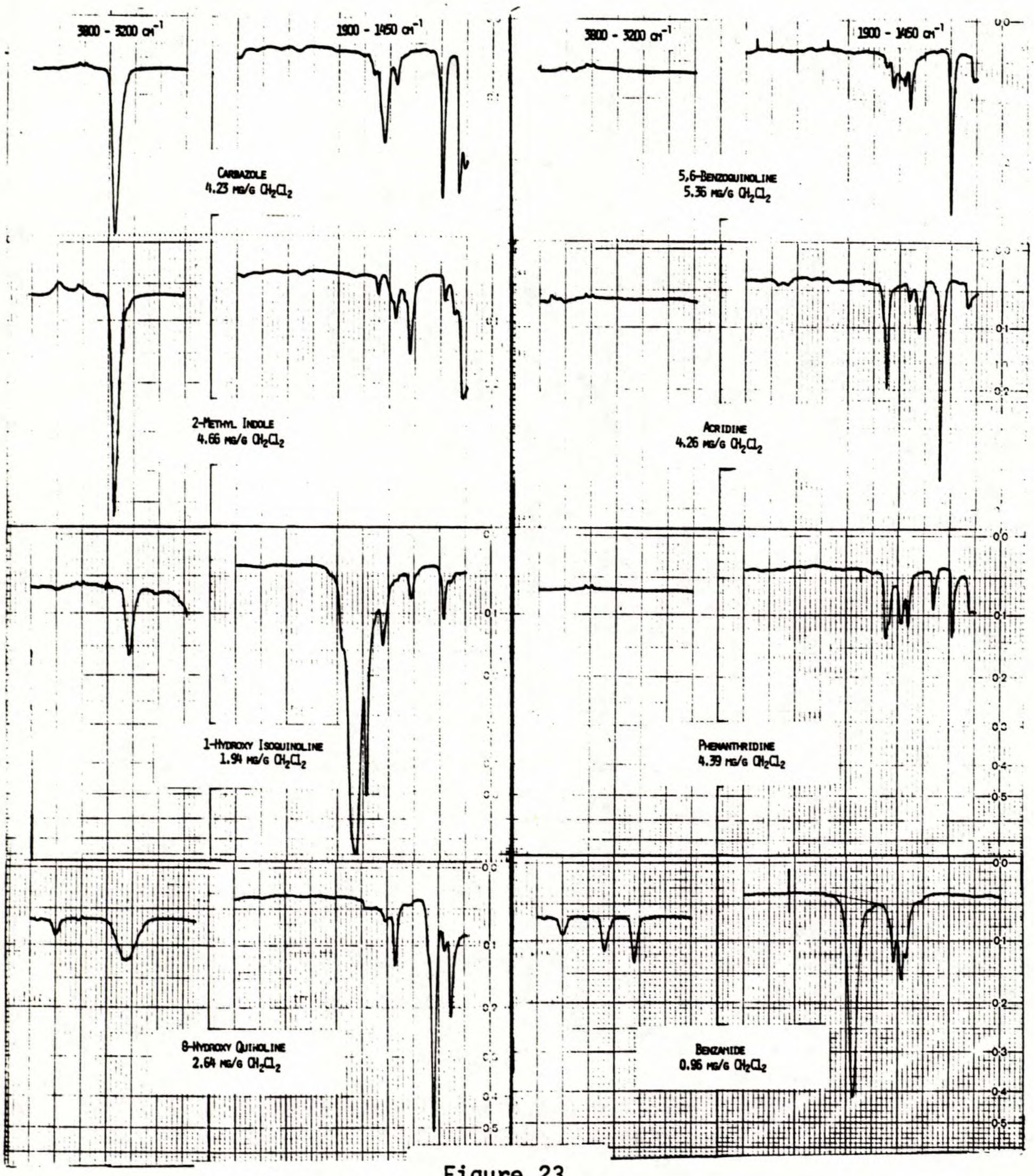


Figure 23

Infra-red Spectra of Model Compounds - Carbazole, 2-Methyl Indole, 1-Hydroxy Isoquinoline, 8-Hydroxy Quinoline, 5,6-Benzoquinoline, Acridine, Phenanthridine and Benzamide in CH_2Cl_2

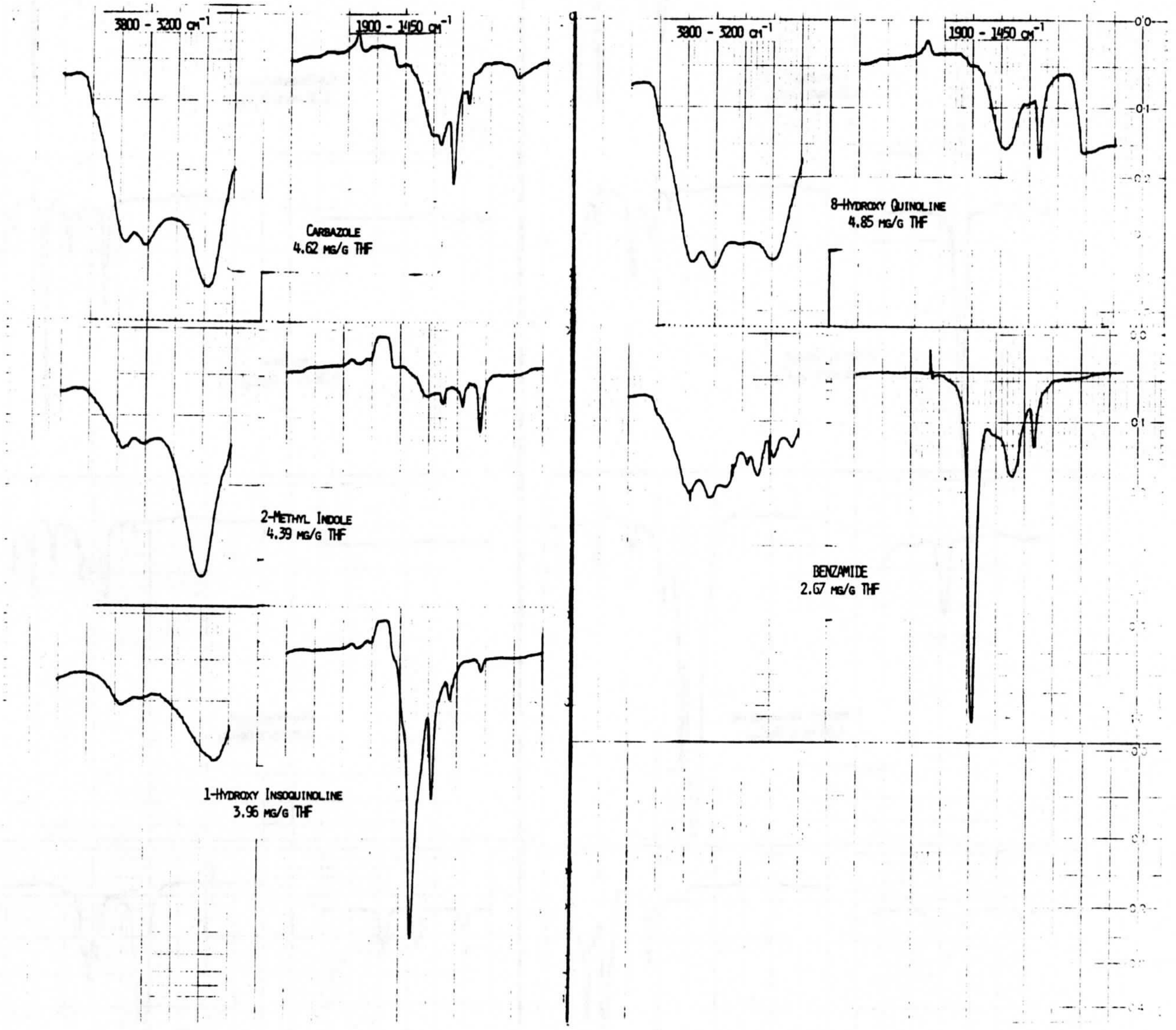


Figure 24

Infra-red Spectra of Model Compounds -
Carbazole, 2-Methyl Indole, 1-Hydroxy
Isoquinoline, 8-Hydroxy Quinoline
and Benzamide in THF

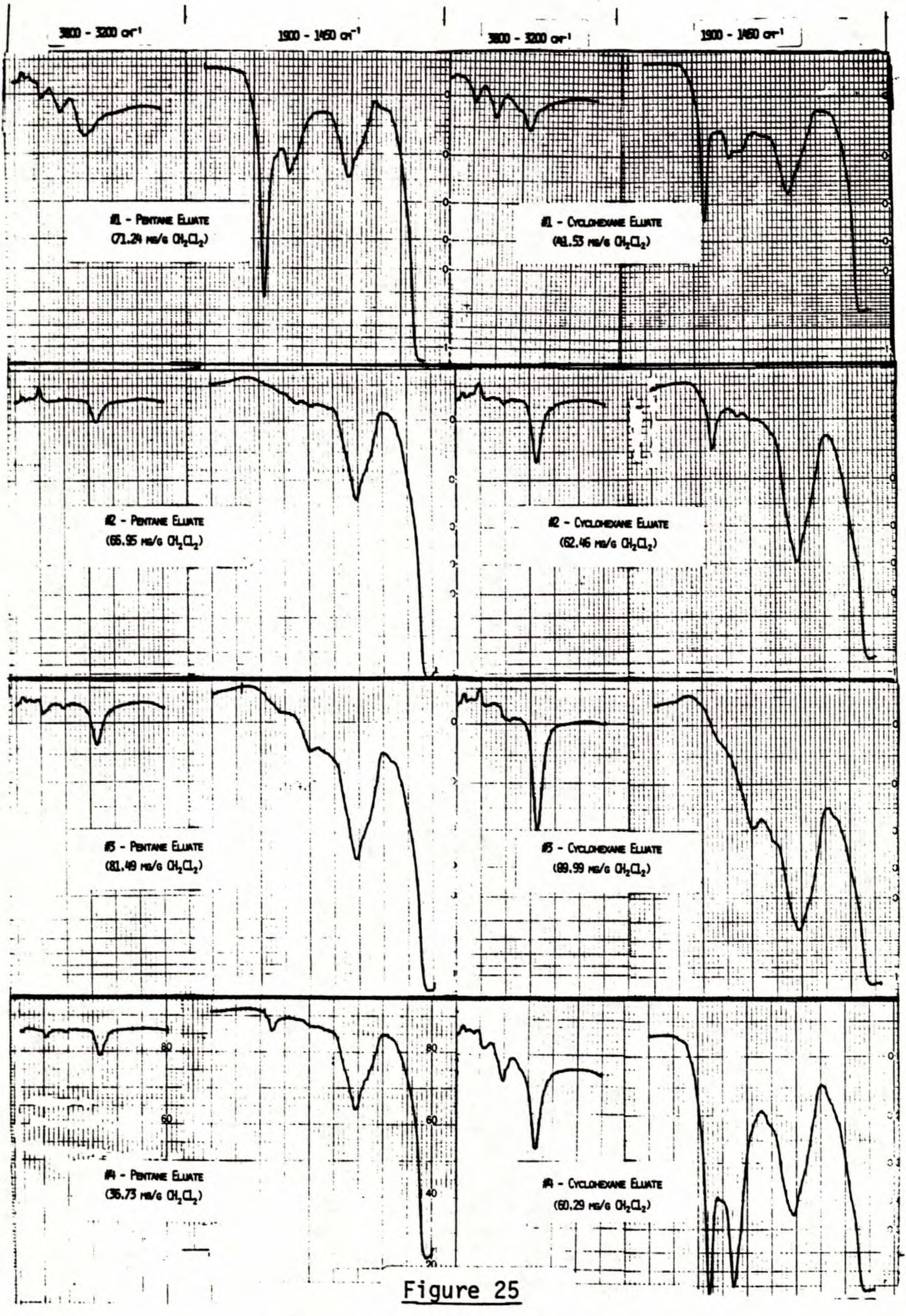


Figure 25

Infra-red Spectra of Ion-Exchange Pentane- and Cyclohexane Eluates of Pitch Maltene Samples #1, 2, 3 and 4 in CH_2Cl_2

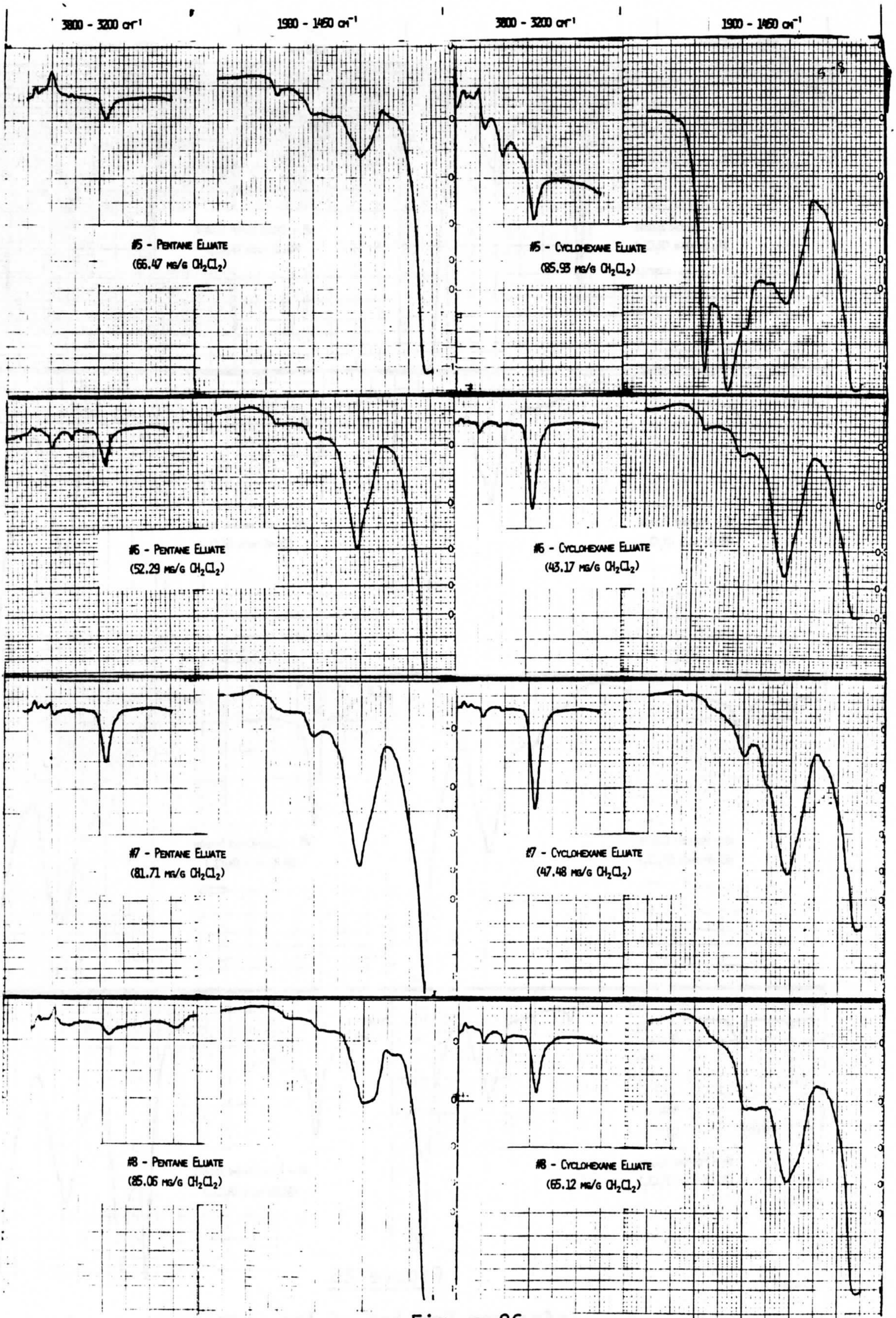


Figure 26

Infra-red Spectra of Ion-Exchange Pentane- and Cyclohexane Eluates of Pitch Maltene Samples #5, 6 7 and 8 in CH_2Cl_2

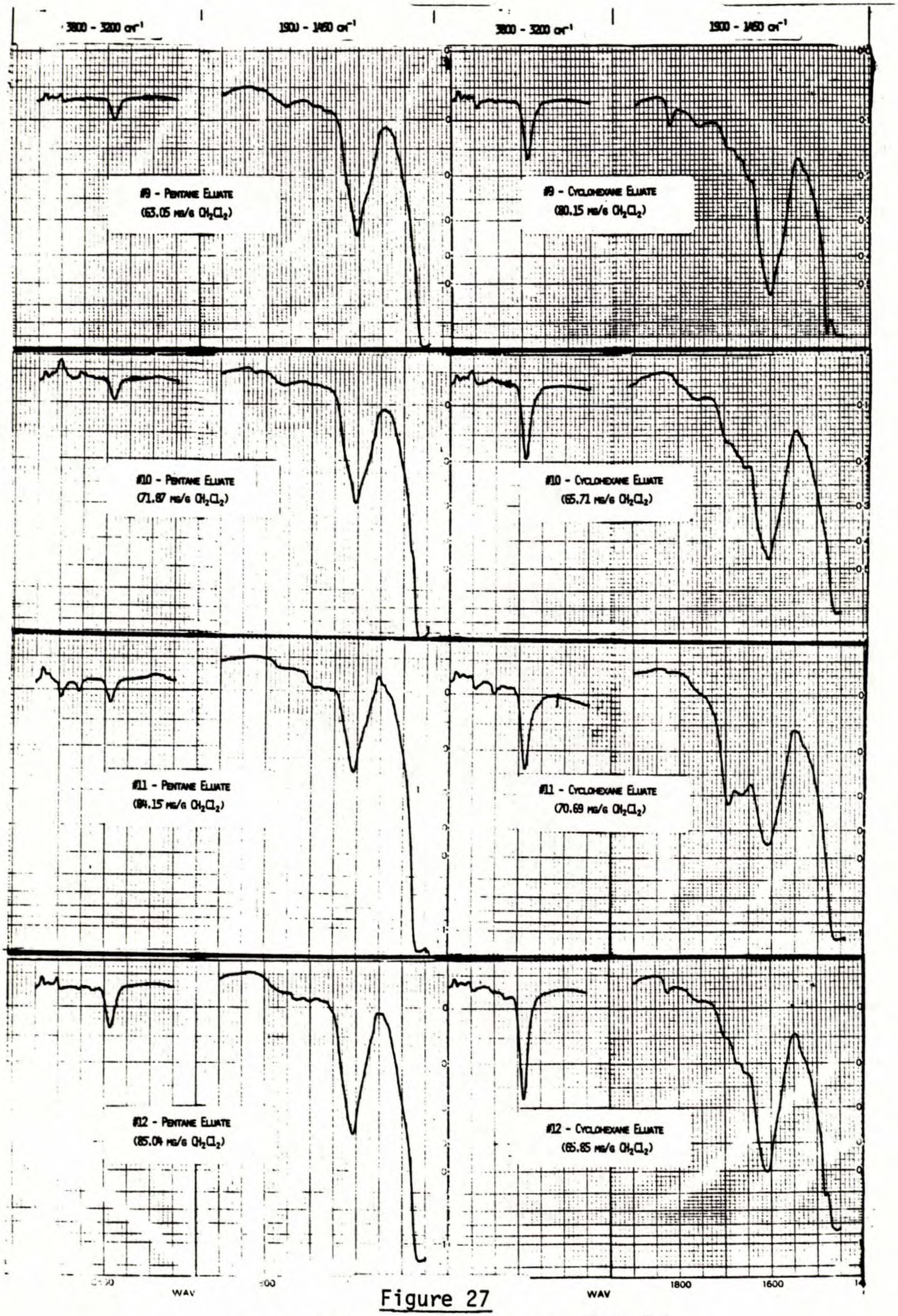


Figure 27

Infra-red Spectra of Ion-Exchange Pentane- and Cyclohexane Eluates of Pitch Maltene Samples #9, 10, 11 and 12 in CH_2Cl_2

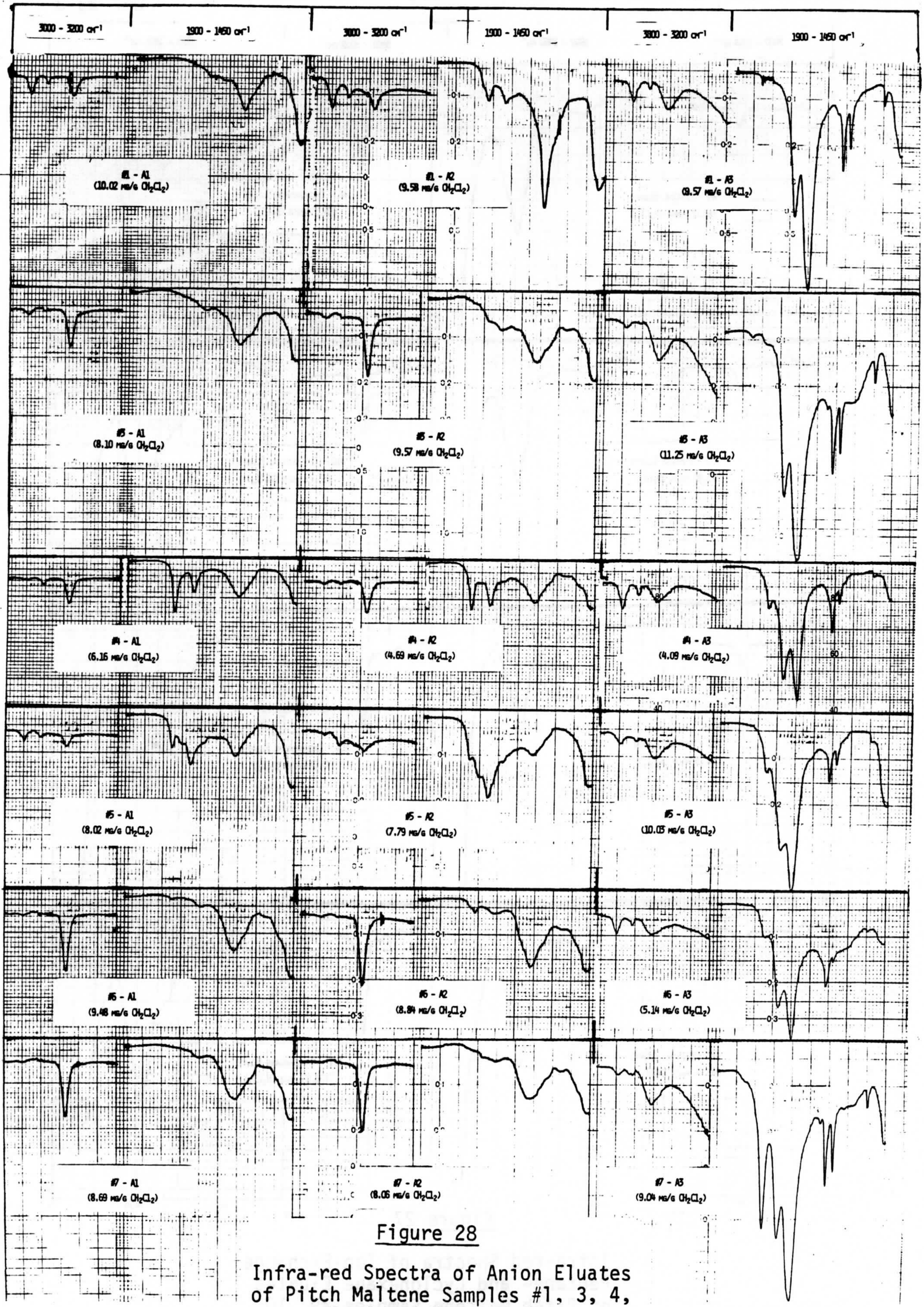


Figure 28

Infra-red Spectra of Anion Eluates of Pitch Maltene Samples #1, 3, 4, 5, 6 and 7 in CH_2Cl_2

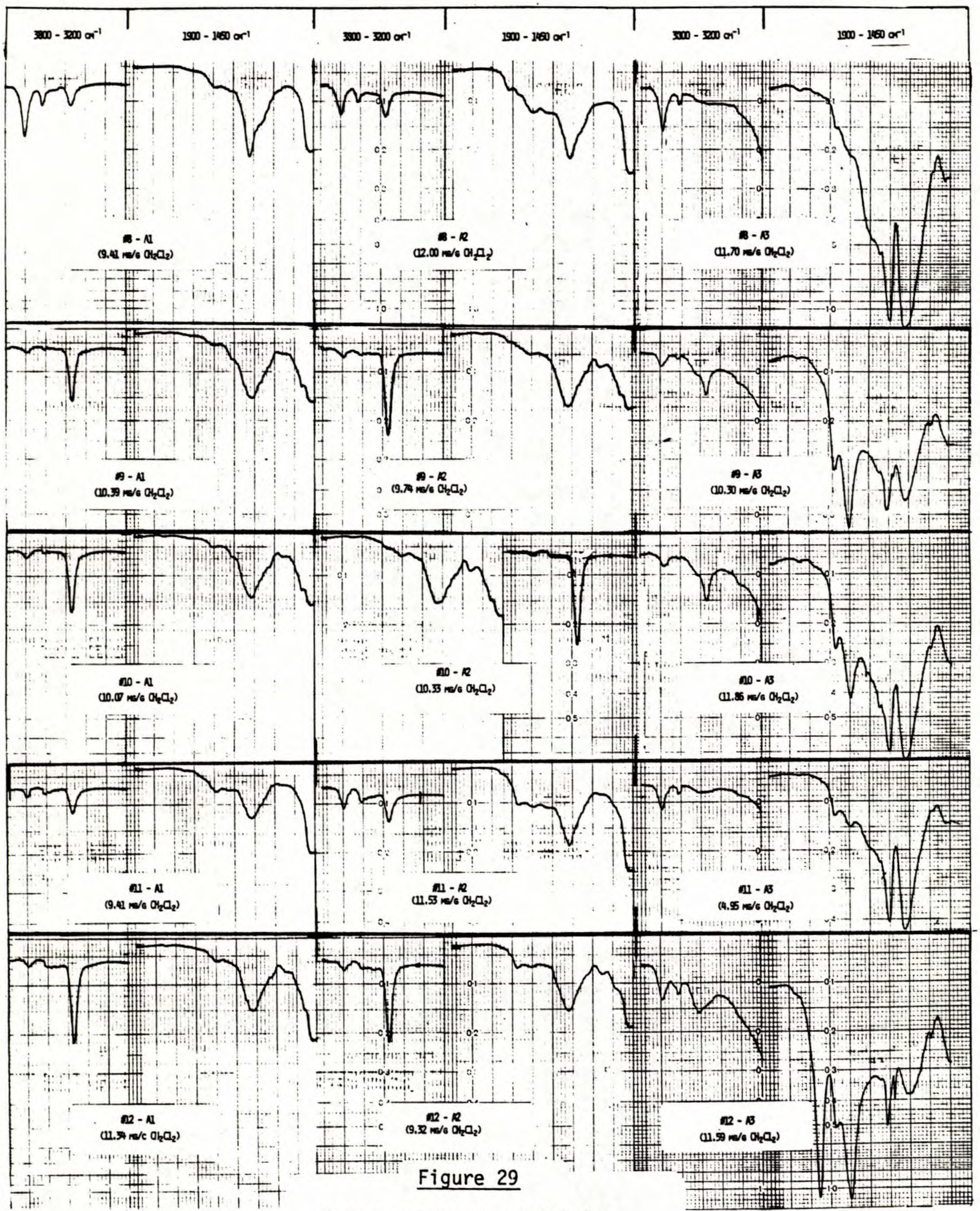


Figure 29

Infra-red Spectra of Anion
Eluates of Pitch Maltene Samples
#8, 9, 10, 11 and 12 in CH_2Cl_2

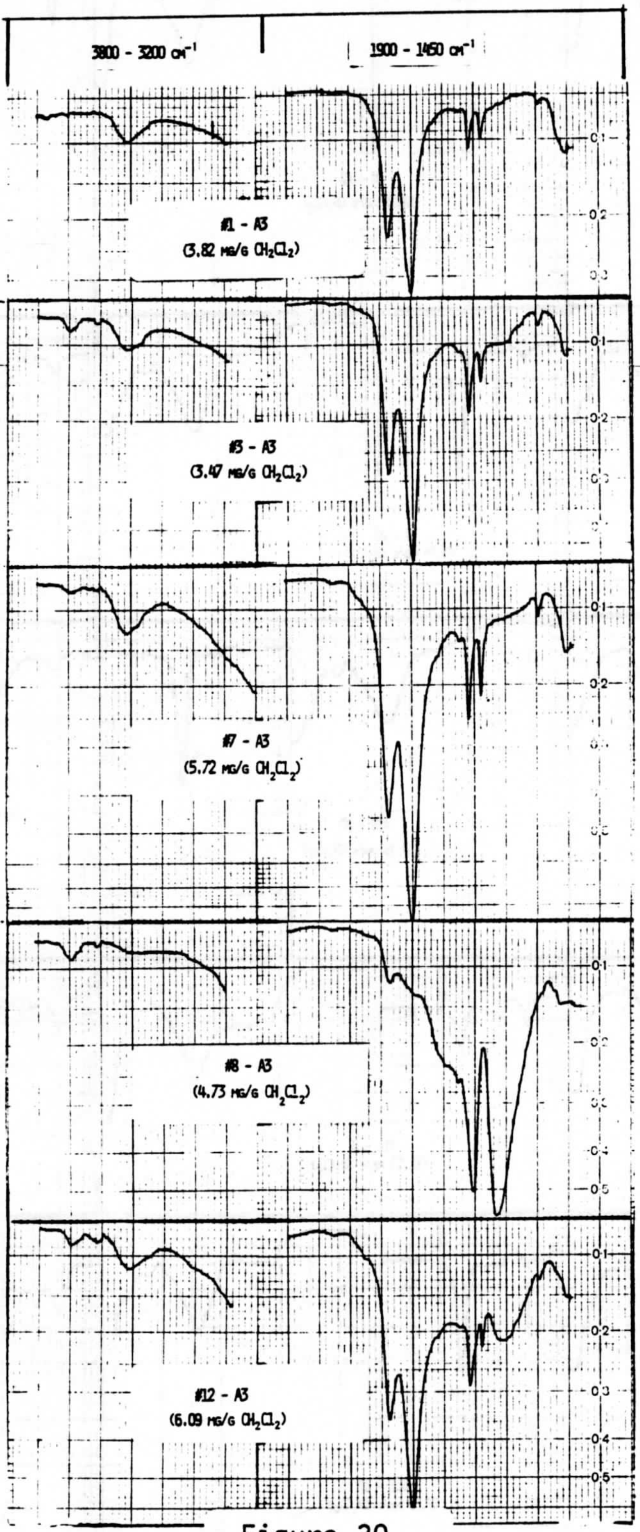
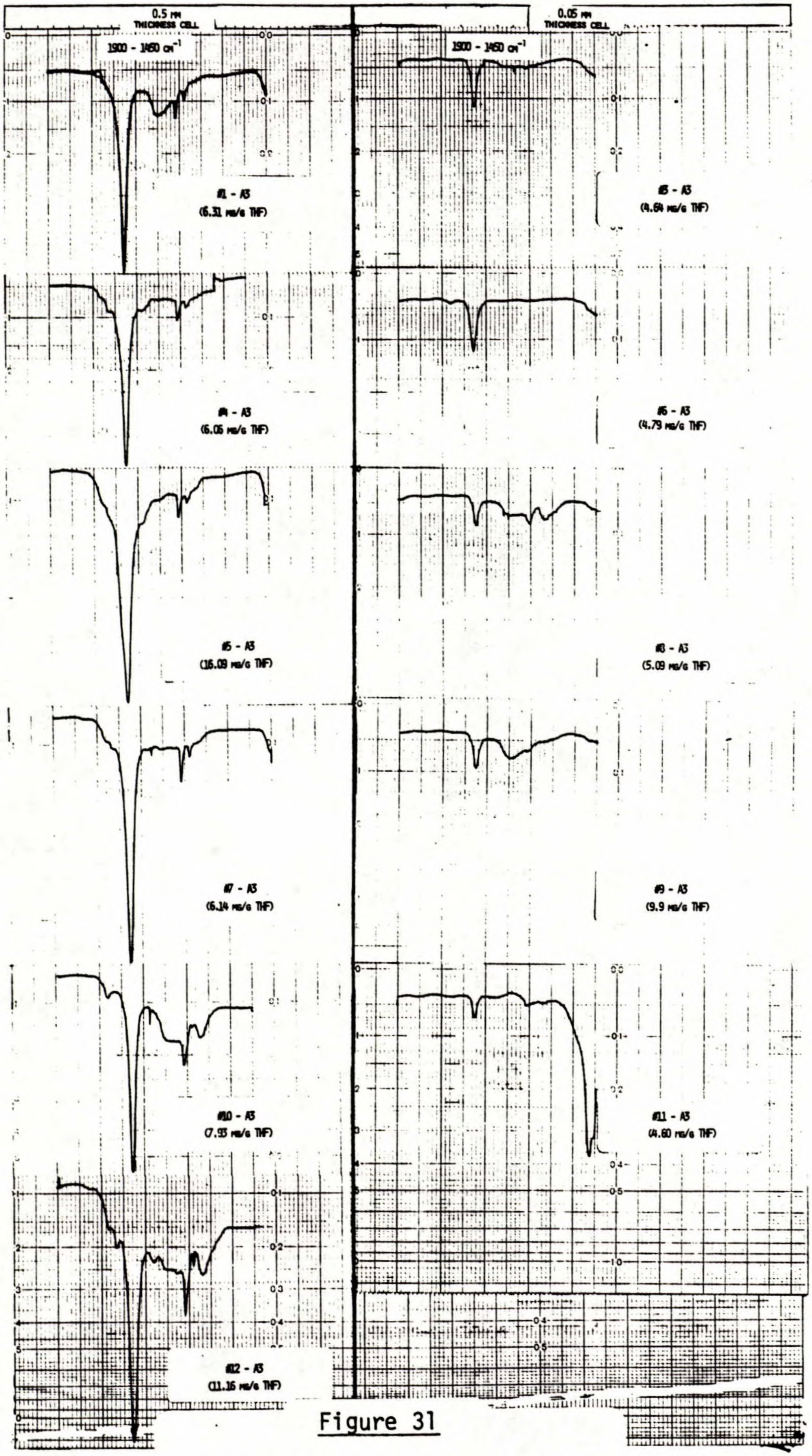


Figure 30

Infra-red Spectra of Dilute Solutions of A-3 Anion Eluates of Pitch Maltene Samples #1, 3, 7, 8 and 12 in CH_2Cl_2



<u>Figure 31</u>

Infra-red Spectra of A-3 Anion Eluates of Pitch Maltene Samples #1,3,4,5,6,7,8,9,10,11 and 12 in THF

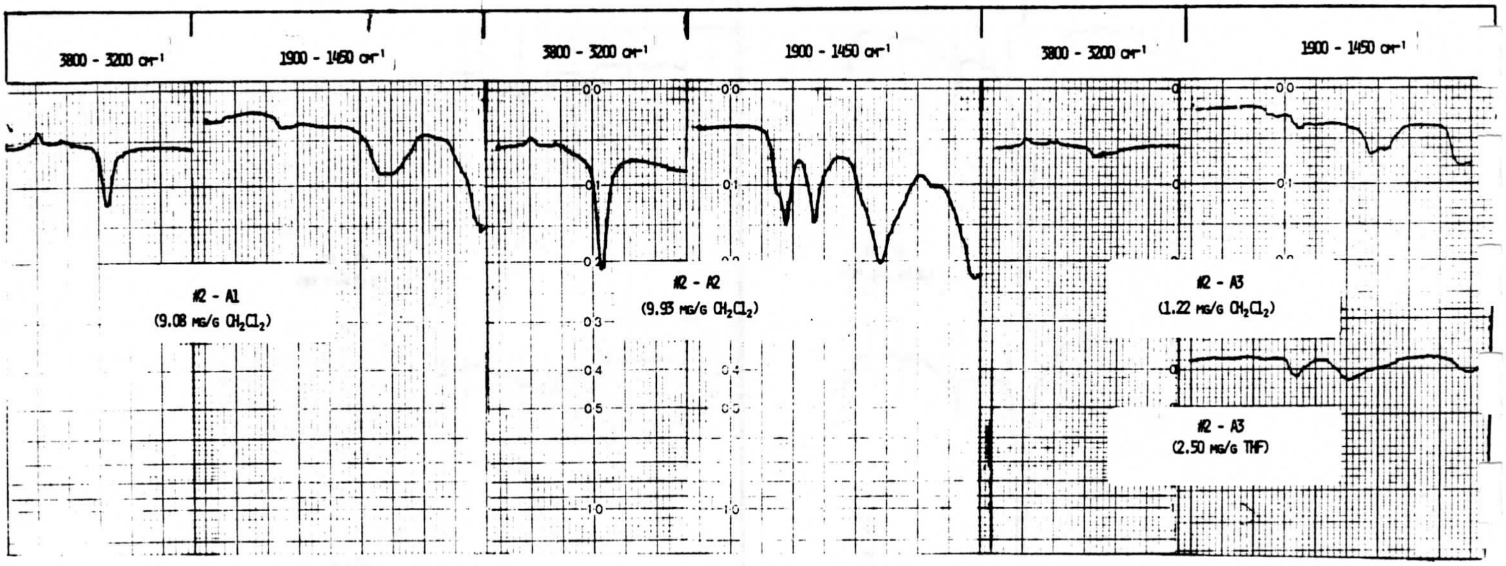


Figure 32

Infra-red Spectra of Three (A-1, A-2, A-3) Anion Eluates of Pitch Maltene Samples #2 in CH_2Cl_2 and THF

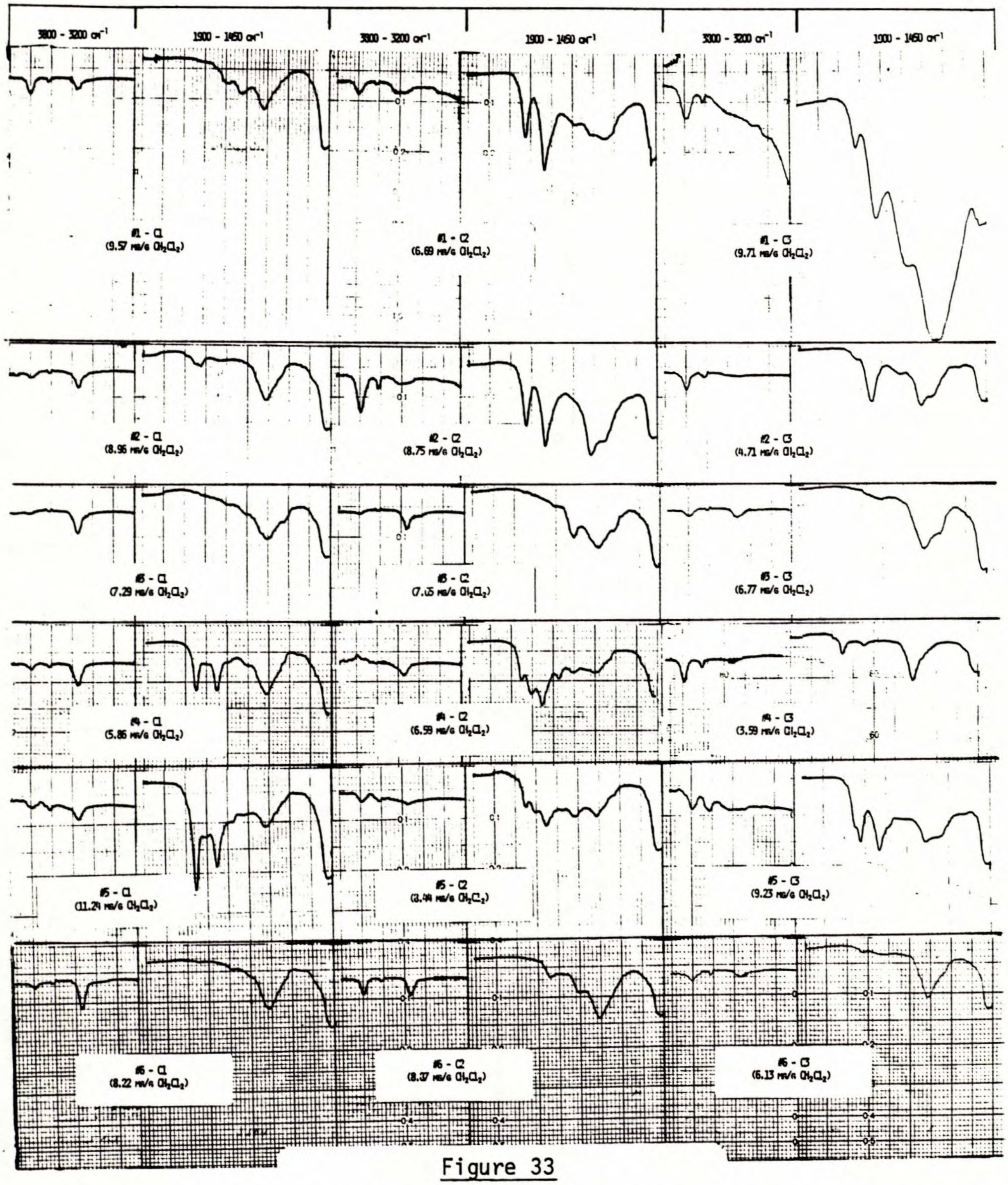


Figure 33

Infra-red Spectra of Cation Eluates of Pitch Maltene Samples #1,2,3,4,5 and 6 in CH_2Cl_2

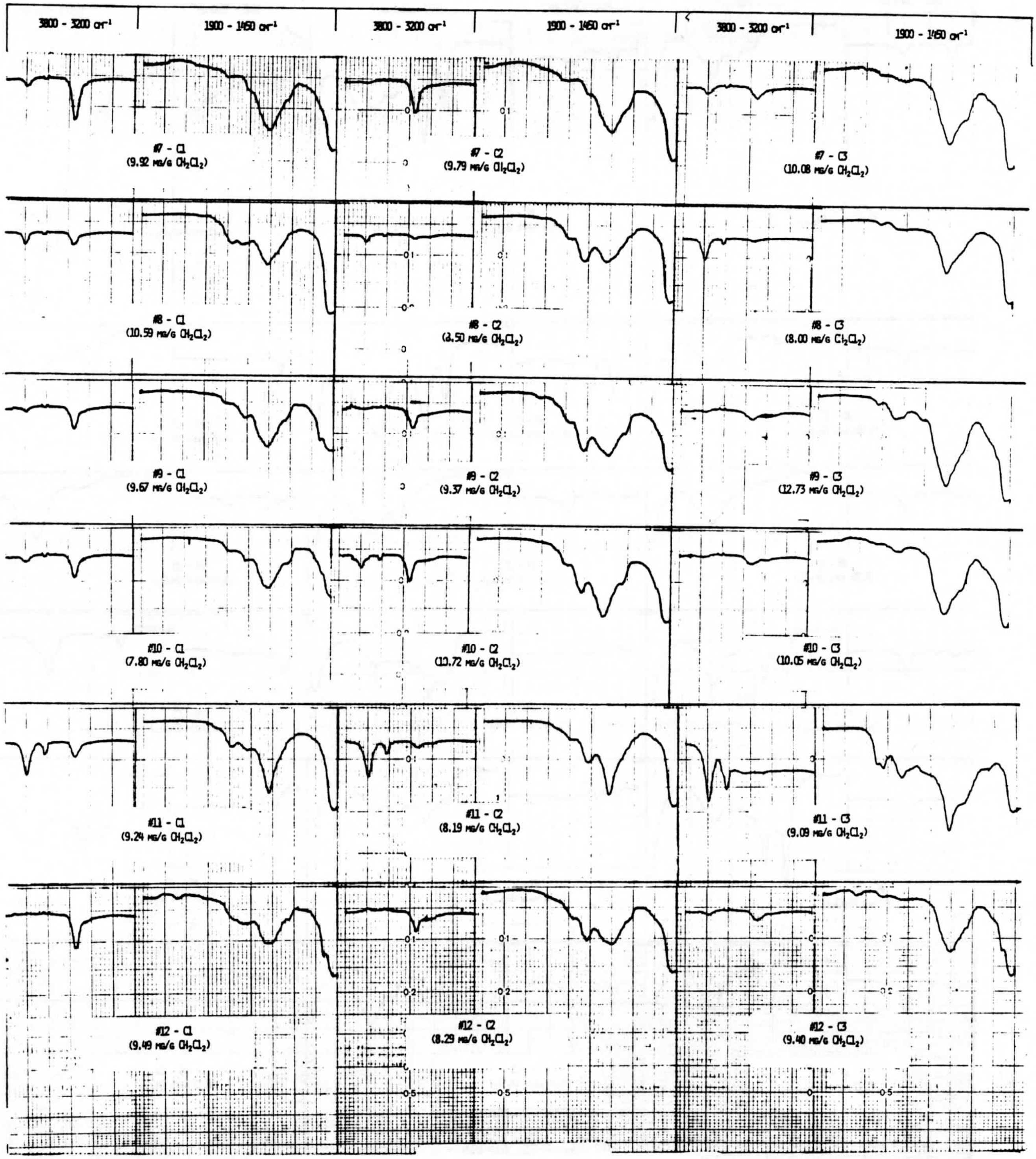


Figure 34

Infra-red Spectra of Cation Eluates of Pitch Maltene Samples #7,8,9,10,11 and 12 in CH_2Cl_2

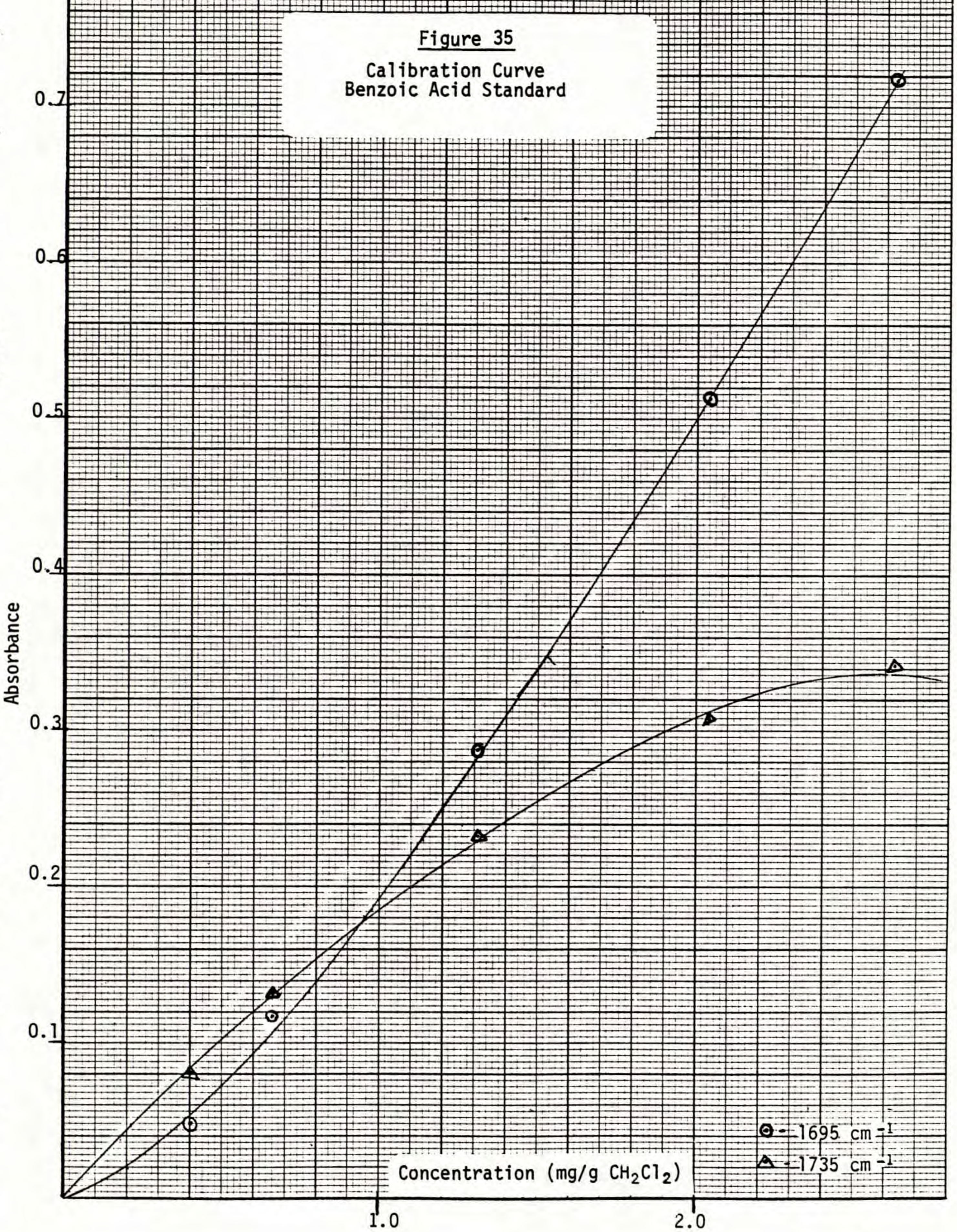


Figure 35

Calibration Curve
Benzoic Acid Standard

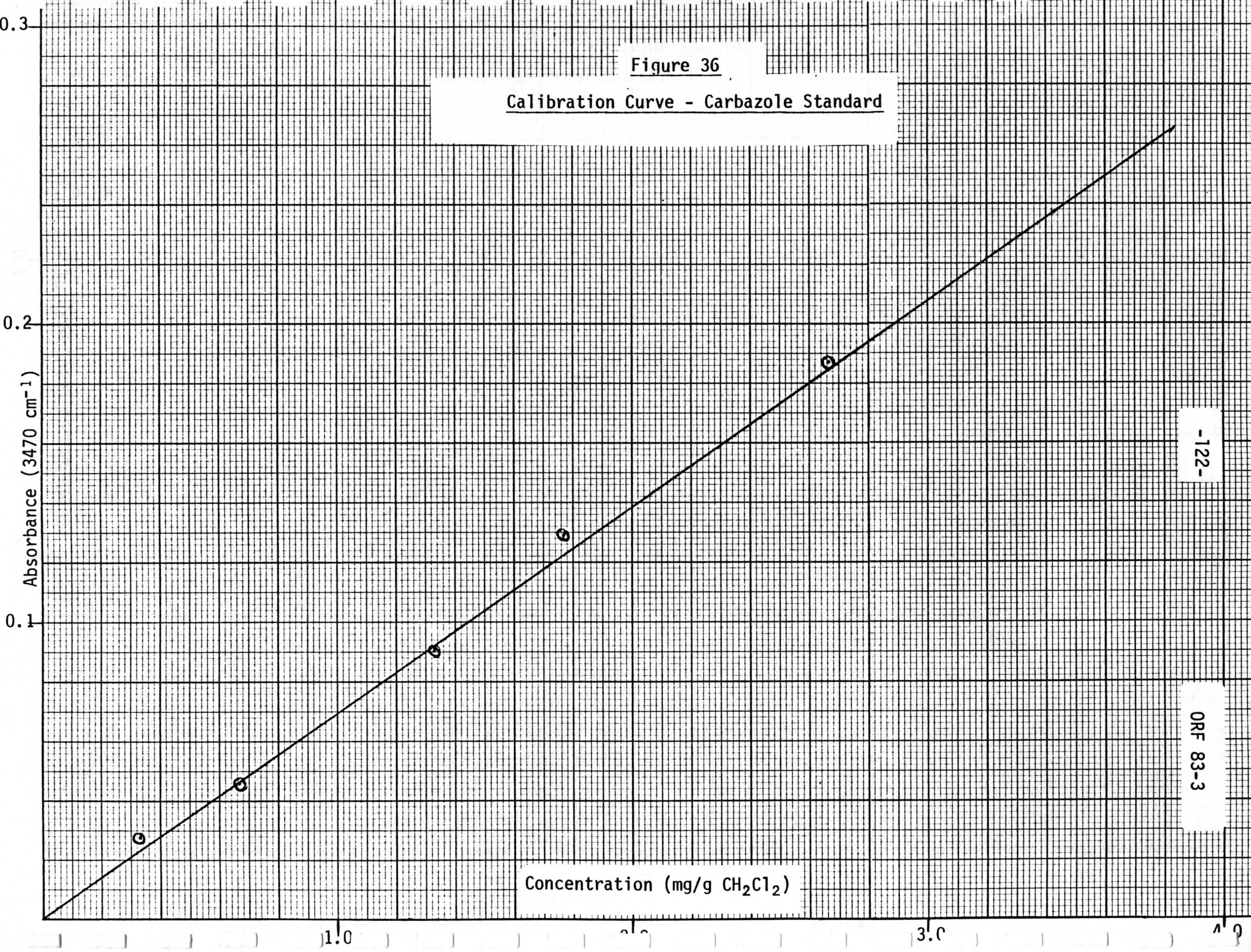
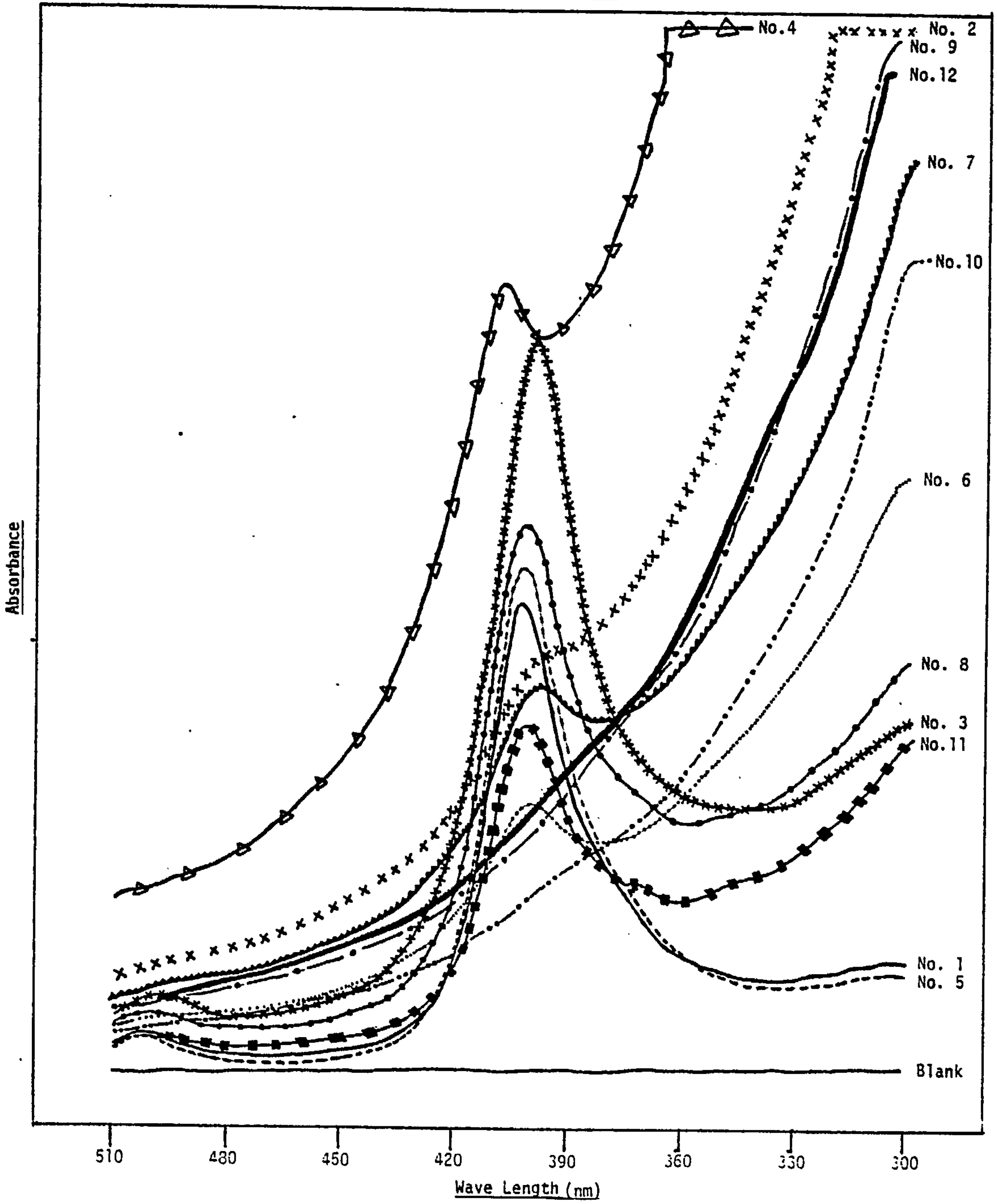


Figure 36

Calibration Curve - Carbazole Standard

Figure 37

UV-Vis Scan of Residual Pitch Benzene Solubles in Porphyrin Analysis



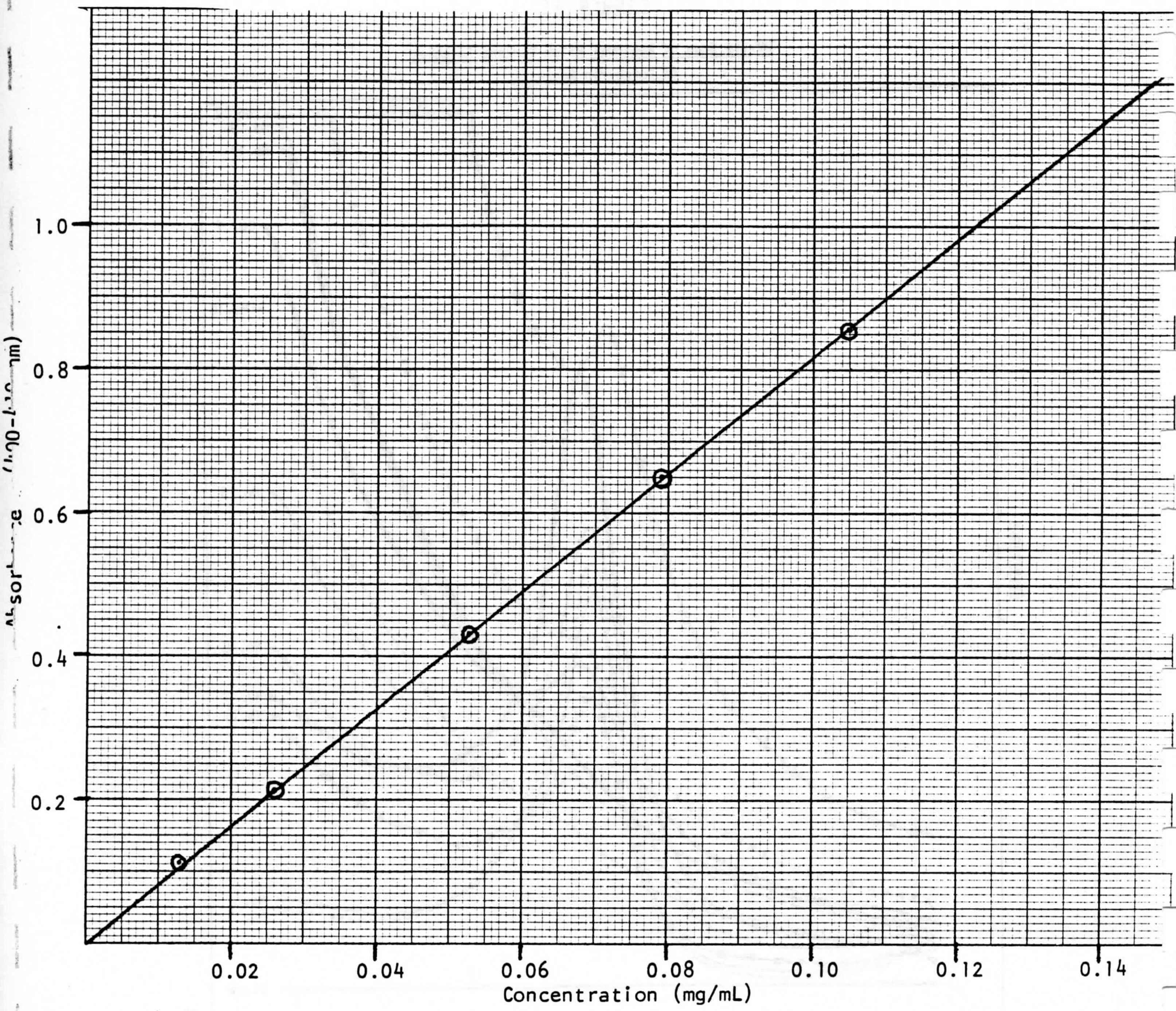


Figure 38 Calibration Curve - Porphyrin Standard (Sample No. 8)

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