CONVERSION OF

OKLAHOMA WASTE COAL

INTO ROAD ASPHALT

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16. ABSTRACT

This report has been prepared to inform the Oklahoma Department of Transportation the progress on the project: Conversion of Oklahoma Waste Coal into Road Asphalt, as well as to provide enough information so that co-workers at the ODOT can readily duplicate the described procedures.

Part I provides background material which introduces the techniques normally used to separate and characterize chemical samples, as well as examples of asphalt fingerprinting using these concepts. This initial effort clearly demonstrates that when a reference library of asphalts and their separation and spectroscopic properties is established, effective fingerprinting will be available.

Part II describes the major effort of this project; a study of the laboratory feasibility of converting waste Oklahoma coal into an asphalt extender. This effort confirms the hypothesis that this coal can be converted into a liquid material by hydrogenation. This substance however, has no miscibility with petroleum asphalt. When animal fat or linseed oil is added to the reaction mixture prior to hydrogenation, a material is obtained which has short term miscibility with petroleum asphalt. This product has excellent chemical properties; however, it has a low penetration and ductility parameters which indicate that it would best serve as an asphalt extender. It is reasonable assume that the fat or oil serves as a source of straight chain hydrocarbons which interact with the aromatic coal structure which compatible with petroleum asphalt.

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Conversion of Oklahoma Waste Coal

into

Road Asphalt

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State of Oklahoma
Department of Transportation
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EXECUTIVE SUMMARY

This report has been prepared to inform the Oklahoma Department of Transportation of the progress on the project:

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as well as to provide enough information so that co-workers at the OkDOT can readily duplicate the described procedures.

Part I provides background material which introduces the techniques normally used to separate and to characterize chemical samples, as well as examples of asphalt fingerprinting using these concepts. This initial effort clearly demonstrates that when reference library of asphalts and their separation and spectroscopic properties is established, effective fingerprinting will be available.

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Future work should include the hydrogenation of waste coal in the presence of additional renewable resources, e.g., corn oil, fish oil, soybean oil. The synthetic asphalt should then be blended with petroleum asphalt and tested for long term miscibility and rheological properties. During this stage of work, large scale synthesis (2-5 pound) procedures for synthetic asphalt should be developed.

It would appear to be meaningful to examine the products from current coal liquefaction processes for potential use as road asphalt. A long range study to obtain solubility profiles for a wide range of petroleum asphalt and synthetic asphalts should be planned. These profiles would be correlated with rheological, chemical, and spectroscopic properties of the profiled materials.

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I. THE CHARACTERIZATION OF COMMERCIAL ASPHALT

A. Introduction

The overall performance of a bituminous roadway is dependent on several factors; including, but not limited to, subgrade and base course quality, construction quality, aggregate type, age of road, environmental conditions, traffic load, and asphalt quality. It is reasonable to assume that chemical composition is directly related to asphalt quality. Asphalt has, therefore, been characterized by physical, chemical, and spectroscopic procedures to ascertain the composition of asphalt.

Current standard specifications for asphalts and road tars can be divided into two groups:

(1) Physical tests (e.g., penetration, ductility, and viscosity) to classify the asphalt and as a means of estimating the performance of the material.

(2) Chemical tests (e.g., solubility in various solvents) to ensure that the material is composed of acceptable components.

The problem with physical tests is that they tend to be empirical. It is well known among asphalt researchers that many asphalts of entirely different origin and chemical composition can meet the same specification requirements; e.g., penetration, ductility, and viscosity. These parameters may no longer be sufficient for establishing asphalt quality. It is therefore, essential to develop methods which quickly and more accurately describe the chemical composition of asphalts used in Oklahoma and the Southwest region. A thorough literature search of the research currently being done in analyzing the chemical composition of asphalt bitumen reveals a wide diversity of tests and resulting data.

Agreement on the significance of any chemical tests analyzing the quality of asphalts and on exact specifications to guarantee the performance of a bitumen, do not exist. Since functional group characteristics of chemicals are more difficult to alter by blending than are physical property characteristics. we have examined elemental analysis, proton nuclear magnetic resonance (^{1}H-NMR), infrared spectroscopy (IR), and mass spectroscopy (MS) characteristics of the whole asphalt and asphalt fractions in an attempt to develop new techniques for characterizing asphalt.

The objectives of this research are to (1) develop a rapid and accurate method of analyzing the composition of asphalt, (2) to compare this data with physical specifications already in use and those being developed by other researchers, (3) to relate this data to the performance of a given road, (4) to use this data to predict the possible characteristics of a road's performance, and (5) if possible, to obtain new specifications for asphalts to be used in Oklahoma/Southwest roads.

The characterization of commercial asphalts was done in two phases. The first phase consisted of separating asphalts into fractions of similar physical or chemical composition. The second phase consisted of analyzing the whole asphalt and these fractions by modern spectroscopic techniques, proton nuclear magnetic resonance (^{1}H-NMR) spectroscopy, infrared (IR) spectroscopy, mass spectroscopy (MS), and by elemental analysis.

B. Fractionation of Asphalts

The purposes of separation are to find a chemical grouping which may be related to asphalt performance, as well as to provide more uniform samples for futher analyses. The five principle methods of fractionation are distillation, extraction, precipitation, absorption, and chromatography.

While none of these techniques by itself has proven to be most effective in the fractionation of asphaltic bitumens, combinations of these operations have proven very useful for the separation of asphalt.

1. Distillation

The first step in determining the fractional composition of asphalt has often been distillation (1). Two fractions are obtained: the fugitive petrolenes (a relatively low-boiling fraction of crude oil soluble in low-boiling saturated hydrocarbons -- e.g., n-pentane) and residual asphaltic bitumen (bitumen consisting of a mixture of non-distillable components and relatively high-boiling components. However, this fractionation is not sufficient to obtain chemical subdivisions since the chemically different fractions of the n-pentane soluble portion are in the same boiling range. Chemical fractionation by distillation can also be obtained by azeotropic distillation or by extractive distillation. These methods, while successful in the industrial separation of low-boiling hydrocarbons systems of few components, have not been useful in the analytical separation of multicomponent and high-boiling mixtures such as that found in asphalt (2).

2. Chemical Precipitation

The distinct feature of chemical precipitation is the stepwise precipitation of fractions. Chemical precipitation is based on the general principle of quantitative analysis which requires the use of an excess of a reagent to complete remove one component from the system. Thus, this concept consists of separating into fractions, quantitatively, groups of components of distinctly different chemical reactivity. It is important to note, however, that when these chemical interactions occur, the asphalt will be modified.

A three step precipitation method was developed by Marcusson and Eickmann (3) in which the asphaltene fraction was first separated from the asphalt by precipitation in naptha, followed by precipitation of the naptha soluble portion with sulfuric acid. This method was valuable in demonstrating the sharpness of the separations attainable by chemical precipitation.

The Rostler-Sternberg method (4,5) of chemical precipitation separates asphalts into five fractions (Figure 1).

- paraffins - saturated unreactive fractions.
- second acidaffins - a group of hydrocarbons having affinity for strong acid fuming sulfuric 30%.
- first acidaffins - hydrocarbons with affinity for ordinary concentrated sulfuric acid.
- Nitrogen bases - separated by 85% sulfuric acid, contains the most reactive components and believed substantially to be nitrogen containing compounds.
- Asphaltenes - insoluble in (40+ vol) low-boiling saturated hydrocarbons, e.g., n-pentane.

The five main fractions of asphalts can further be subdivided by molecular weight and/or response to chemical reagents. This method was designed as a simple analytical technique for identifying the asphalt fractions. It is also used quantitatively to define asphalts by percentage composition to correlate with performance (5,6).

Because the Rostler-Sternberg (5) separation scheme is so highly cited, this procedure was initially used in this study to fractionate the asphalts (Appendix B). However, the separation results obtained by using the Rostler-Sternberg scheme were difficult to reproduce due to the erratic scattering of data which can occur in this method of fractionation. This has been noted in this study, as well as by other research groups. G.L. Oliensis (4,6,7) comments in Rostler's papers on asphalt composition should be noted,

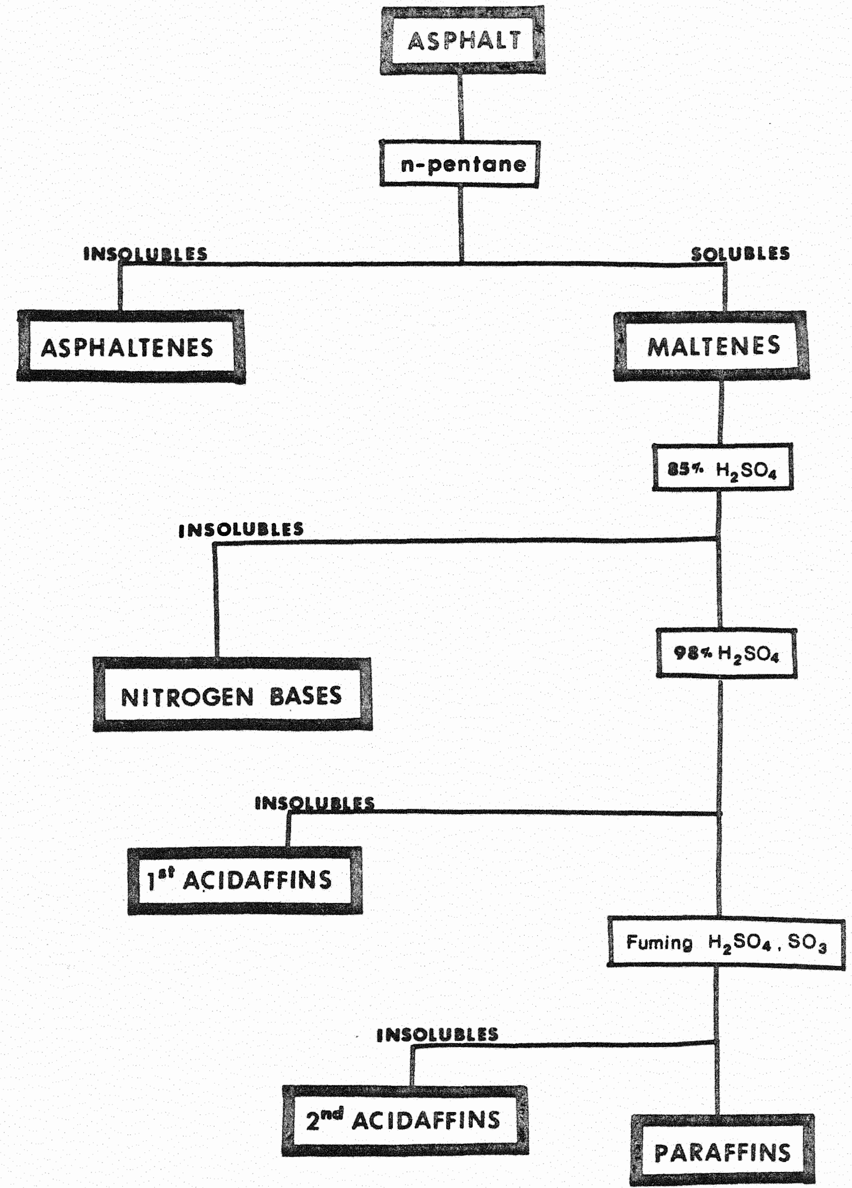


Figure 1: Rostler-Sternberg Separation Procedure

where he points out erratic scattering of the data along with other problems with this method. Another problem with the Rostler-Sternberg scheme is that it cannot be used when further analyses of each fraction are needed.

Although there are problems with the precipitation method, it is useful for defining asphalts by percentage composition, and it does correlate with asphalt performance.

3. Solvent Extraction

The first to suggest a method of asphaltic bitumen separation from organic material by solvents was Richardson around 1914 (2). Bitumen (i.e., road asphalt) was first defined as material which is soluble in carbon disulfide. The carbon disulfide soluble portion was then subdivided into low-boiling petrolenes and residual asphalt by distillation. The residual asphalt was then separated into asphaltenes (high molecular weight components) and maltenes (lower molecular weight components) by solubility in 88% Baumé naptha (a mixture of relatively low-boiling saturated hydrocarbons, i.e., n-pentane, isopentane, and cyclopentane). This early work led the way to the now common separation of asphalt with n-pentane. In this procedure the more complex and high molecular weight compounds (asphaltenes) are believed to be precipitated by 40+ volumes in low-boiling saturated hydrocarbons, n-pentane being the preferred solvent. Variations of this method are extensively used today as the primary subdivision in most fractionation techniques.

Rostler and White have reviewed and compared several available analytical methods based on the solubility technique (8). The techniques compared include methods by Rostler and Sternberg (5), Marcusson and Eickmann (3), Hubbard and Stanfield (9), Traxler and Scheveyer (10) and Kleinschmidt (10). They found good correlation between four of the methods for the rough separation of asphalt into three groups; asphaltenes, resins, and oils, but much overlap when separating asphaltenes, resins and oils into subfractions. Thus, the literature suggests that like chromatography (12), much overlap between fractions is found as division into subfractions increase.

Several solvent extraction schemes were examined in attempting to find a procedure that was simple, yet complete enough for our spectroscopic measurements (11,13,14). The well established n-pentane extraction, was selected to remove the asphaltenes and was combined with absorption on Fuller's earth to further separate the remaining maltenes fraction into resins and oils (Figure 2) (9). Table 1 lists the percent asphaltenes, resins, and oils for various asphalts obtained by this fractionation scheme. This separation scheme permits the utilization of each fraction for further analytical work including elemental analysis, ^{1}H-NMR, IR, and mass spectroscopy.

4. Absorption

For at least 80 years, the fractionation of asphalts by absorption on Fuller's earth, animal charcoal, and mixtures of animal charcoal with sand has been carried out. An important example in apshalt analysis is the Corbett separation technique (15) which separates asphalt into its four generic components. The method involves solvent deasphalting to recover asphaltenes followed by elution-absorption chromatography to yield saturates, napthalene, aromatics, and polar aromatics. Corbett used this method to study the physical properties of asphalt as related to its composition (16).

Although most absorption methods are no longer used today, they should be considered the forerunners of modern chromatographic techniques which use the principles of both solvent extraction and absorption.

5. Chromatography

Originally, chromatography was designed to separate mixtures of chemical compounds of different color by eluting them with a suitable solvent through

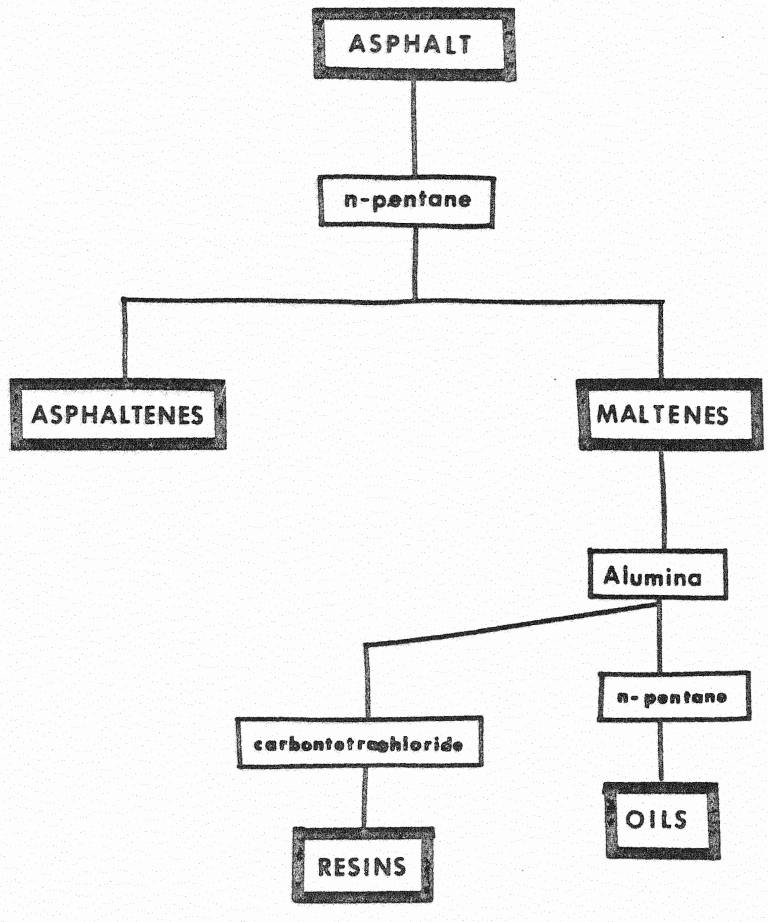


Figure 2: n-Pentane Fractionation Scheme

TABLE 1

Percent Asphaltenes, Resins and Oils of Various
Batch and Core Extracted Asphalts

Sample	Number	% Asphaltenes	% Resins	% Oils
<u>Batch Asphalts</u>				
AC-3	102	18.0	69.9	12.1
AC-4	103	12.3	67.9	19.8
CRS-2	112	23.8	59.4	16.8
Emulsion SS-1	114	42.4	52	5.6
<u>Core Extracted Asphalts</u>				
Beaver #1	401	39.5	51.0	9.5
Beaver #2	402	33.9	58.9	7.2
Beaver #2A	403	38.4	52.4	9.2
Beaver #3	404	45.0	42.7	12.3
CMS-1 Highway	406	29.8	61.4	8.8
Abson #1	415	26.8	61.4	11.8
Abson #2	416	28.8	61.4	9.8
Abson #3	417	32.4	60.0	7.6
Abson #4	418	35.8	53.4	10.8

a column of solid powder. Today, the theory of solvent extraction and absorption are combined for use in chromatographic techniques. These procedures, if kept within theoretical and practical limits, can prove very useful. Several liquid chromatographic schemes have been developed for asphalt analyses.

One chromatographic method separates asphaltic bitumens into four fractions (11) - asphaltenes, asphaltic resins, dark oils, and water white oils by precipitation of asphaltenes with 40 volumes of n-pentane and followed by the elution of the pentane soluble fraction from a chromatographic column of Fuller's earth successively to obtain a) water white oils with n-pentane, b) dark oils with methylene chloride, c) asphaltic resins with methy ethyl ketone, and d) acetone chloroform desorbed with acetone chloroform mixture. Although the method in general is not limited by sample size, it is especially suited for samples of 3 to 6 grams and required 6 to 8 hour fractionation time.

The strong affinity of silica gel for aromatic compounds has been used in an accurate relatively rapid method of analysis of the maltene fraction of an asphalt. This fraction was separated by elution with n-pentane from silica gel into aromatics and non-aromatics (13).

Another method separates the maltene fraction also using silica gel (14). The separated fractions are:

1) Non-aromatics with n-heptane
2) Aromatics with benzene
3) Oxy-compounds containing also, according to Eby (14), as well as S and N eluted with pyridine.

The above methods are considered rapid and simple ways of separating by chromatography. A very elaborate method by O'Donnell employs a combination of fractionation procedures (17):

1) Molecular distillation, separation on basis of molecular size.
2) Silica gel chromatography to separate saturates, aromatics, and resins.
3) Solvent dewaxing of saturates.
4) Urea complex formation to separate long chain paraffins.
5) Alumina chromatography of aromatics to separate monocyclic and dicyclic aromatics.
6) Peroxide oxidations followed by chromatography to remove benzothiophene homologs.
7) Thermal diffusion of segregate napthanes on basis of ring numbers.

However, like all chromatographic methods proposed for fractionation of asphaltic bitumens, they are strongly dominated by equilibrium conditions and do not give fractions which are different components but merely blends of the same component in different proportions. Simpson, Griffin, and Miles indicate that even in the elaborate and very complicated operations of the O'Donnell method, the fractions obtained overlap substantially in composition (12).

Another limitation of chromatographic procedures for asphalt analysis is that the separation is selective only as to shape or size of the molecules but not as to both simultaneously; thus, the fractionation is confined to reaching a state of equilibrium distribution of all the components present.

High performance liquid chromatography has been used to separate asphalts into saturates, aromatics, polar aromatics, monophenols, nitrogen heterocyclic aromatics polyphenols, and high molecular weight highly functional molecules. The separation scheme uses High Performance Liquid Chromatography (HPLC), preparative and analytical scale, for functional group separation that may relate to asphalt properties.

Inverse Gas-Liquid Chromatography (IGLC) is used to measure functional group interactions between volatile test compounds and the chemical functionality of asphalt (19). In this method, asphalt serves as the stationary phase in the column and the retention characteristics of the test compounds are observed. By this technique differences in the chemical composition of asphalts were noted.

Pyrolysis, hydrogenation and gas-liquid chromatography have also been used for the fingerprinting and characterization of the bitumens (20). From this analysis information on the number and lengths of paraffinic side chains gives some insight as to the structure of these bitumens.

Ordinary fractionation methods such as distillation, precipitation, extractions, and absorption permit the separation of asphalt both chemical structure and molecular weight. Gel permeation chromatography (GPC), a more specific technique that separates molecules according to molecular size, is now being used to evaluate asphalts.

Altgelt, in 1965, was the first to report the fractionation of asphaltenes by GPC techniques (24). By this technique, a definite molecular weight separation was achieved and preliminary infrared spectroscopic studies suggested that systematic changes in structural characteristics could be monitored.

The technique for determining molecular weight distribution of macromolecular substances by GPC was introduced by J.C. Moore in 1963 (22), and developed and commercialized by Waters Associates of Framingham, Massachusetts (18). Altgelt, in his paper on "Gel Permeation Chromatography of Asphalts and Asphaltenes" gives the experimental details of fractionation of asphalts and asphalt constituents by GPC (23). Gel preparation, column design and packing procedures are described at length. The GPC separation of a number of crude petroleums was later reported giving further evidence that asphalt could be fractionated by molecular size (24).

Kiet, Blanchard, and Molhotra reported in the GPC fractionation of asphalts and the characterization of its fractions in terms of molecular and unit sheet weights (25). The asphalts were dissolved in toluene then fractionated on preparative gel permeation chromatograph (prep-CPC). Twenty-three fractions differing widely in molecular weight were collected and characterized by, analytical GPC, viscometry, vapor pressure osometry (VPO), element analysis IR, and NMR.

Such data as obtained by GPC is used to define how molecular structure correlates with performance or physical properties. From preliminary observation, however, it appears that the difference between "good" and "bad" road asphalts appears to be more a function of intermolecular associations than of relative molecular weight distribution. This does not distract from the possible use of GPC in the study of asphalt quality, but it does emphasize the importance of sample size rather than some complex property such as absorbtivity or solubility. This has proven to be one of the greatest advantages of Gel Permeation Chromatography analysis. This simultaneous use of GPC (preparative and analytical) and HPLC make it possible to define important compositional characteristics of bitumen. This method also provides low response time with a large degree of precision and reproducibility (26).

Changes in molecular weight distribution caused by environmental factors during service in the pavement are also detected by GPC. Relation to GPC analysis to asphalt properties is, however, severely hampered by lack of adequate standards to calibrate the chromatograms. The uses of GPC is also limited by two detrimental influences; one being absorption, and the other an opposite effect called negative absorption. In absorption, the sample is absorbed to the column and delayed, opposing the fractionation process. In negative absorption, the sample runs through column without delay and without fractionation.

The most important new advances in the use of chromatography for characterizing asphalts has been described by Jennings (24) at Montana State University (27,28). The method uses high performance liquid chromatography in the gel permeation mode and appears to be a promising new tool for asphalt consumers and producers. Analysis of asphalt extracted from nearly 50 established roads indicates that HPLC in the gel permeation mode can distinguish between asphalts and that differences between chromatograms may be related to quality. However, the effects of roadway aging are as yet unknown due to lack of samples of the original asphalts from the established roadways studied. The model currently being used for excellent asphalt assumes there has been little or no change in the chromatogram once the roadway is constructed.

Fractional analysis of asphalts is still far from being fully developed. However, it represents considerable progress in the research to elucidate the chemical make-up of asphalts and to correlate composition with the functions of the components that make up asphalts. While it would be reasonable for this research effort to initially utilize modern physical techniques such as liquid chromatography to separate asphalt fractions it is anticipated that correlating our separate spectroscopic findings with work such as is being done at Montana State University will be more beneficial in predicting asphalt performance with aging. (27,28).

C. Analysis of Asphalts

Proper fractionation in asphalt analysis is very important; however, without a characterization of the fractions it has no meaning. The most useful analytical methods for heavy petroleum fractions are, elemental analysis, nuclear magnetic resonance (^{1}H-NMR), infrared (IR), and mass spectroscopy (MS).

1. Elemental Analysis

Elemental or Ultimate Analysis is the determination of carbon and hydrogen in the material as found in the gaseous products of its complete combustion, the determination of nitrogen, sulfur, and ash in the material as a whole and the calculation of oxygen by difference (29-33). Of the five elements (C, H, N, S, and O) which in various combinations compromise the organic substance of fossil fuels, carbon and hydrogen account for 70-95% and 2-6%, respectively, (on a dry ash-free basis) and are thus major constituents of coal and petroleum.

a. Carbon and Hydrogen

The determination of carbon and hydrogen is made by combustion in a closed system and subsequent determination of the CO_2 and H_2O products in an absorption train after complete oxidation and purification from interfering substances. This method gives the total percentages of carbon and hydrogen in the coal as analyzed and includes the carbon in carbonates and the hydrogen in the moisture and in the water of hydration of silicates.

b. Nitrogen

The determination of nitrogen is made by either of two methods (30). In these procedures, destructive digestion of the sample with a hot catalyzed mixture of concentrated sulfuric acid and potassium sulfate converts nitrogen into an ammonium salt, which is subsequently decomposed in a hot alkaline solution. The ammonia is recovered by distillation and determined alkalimetric or acidimetric titration.

Due to the exceptional stability of most nitrogen forms in coal and coal derivatives, these procedures often yield low results.

c. Sulfur

Sulfur occurs in both the organic and inorganic matter of coal. Total (organic plus inorganic) sulfur contents can be found in the range 0.5 - 2.5%, but may be as high as 7-8%, which can affect coal properties, especially in use as road tar.

Routine determination of sulfur involves conversion of S-forms into water soluble sulfates and subsequent determination of SO_4^{2-} by one of three procedures (31):

(1) Eschka Method - The sample and Eschka mixture are ignited and the sulfur is precipitated as barium sulfate ($BaSO_4$) (ASTM D3177-75 Sec 5-8)

(2) Bomb Washing Method - Sulfur is precipitated as $BaSO_4$ from oxygen-bomb calorimeter washings (ASTM D3177-75 Sec 9-11)

(3) High Temperature Combustion Method - the sample is burned in tube furnace at 1350°C in stream of oxygen. Absorption in hydrogen peroxide H_2O_2 solution yields H_2SO_4 and HCl. H_2SO_4 is determined by titration.

d. Ash

Ash is determined by weighing the residue after extensive combustion of the sample under rigidly controlled conditions of sample weight, temperature time and atmosphere.

e. Oxygen

Because oxygen occurs in the mineral matter as well as in organic combustions, precise determination of oxygen is difficult. Thus, in most cases (including ASTM Standards Methods) oxygen is calculated by difference (33) i.e., 0% = 100%(C+H+N+S+Ash). Oxygen, so reported contains the resultants of all experimental errors. For this reason, much interest has been taken in developing a direct method of analysis of oxygen (34). The utility of these methods has been exhaustively tested (35-37), yet by no means are they troublefree. Other direct oxygen determinations employ photon or neutron activation reactions which presents problems with time, amount of sample and economics of experiment (38).

Elemental analysis of several typical asphalts (Table 2) were performed by Huffman Laboratories, Inc., of Wheat Ridge, Colorado. American Society of Testing and Materials (ASTM) Standards Methods were used in analyzing our samples for carbon and hydrogen, nitrogen, sulfur, and oxygen (29-33).

The carbon to hydrogen (C/H) ratio obtained by elemental analysis is an important parameter for hydrocarbons since it indicates to what degree the hydrocarbons deviate from paraffinic structures of the general formula C_nH_{2n+2}. The C/H ratio of the batch asphalts AC-3, AC-3A, and AC-4 is about the same as that found for asphalt extracted from cores taken from the "in-service" roads. A large difference is seen, however, in the carbon to oxygen (C/O) ratio of the batch asphalts versus the core extracted asphalts. The decrease in (C/O) ratio for "in-service" road asphalt is characteristic of an increase in oxygen content due to oxidation of the asphalt.

2. Nuclear Magnetic Resonance Spectroscopy

In nuclear magnetic resonance (^{1}H-NMR) analysis chemical shift and spin-spin splitting are specific for the conditions of certain nuclei and hence, can be used to determine the possible environment of the nucleus being analyzed. The intensity of area of peaks can be used to calculate the relative abundance of each environment. Thus, in NMR asphalt analysis,

TABLE 2

Elemental Analysis and their Atomic Ratios for Typical Asphalts

Sample[a]	Number	C %	H %	N %	S %	O %	C/H (Atomic Ratio)	C/O (Atomic Ratio)	$\frac{C}{O+S+N}$ (Atomic Ratio)
AC-3	102-01	87.2	10.8	0.5	0.7	0.6	8.1	145	48.4
AC-3A	103-01	86.6	10.8	0.8	1.5	0.5	8.0	173	30.9
AC-4	101-01	86.8	10.9	0.6	1.4	<0.5	7.9	<173	34.8
Styrelf A1	411-01	82.6	10.3	0.6	0.9	5.6	8.0	14.7	11.6
Styrelf A2	412-01	83.6	10.4	0.6	2.1	3.3	8.0	25.3	13.9
Styrelf B1	413-01	82.8	10.5	0.6	0.9	5.1	7.9	16.2	12.5
Styrelf B2	414-01	83.9	10.5	0.6	0.9	3.9	8.0	21.5	15.5
June P	408-01	83.9	10.5	0.5	1.1	3.9	8.0	21.5	15.3
June Q	409-01	82.4	9.8	0.5	2.8	4.6	8.4	17.9	10.4
DOT 60 Mesh Coal		69.3	4.6	1.5	7.4	6.2	15.0	0.3	4.6

[a] See appendix D for sample descriptions.

analyzed. The intensity or area of peaks can be used to calculate the relative abundance of each environment. Thus, in NMR asphalt analysis, important information about specific molecular environments or compound types of asphalt components, can be determined.

In 1958, R. Williams used proton NMR in the characterization of saturate, aromatic and olefinic petroleum fractions (39). Although the spectra was of poor quality and low resolution, valid empirical relationships were obtained. Saturates were characterized by a "branchiness index" (BI) defined as the ratio of heights of ^{1}H-NMR absorption bands due to methyl and methylene groups, respectively. Aromatic analysis by ^{1}H-NMR provided determination of alkyl and aromatic ring carbon; extent of alkyl group substitution of aromatic rings; average number of aromatic rings per molecule; number of carbons per alkyl group; and structural weight. Similar empirical relationships based on observable proton resonances were reported by Brown and Ladner (40,41). Both studies were performed at low frequency (30-40 MHz) and on low resolution instruments.

The first application of 60 MHz high resolution ^{1}H-NMR techniques to petroleum characterization was reported by Yen and Erdman in 1962, for the characterization studies of several unfractionated asphalt samples (42). In 1967, Ramsey, McDonald and Peterson reported ^{1}H-NMR structural studies on various asphalts fractionated by elution techniques (43). Altgelt, in 1965, applied ^{1}H-NMR analysis to asphalts fractionated by GPC (23). Here was the opportunity to utilize methods and empirical relationships already developed for both ^{1}H-NMR and GPC, to observe systematic changes in the asphalts. Proton-NMR techniques on GPC fractions yield data not only on the characterization of petroleum residual, but also information relative to much of the GPC separations. Trends in the fractionation of molecular types were observed.

^{1}H-NMR studies, when combined with separation procedures and additional spectroscopic analyses, have shown that the weight of unit sheets in petroleum residues may be calculated from the ^{1}H-NMR data (25,42,44,47). However, there appears to be little correlation between weights calculated by ^{1}H-NMR and vapor pressure osmometry molecular weights in the high molecular weight region. This could be due to the belief that factors in addition to molecular size influence the fractionation process which is apparently dependent on the experimental method employed. Possibly measured molecular weight is a function of the entity measured, -- e.g., micelle, particle or sheet. It does, however, support the theoretical picture of the macrostructure of asphaltic materials proposed by researchers (24,48,49).

The ^{1}H-NMR spectra of the petroleum asphalts are qualitatively similar. The region of stronger resonance between 0.5 and 3 ppm corresponds to hydrogens attached to saturated carbon atoms and the region of weaker resonance between 6.5 and 8 ppm to hydrogens attached to aromatic ring systems. The absence of absorption between these regions rules out the presence of hydrogens attached to carbons of isolated olefinic bonds (43). The ^{1}H-NMR spectrum of a typical asphalt AC-3 fraction is shown in Figure 3. The centers of absorption for different types of protons are $\delta = 7.25$, H_{ar} aromatic protons; $\delta = 2.0 - 3.0$ H_α protons $(-CH)_\alpha$ to aromatic rings; $\delta = 1.0 - 2.0$, H_β protons ($-CH_2-$) and $\delta = 0.5 - 1.0$, H_γ protons ($-CH_3$) saturated methyl protons (Figure 4) (22). Tables III and IV present the data obtained from the ^{1}H-NMR analyses in terms of α, β, γ, and aromatic protons, presented in the form of ratios H_α/H_T, H_β/H_T, H_γ/H_T, $(H_\beta + H_\gamma)/H_T$, H_γ/H_β and H_{ar}/H_T where H_T is total number of protons. Values for each was determined from the area under the peak by the cut and weigh method. Several NMR's were taken on a few selected samples using

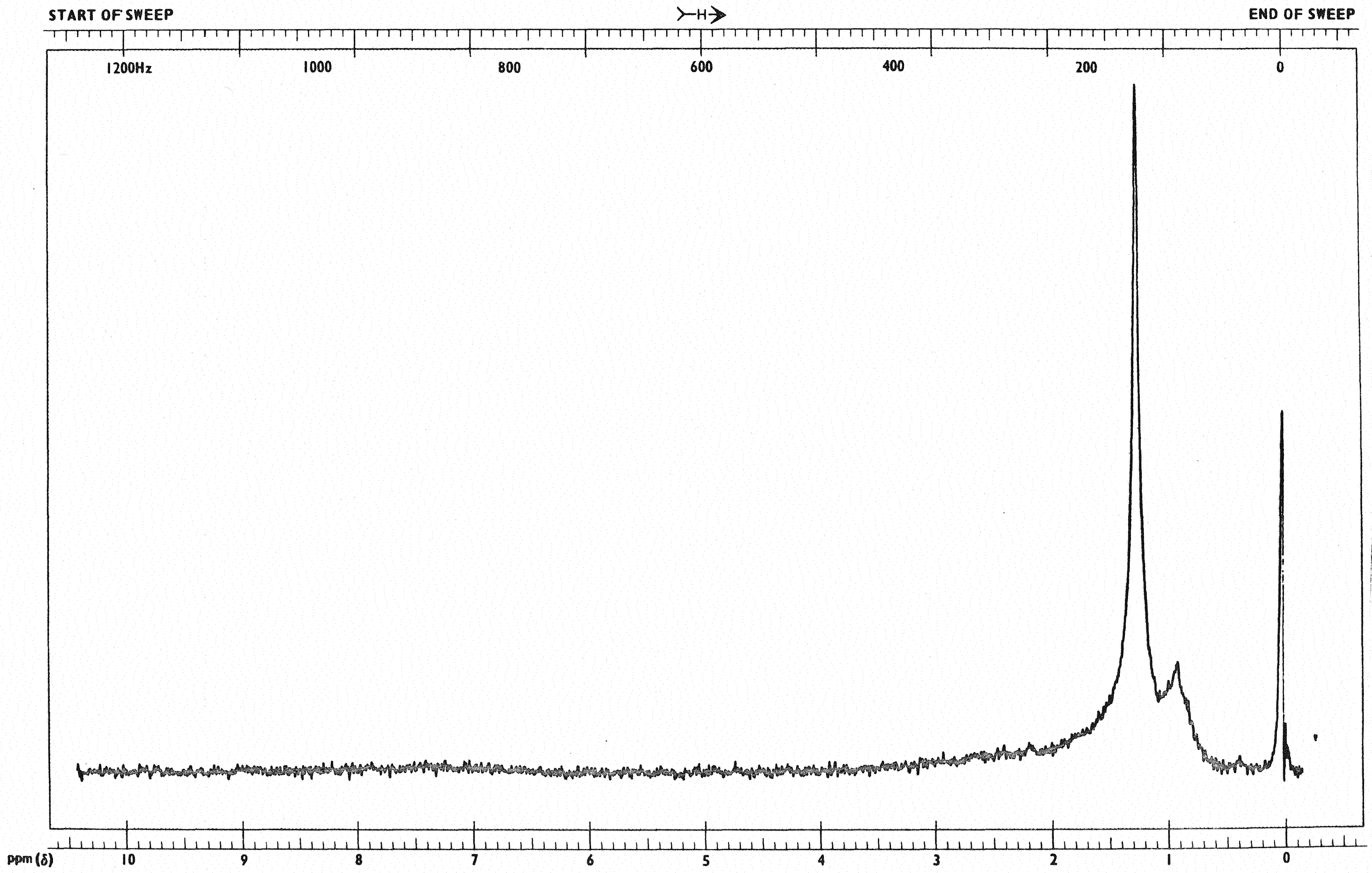


Figure 3: Typical Asphalt ^{1}H-NMR AC-3 (101-01)

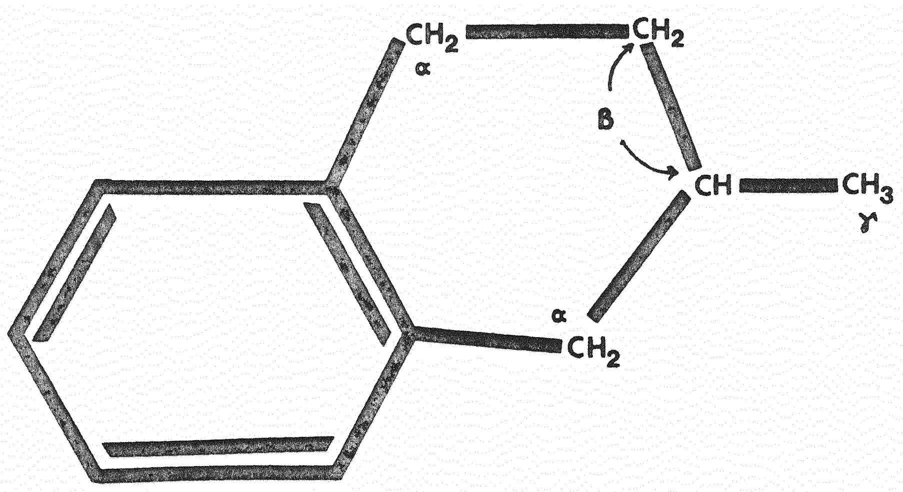


Figure 4: Definition of α, β, and γ positions

the cut and weigh method. Several NMR's were taken on a few selected samples using the same and different instruments. A standard variation on the ratio H_α/H_T, H_β/H_T, H_γ/H_T, $H_\beta + H_\gamma/H_T$, and H_γ/H_β was determined to be ± .02.

Using Brown-Ladner equations (41) three important structural parameters for the samples can be obtained and compared (f_a, σ, H_{aru}/C_{ar}). f_a is the aromaticity defined as the ratio of aromatic carbon to total, σ is the degree of substitution of the aromatic system, and H_{aru}/C_{ar} is the atomic hydrogen to carbon ratio of the hypothetical unsubstituted aromatic material.

These quantities are given by the following equations:

$$(f_a) = \frac{\frac{C}{H} - \frac{H\alpha^*}{x} - \frac{Ho^*}{y}}{C/H} \qquad (1)$$

$$\sigma = \frac{\frac{H\alpha^*}{x} + \frac{O}{H}}{\frac{H^*}{X} + \frac{O}{H} + H_{ar}} \qquad (2)$$

$$\frac{H_{aru}}{C_{ar}} = \frac{\frac{H\alpha^*}{X} + H_{ar} + \frac{O}{H}}{\frac{C}{H} - \frac{H\alpha^*}{x} - \frac{Ho^*}{y}} \qquad (3)$$

Where C/H and O/H are atomic ratios determined directly from the elementary analysis and $H\alpha^*$, H_0^*, H_{ar}^* were determined from areas under NMR peaks using the formulas.

$H\alpha^* = \frac{H\alpha}{H_T}$ is the fraction of the total hydrogen on α carbon atoms.

$H_0^* = \frac{H_0}{H_T}$ is the fraction of the total hydrogen on other nonaromatic carbon atoms.

$H_{ar}^* = \frac{H_{ar}}{H_T}$ is the fraction of the total hydrogen on aromatic carbon atoms.

$x = y = 2$ as determined by Brown & Ladner (41).

where:

x = average atomic H/C ratios of α-carbon structures

y = average atomic H/C ratios of non-aromatic carbon system

These parameters are based on two assumptions: (a) all oxygen is attached directly to aromatic systems as phenol or aryl ether groups, and (b) no aromatic rings are joined by a single C-C bond.

Aromatic hydrogens were not seen on spectra obtained by either the T-60 continuous wave instrument, or the NR-80 Fourier Transform ^{1}H-NMR spectrometer. This is probably due to the structure of the asphalts. According to researchers (24,48,49), asphalt is composed of flat sheets of condensed aromatic rings which are highly substituted with aliphatic side chains. Thus, there is very little aromatic hydrogen to be seen on a ^{1}H-NMR spectra.

Fourier Transform Carbon-13 NMR, however, would be a reasonable method of analysis to determine the aromaticity of asphalt samples for several reasons: (1) the ^{13}C chemical shift range is about 200 ppm compared to that for ^{1}H's

TABLE 3

The Proportions of the α , β, γ and Aromatic Protons in the Various Batch Asphalt Fractions Computed from their NMR Spectra

Sample[a]	Number	H_α/H_T	H_β/H_T	H_γ/H_T	$(H_\beta+H_\gamma)/H_T$	H_γ/H_β
AC-4	101-01	.12	.69	.18	.88	.26
AC-3	102-01	.11	.72	.18	.89	.25
AC-3A	103-01	.04	.77	.19	.96	.25
MC-3000	104-01	.12	.66	.22	.88	.33
MC-800	105-01	.11	.64	.25	.89	.39
MC-30	106-01	.04	.64	.32	.96	.50
CMS-1	110-01	.06	.72	.22	.94	.30
CMS-2	111-01	.10	.68	.22	.89	.32
CRS-2	112-01	.09	.72	.19	.91	.27
Emulsion-1	113-01	.10	.69	.21	.90	.30
Emulsion SS-1	114-01	.06	.73	.21	.94	.29
SOX	120-01	.04	.72	.24	.95	.33
SCCa	121-01	.12	.68	.20	.88	.29
SCCb	122-01	.13	.67	.20	.87	.29
BST	123-01	.14	.66	.21	.86	.32
BSTa	124-01	.11	.68	.20	.89	.29
Rubber Asphalt	126-01	.05	.66	.28	.95	.43

[a] See Appendix D for explanation of sample names

TABLE 4

The Proportions of the α, β, γ and Aromatic Protons in the Various Road Core Asphalt Fractions Computed From their NMR Spectra

Sample[a]	Number	$H\alpha/H_T$	H_β/H_T	$H\gamma/H_T$	$(H_\beta+H\gamma)/H_T$	$H\gamma/H_\beta$
Beaver Co. #1	401-01	.04	.72	.24	.96	.34
Beaver Co. #2	402-01	.06	.71	.23	.94	.33
Beaver Co. #2A	403-01	.05	.78	.17	.95	.22
Beaver Co. #3	404-01	.08	.71	.20	.92	.29
25-1 Highway	407-01	.03	.75	.21	.97	.28
June P	408-01	.13	.67	.20	.87	.29
June Q	409-01	.11	.69	.20	.89	.29
Styrelf A1	411-01	.12	.58	.30	.88	.53
Styrelf A2	412-01	.13	.55	.32	.87	.58
Styrelf B1	413-01	.08	.68	.23	.91	.33
Styrelf B2	414-01	.11	.59	.29	.88	.49
Abson #1	415-01	.11	.67	.22	.89	.32
Abson #2	416-01	.11	.68	.21	.89	.30
Abson #3	417-01	.09	.69	.22	.91	.31
Abson #4	418-01	.10	.69	.21	.89	.30

[a] See Appendix D for explanation of sample names

of about 10 ppm; (2) the carbon atoms give information about the backbone of the molecules making up the asphalt fraction; and are often more sensitive than protons to the intromolecular environment and the electronic structure of the molecule and less sensitive to the intermolecular environment; and (3) the C-H dipolar interaction is about 20 times smaller than H-H dipolar interactions allowing sharper spectral lines and more detail in the ^{13}C-NMR spectra (Figure 5).

These asphalts were also characterized in terms of a "branchiness index" defined by Brown as the ratio of NMR absorption bands due to methyl and methylene groups, respectively, (H_γ/H_β). Table 5 contains the BI for a selected group of batch and core asphalts.

Ramsey, McDonald and Petersen (43) evaluated the NMR methods of Brown and Ladner for determining average structural parameters and formula weights. The formula weights calculated were compared to molecular weights obtained by other methods and show fair agreement in the majority of cases. They also compared it to data from other investigators who studied the same samples. Their conclusions: "Structural parameters obtained from NMR data appear to be as reliable as those obtained by other methods."

3. Infrared Spectroscopy

The unambiguous establishment of the identity or structure of any compound by infrared spectroscopy (IR) alone is seldom possible.[50] Uncertainties arise from overlapping group frequencies; spectral variations due to the physical state of the sample, and instrumental limitations. The classifications, therefore, of multi-component petroleum fractions solely by their infrared absorption spectra is indeed a difficult task. Infrared spectroscopy is useful, however, as an analytical technique for asphalt analysis since it

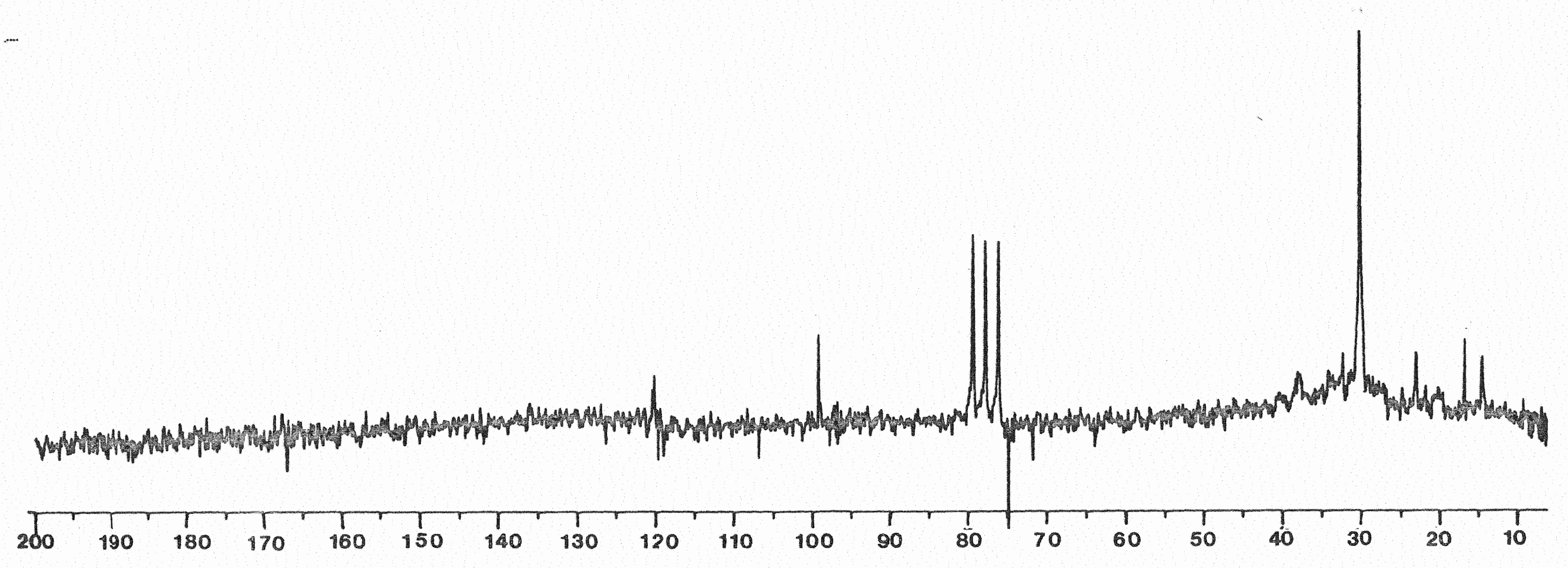


Figure 5: Carbon-13 NMR of AC-3 Asphalt

TABLE 5

NMR - Derived Branchiness Index (B.I.) for Batch Asphalts Compared To Core Extracted Asphalts

Batch Asphalt Sample	Number	B.I.	Core Asphalt Sample	Number	B.I.
AC-4	101-01	.26	Beaver Co. 1	401-01	.34
AC-3	102-01	.25	Beaver Co. 2	402-01	.33
AC-3A	103-01	.25	Beaver Co. 2A	403-01	.22
MC-3000	104-01	.33	Beaver Co. 3	404-01	.28
MC-800	105-01	.30	25-1 Highway	407-01	.28
MC-30	106-01	.34	June P	408-01	.29
CMS-1	110-01	.30	June Q	409-01	.29
CMS-2	111-01	.32	Styrelf A1	411-01	.53
CRS-2	112-01	.27	Styrelf A2	412-01	.58
Emulsion-1	113.01	.30	Styrelf B1	413-01	.33
Emulsion SS-1	114-01	.28	Styrelf B2	414-01	.49
SOX	120-01	.32	Abson 1	415-01	.32
SCCa	121-01	.29	Abson 2	416-01	.30
SCCb	122-01	.26	Abson 3	417-01	.31
BST	123-01	.32	Abson 4	418-01	.30
BSTa	124-01	.29			
Rubber Asphalt	126-01	.43			

does provide information on the aliphatic, aromatic, carbonyl and organo sulfur components of these compounds.

Several workers have used infrared analysis to solve asphalt problems. In an attempt to understand the chemical composition of asphalt and the interaction forces that exist within and between molecules, hydrogen banding was investigated by studying the OH and NH stretching bands of whole and diluted samples of asphalt (51).

In addition, it has been used as a method for the quantitative and qualitative determination of compound types absorbing in the carbonyl region of asphalt (52-55). Infrared spectroscopy has also been used to fingerprint oil spills and to describe asphaltic pitches (56,57). An established statistical technique was successfully applied to this infrared procedure for heavier petroleum products to provide a useful and powerful technique for classification of samples (57). Mattson applied patter recognition techniques to infrared spectra in the classification and fingerprinting of petroleum oils (crude oils, lubricants, distillate and residual fuels (58).

Infrared spectroscopy has been combined with other data such as MS, NMR, and elemental analysis for the fingerprinting and characterization of asphalts (46,47,59). Asphalts obtained from a refinery in Montreal were collectively dissolved in toluene and fractionated on preparative gel permeation chromatography (25). IR was then used in combination with analytical GPC, viscometry, vapor pressure osmometry, elemental analysis, and NMR in characterizing these asphalt samples. Based on the elemental analysis and IR studies a qualitative picture of the asphalt fraction was determined. However, in order to elucidate any structure, NMR analysis was also needed. Brown and Ladner (41) during their studies on coal-like material by elemental analysis, NMR and IR spectroscopy developed equations to compute certain structural parameters for coals, e.g., aromaticity (f_a), degree of substitution (σ) and H_{ar}/C_{ar}, the atomic hydrogen to carbon ratio of the hypothetical unsubstituted aromatic material. Haley derived equations leading to the computations of unit sheet weight for asphaltic fractions (46).

The infrared absorption spectra of samples were determined in the range from 4000-6000 cm^{-1} using a Perkin Elmer 283B Infrared Spectrophotometer and/or a Bechman IR-10 Infrared Spectrophotometer.

Interpretation of the infrared data is complicated by intense paraffinic hydrocarbon absorption bands. In order to use the spectra for the detection of other than carbon hydrogen absorptions it was necessary to use very concentrated solutions (>30%) in CCl_4, losing resolution in the 2800-3000 cm^{-1} range (νCH) in order to see resolution in the mid-range. Samples were normally prepared by forming a film on a KBr disk by the evaporation of a CCl_4 solution of the asphalt (Figure 6).

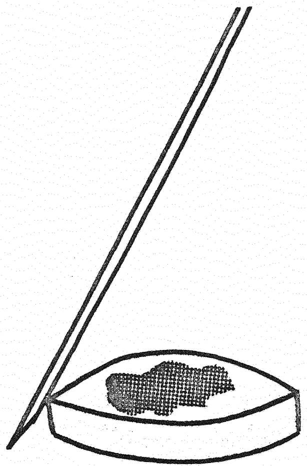


Figure 6

A typical spectrum is presented in Figure 7. Several absorption bands are commonly found in asphalt. The absorption bands in 700-900 cm^{-1} region can generally be assigned to C-H out of plane bonding vibrations in aromatic nuclei (60) and absorptions around 1300 cm^{-1} are often assigned to the stretching vibrations of C-N, $R-NO_2$ and SO_2 groups.

Absorption bands in the 1050-1200 cm^{-1} region often appear in the spectra of asphalt extracted from road cores. This is due to trace silicates present as a result of incomplete removal of aggregate fines from the road cores. This band may be accompanied by carbonate absorption that overlaps in the 1400 cm^{-1} range (61).

The bands which appear at 1380 cm^{-1} as medium broad bands are due to C-H asymmetrical bonding vibrations of methyl group, and the band at 1460 cm^{-1} appearing as a larger broad band can represent the asymmetric bonding vibrations of $C-CH_3$ groups or may also represent the asymmetric deformation vibration of a methylene group in an alkane. The aromatic C=C stretching vibration absorbs at about 1600 cm^{-1} with a shoulder at 1575 cm^{-1} (61).

Strong bands near 1700 cm^{-1} are normally assigned to carbonyl ($>C=O$) absorptions. This band is indicative of oxidized asphalts formed either during air heating or in long term use as road material. A strong peak in this area also is noted in young asphalt samples which have been located with metal complexes selected to increase the polymerization of asphalt (63).

The bands which appear in the region 2850-2960 cm^{-1} are assigned to paraffin side chains on cyclic nuclei. The band at 2850 cm^{-1} represents C-H stretching vibrations of CH_2 or CH_3 groups and those at 2920 and 2960 cm^{-1} represent $-CH_2-$ and $-CH_3$ stretching vibrations of alkanes. At 3060 cm^{-1}, where C-H aromatic stretching vibrations occur, there is an absorption shoulder (56).

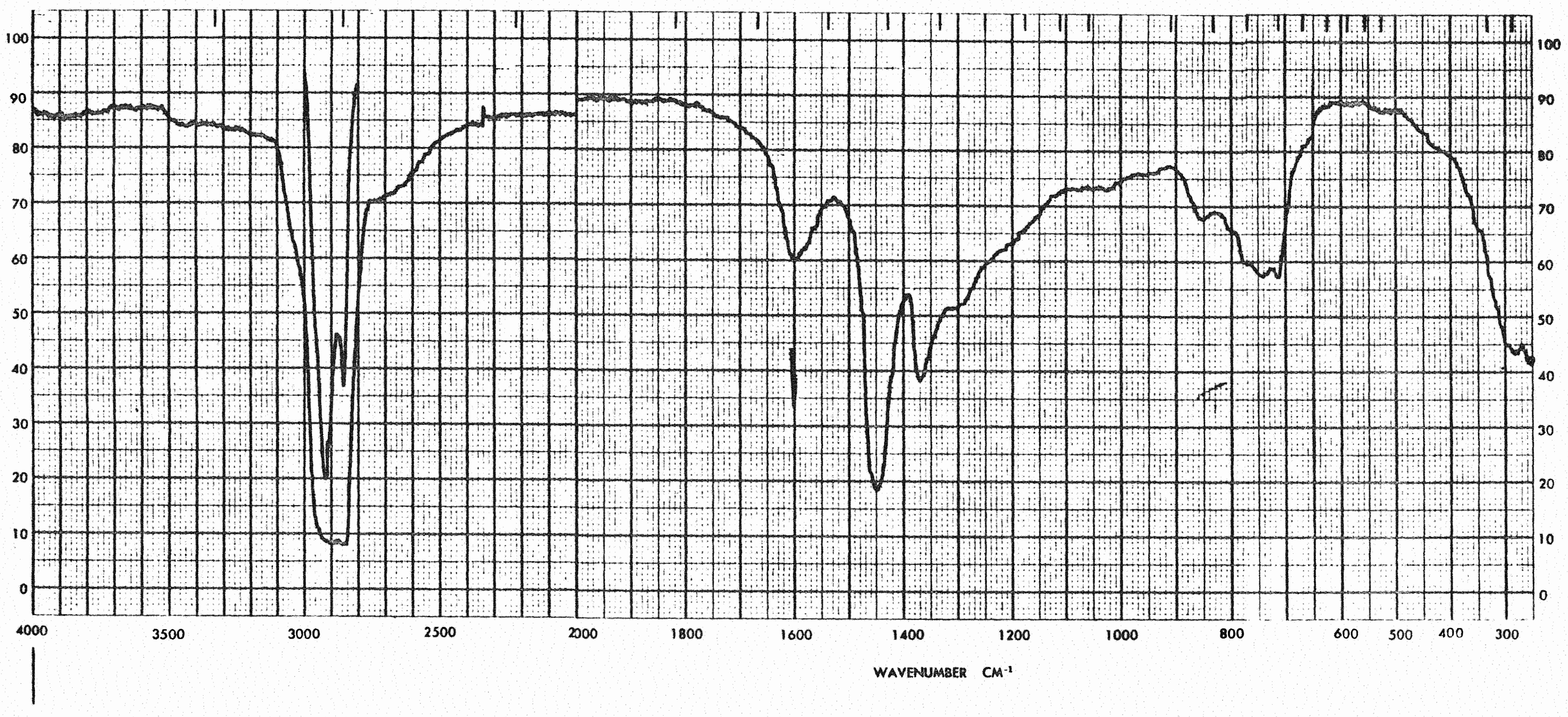


Figure 7: Typical Asphalt IR Spectra AC-3 (101-01)

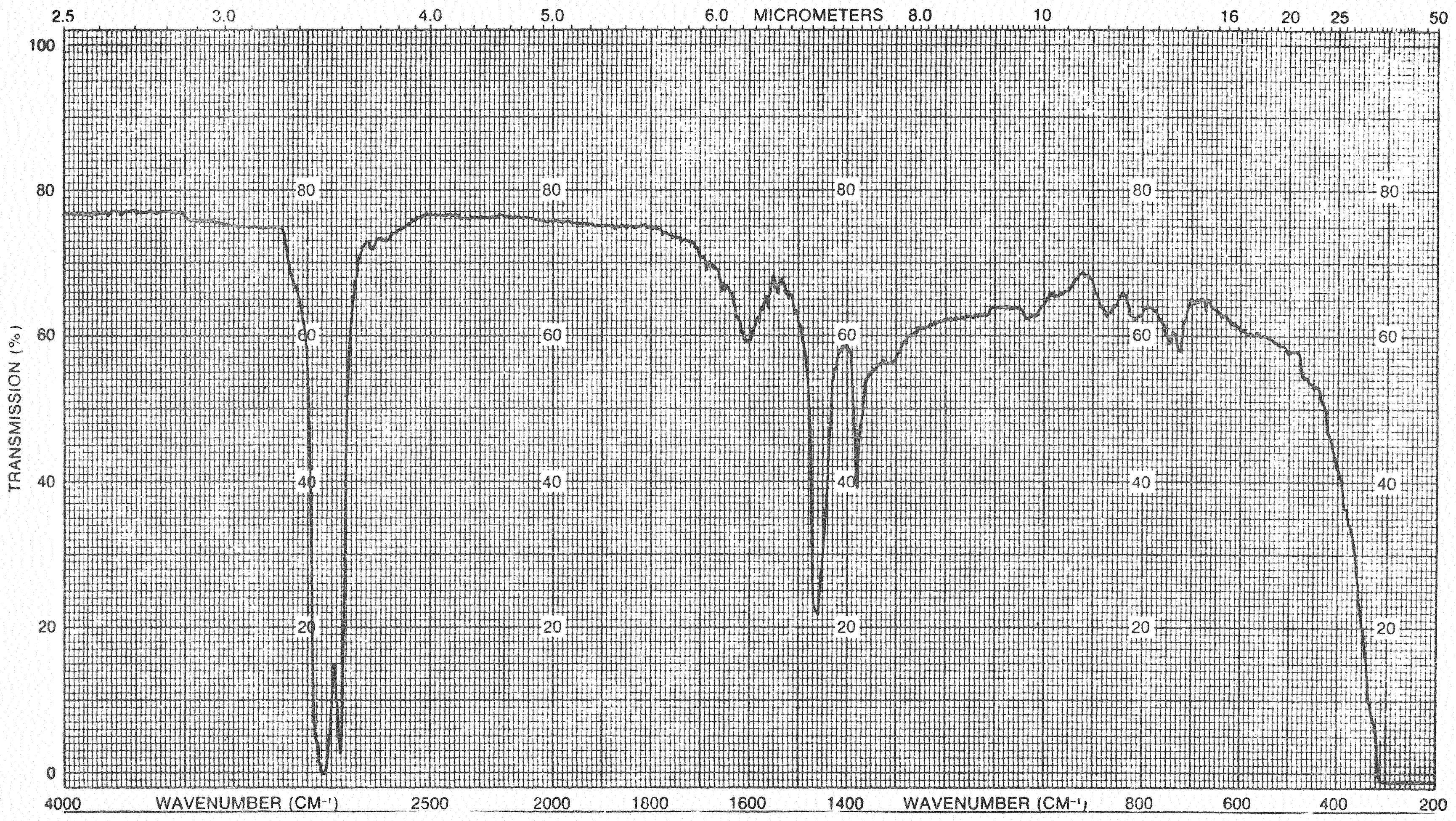


Figure: 8: AC-3 control sample

Aside from establishing the nature of functional groups in asphalts and coal tars, considerable progress has also been made in estimating their relative proportions and deriving H_{ar}/H_{al} ratio of aromatic to aliphatic hydrogen from the spectra of coal tars and asphalts. Also, combination of these data with data obtained from ultimate analysis and proton magnetic resonance has allowed calculation of several structural parameters relating to organic matter of coal and asphalts (25,41).

4. Mass Spectroscopy

Mass spectroscopy, a powerful tool for analysis of volatile samples, is found difficult to interpret on samples containing nonvolative and unstable components. A scheme, however, has been presented for the separation and determination of structural information of fully hydrogenated coal liquification samples using mass spectrometry (64). By utilizing high performance liquid chromatography as a separation tool coupled with quadrapole mass spectrometry as an identification tool, analysis on the functional groups and components of asphalt can be made. By this method, speed and simplicity are obtained without sacrificing selectivity.

Dickie and Yen (24), by X-ray diffraction and mass spectrometry, coupled with molecular weight measured by GPC and VPO, have presented detailed discussion of both resin and asphaltene fraction of asphalt material. They have proposed a possible macro structure, consisting of three basic entities: micelles, particles and unity sheets, in which micelles are made up of the entities called particles, which consist of even smaller unit sheets or layers.

D. Correlation of Results

This section attempts to relate the results of our extended studies to the properties of asphalts. From a limited number of batch and road core asphalt samples, we were able to obtain some correlations as properties and spectral features were observed and compared. As this research continues and additional samples from good and bad roads, as well as samples of the original batch asphalt used on these roads are analyzed, additional trends related to asphalt properties should be seen.

It is generally recognized that failures of asphalt pavements caused by embrittlement and other changes in physical properties during the aging processes are due to chemical reactions of all or some of the asphalt components. Thus, defining the components of asphalts responsible for fundamental properties and uncovering the influence of individual components and their blends on asphalt properties is of major importance.

By using a relatively simple procedure and apparatus the asphalts have been separated into three main groups of components: asphaltenes, resins, and oils (Appendix D and section I.A.2) The asphaltenes (8) are believed to be polycondensation products containing sulfur, oxygen, and nitrogen links probably derived from the resinous components by natural or artificial oxidation and polymerization processes. Thus, they would be expected to be high molecular weight products of limited solubility in saturated hydrocarbons. The resin fraction comprises highly reactive polar compounds which are subject to oxidation and polymerization/condensation reactions under atmospheric conditions. The oil fraction consists of straight chain paraffins, cycloparaffins, and isoparaffins.

Table I (pp. 9) gives the percentage of asphaltenes, resins, and oils for some pure batch asphalts and compares them to asphalts extracted from road cores.

The distinct differences in the amount of asphaltenes between virgin asphalt and that taken from road cores is probably due to oxidation and polymerization of the resinous components into asphaltene-like components while in service.

Nuclear magnetic resonance (NMR) and infrared (IR) spectroscopy studies are being directed towards identifying these groups which are easily oxidized and/or converted to polymeric material. When this information from a wide variety of asphalts and road conditions is compiled, we can probably begin to predict the performance of the asphalt.

The oxidation of in service asphalts can be monitored by IR spectroscopy by noting the appearance of a carbonyl absorption band at $\sim$1700 cm^{-1}. A simple experiment was designed to illustrate this:

> A sample of high grade AC-3 asphalt was prepared on an IR disc for analysis. The initial IR spectrum taken on this sample (Figure 8) shows no absorption at 1700 cm^{-1}. The disc was placed into a 50°C drying oven and IR spectra were taken at various intervals (Figure 9). As one can see from the spectra, an absorption band, near 1700 cm^{-1} begins to appear and its intensity increases with increasing time as the sample oxidizes.

Quantitative monitoring of the oxidation of asphalts with IR spectroscopy could be a meaningful effort.

Elemental analysis data can be used to verify the oxidation of an asphalt by the corresponding decrease in the carbon to oxygen (C/O) ratio of the asphalts from road cores as compared to batch asphalts (Table 2, page 18).

The ^{1}H-NMR data supports the established picture of asphalt as consisting of polynuclear aromatic sheets highly substituted with long chain and branched aliphatics. The ^{1}H-NMR and elemental analysis (C/H ratio $\sim$8) data show the asphalts consist of 60-80% $-CH_2-$ groups (H_β/H_T) with less than 12% of the hydrogen alpha to the aromatic ring indicating the high amount of substitution

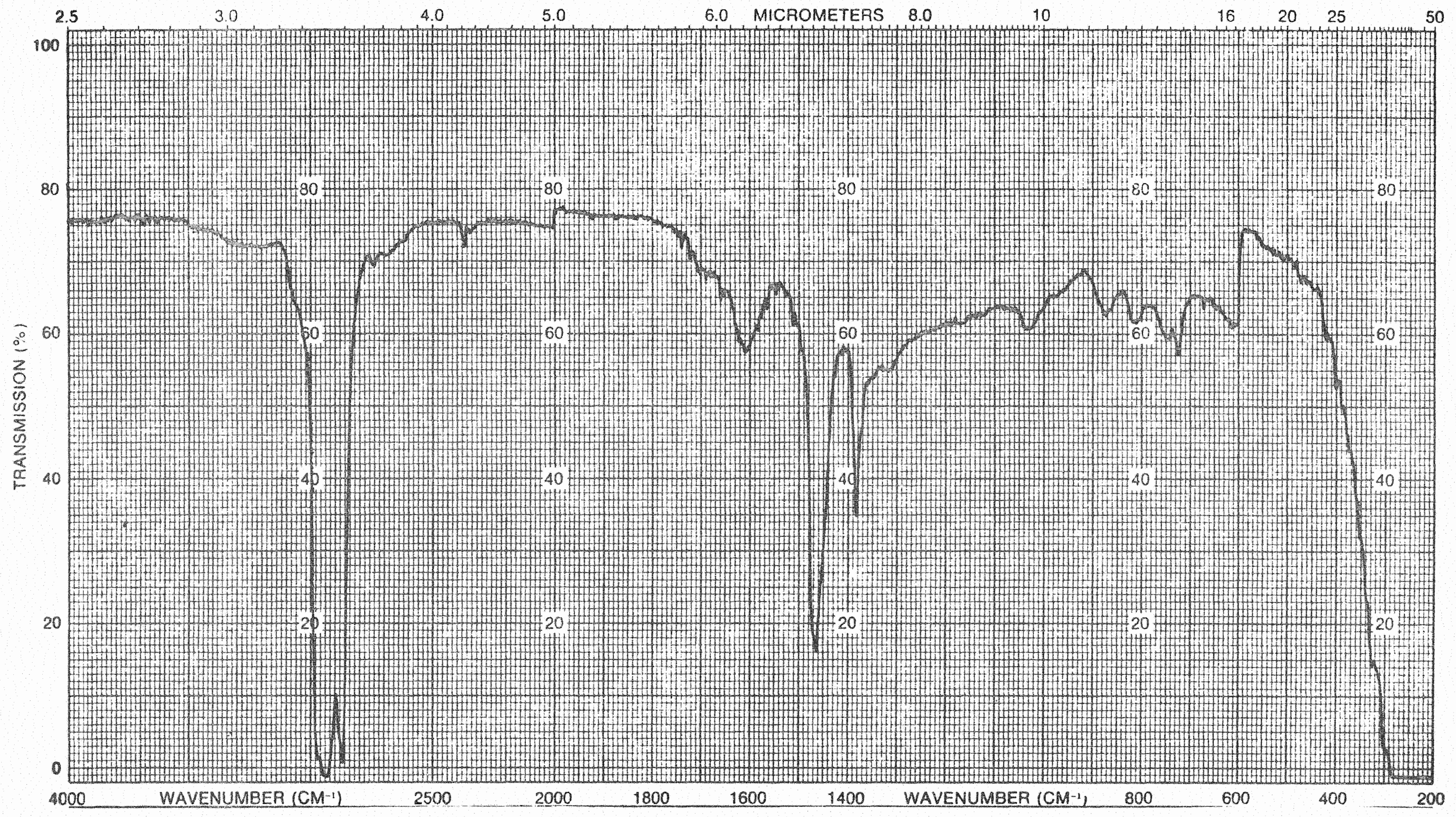


Figure 9a: AC-3 sample after oxidation in a 70°C oven for 2 days.

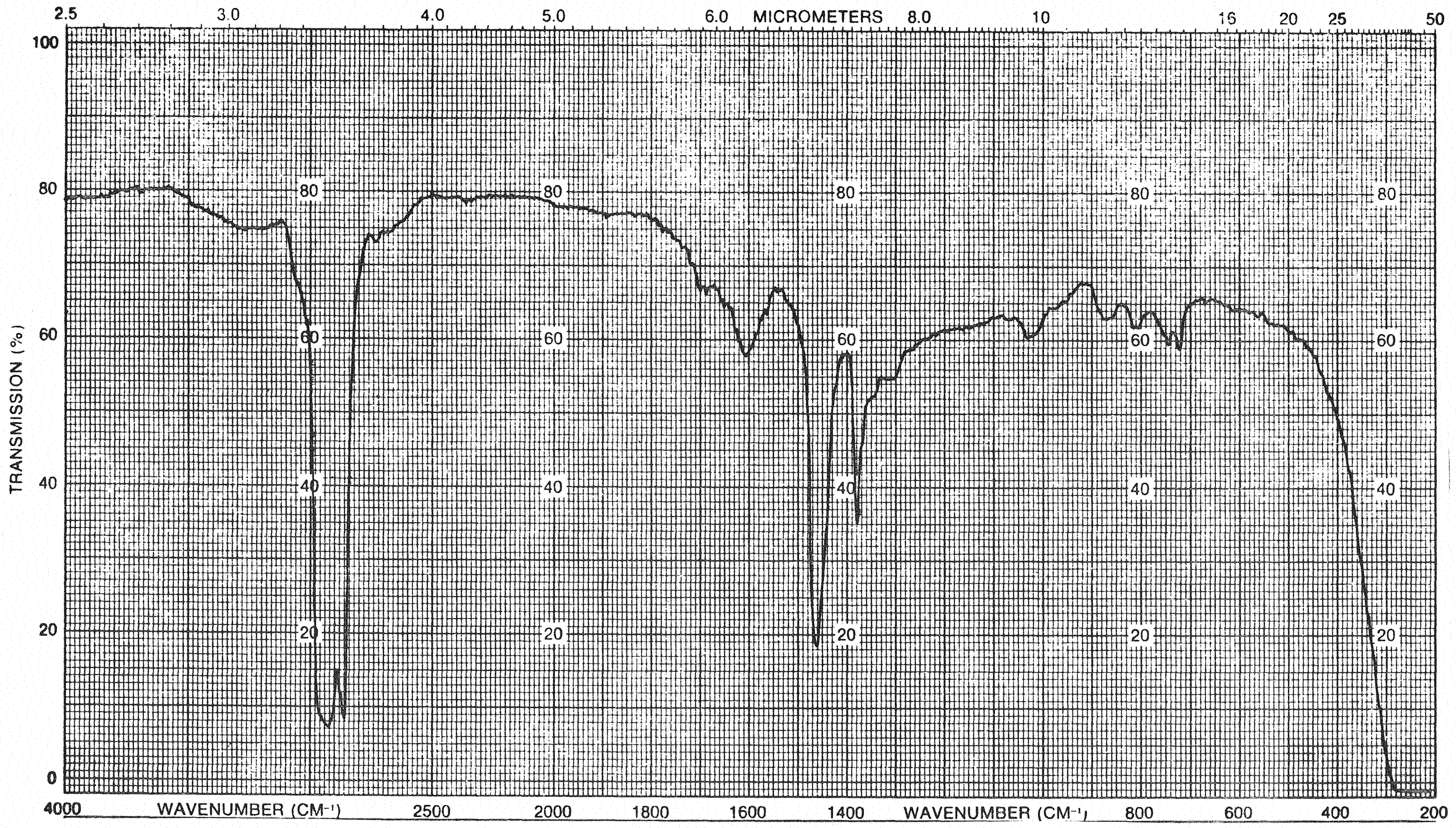


Figure: 9b : AC-3 sample after oxidation in a 70°C oven for one week.

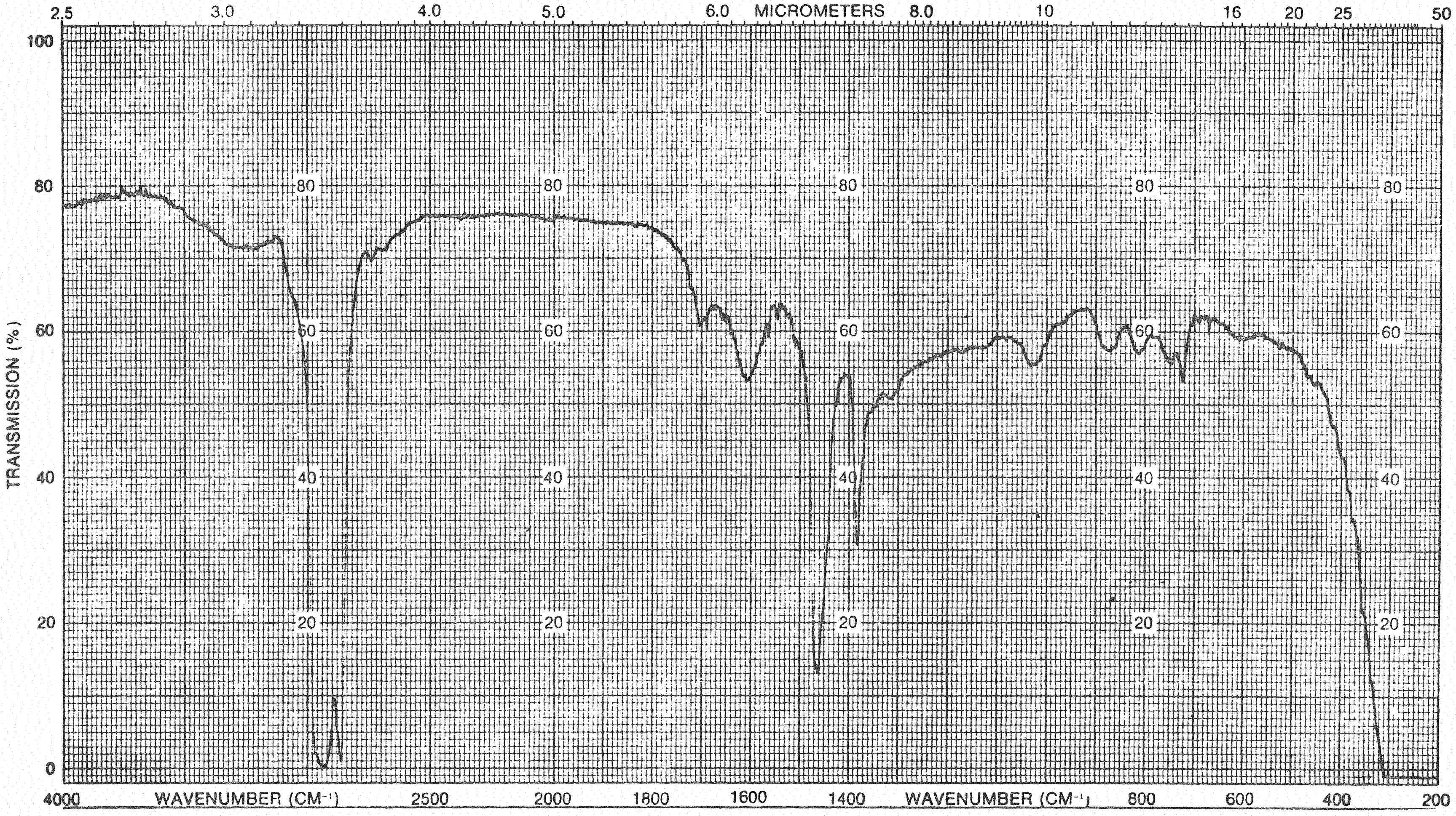


Figure: 9c: AC-3 sample after oxidation in a 70°C oven for one month.

with aliphatic chains. The branchiness index (Table 5, page 29) ratio of CH_3/CH_2 groups of greater than 0.22 indicates that the substituted aliphatic chains in the asphalts analyzed contain greater than 3 carbons per chain.

The importance of NMR spectroscopy in asphalt analysis is not completely evident from limited data obtained in this initial study. As this research continues, however, ^{13}C-NMR analysis of asphalt and its fractions will give valuable information about the carbon skeletal structure of asphalts which when combined with the proton-NMR data will be important in identifying asphalt quality.

Fingerprinting of Asphalts

The physical, chemical and spectroscopic properties of commercial asphalts are also being studied with the goal of establishing a reference library of Oklahoma standard asphalt spectra to aid in the quality control of these materials.

The presence of Chem-crete (63), can be detected in a virgin asphalt by infrared analysis. Since fresh batch asphalt does not have an absorption band at $\sim 1700\ cm^{-1}$, the presence of this absorption band in a virgin asphalt would indicate the presence of Chem-crete (Figures 10-13).

Infrared spectra differences on the fractions obtained by our separation scheme were also observed (Figures 14a, b, c, and d) Figure 14a is an IR spectrum of Beaver County road core asphalt. Figures 14b, c, and d are spectra of the asphaltenes, resins, and oil fractions, respectively. Carbonyl groups appear to be present only in the asphaltenes and resins fractions while the oils fractions appear to be purely aliphatic from its IR. This information can be important in observing the reactivity of the fractions.

The above are all examples of indirect fingerprinting (matching road cores with their original asphalt). However, infrared spectroscopy can also

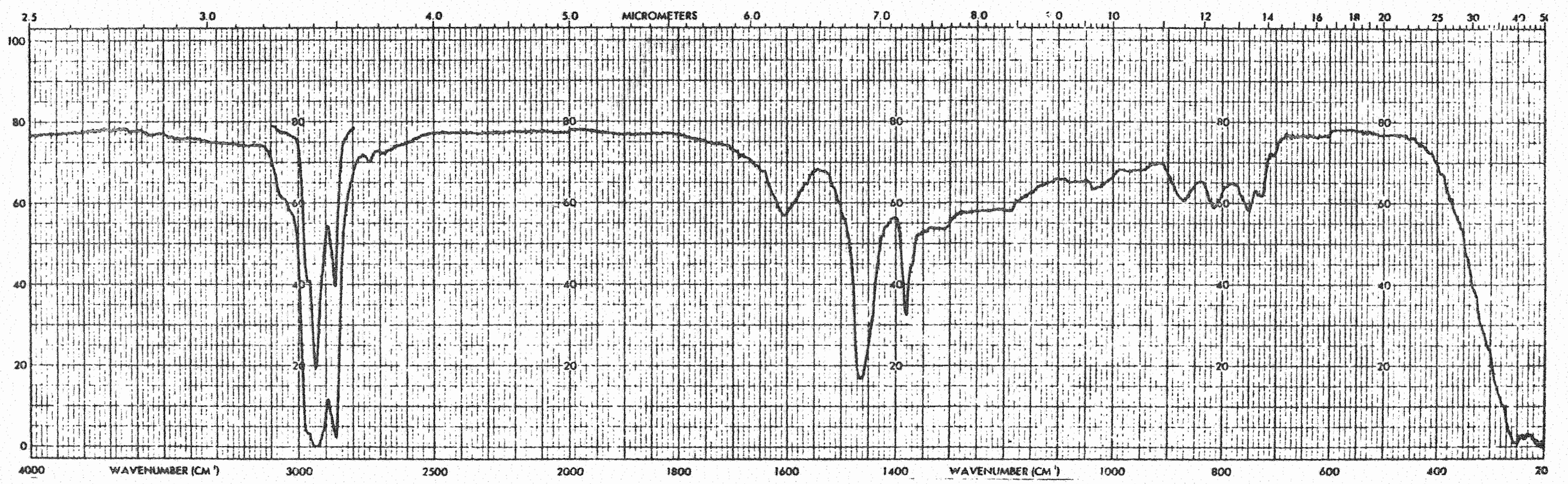


Figure 10: Big Springs, Texas Asphalt No. 123-01

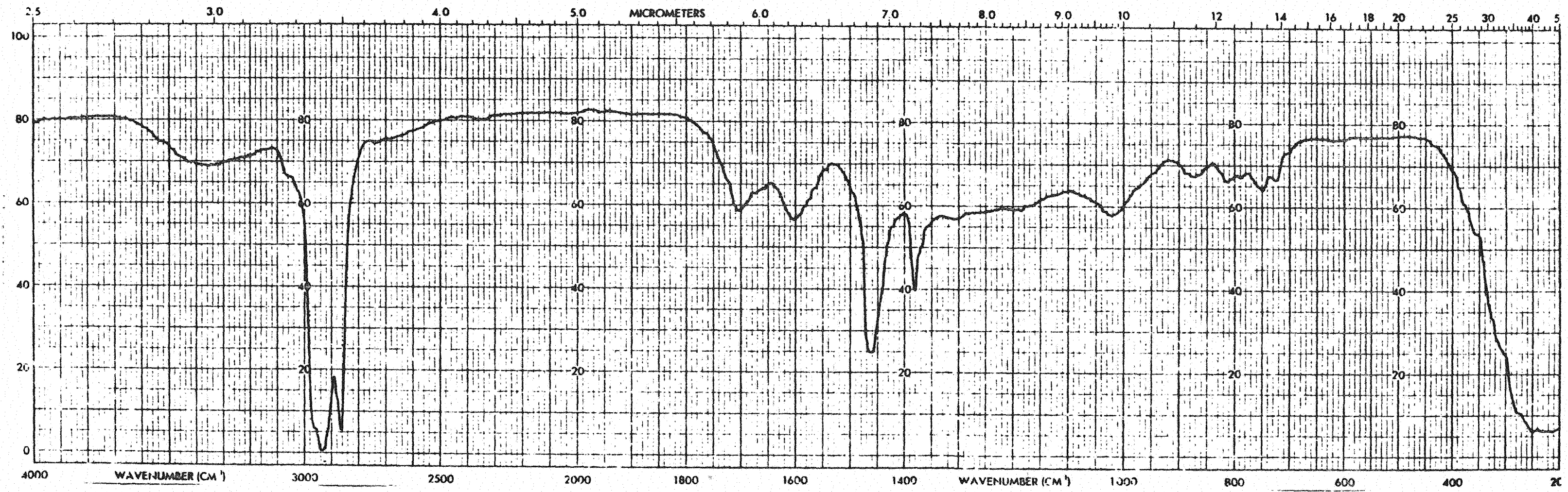


Figure 11: Big Springs, Texas Asphalt with Chem crete No. 124-01

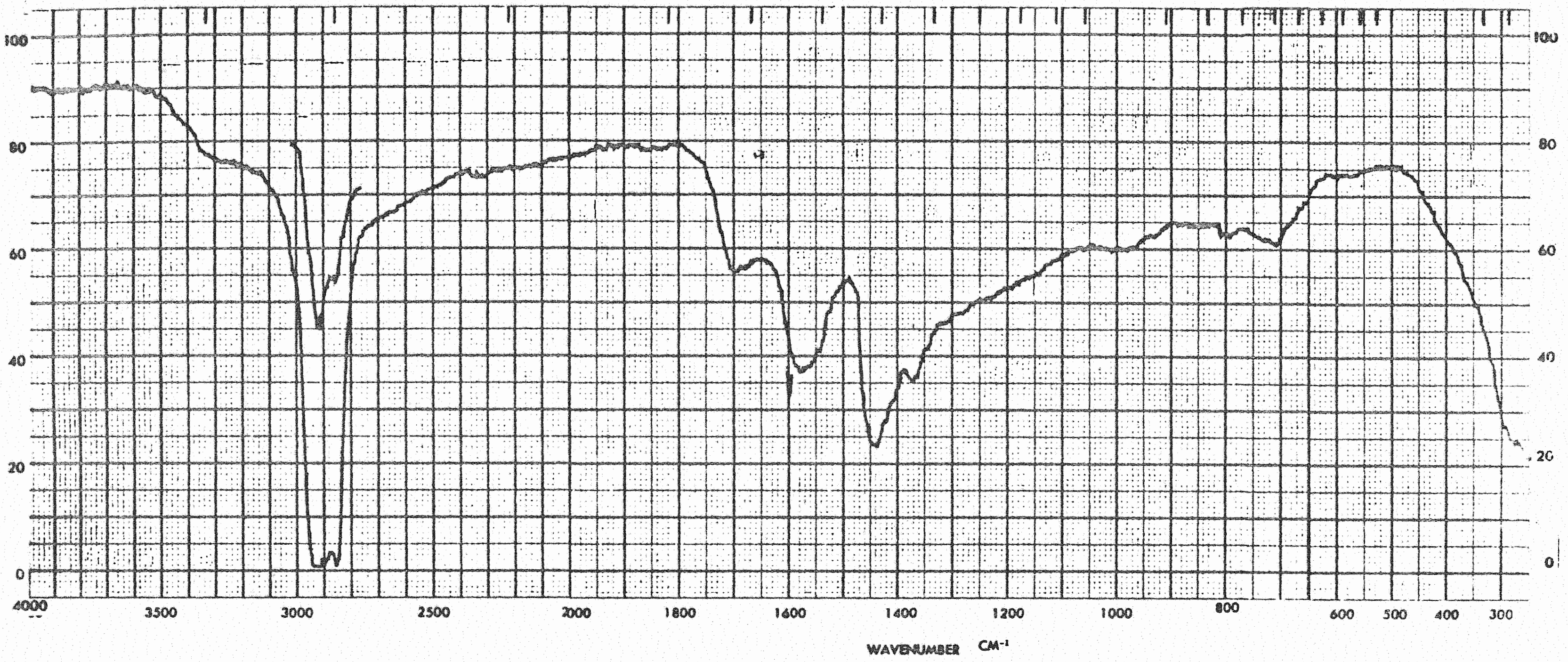


FIG.12 : Chem crete. This product was developed by the Chem-crete Corporation of Menlo Park, California. Chem-crete chemistry involves the addition of a small amount of common metal to promote oxidation and polymerization. This is observed by the presence of absorption at 1700 cm^{-1} for C=O stretch.

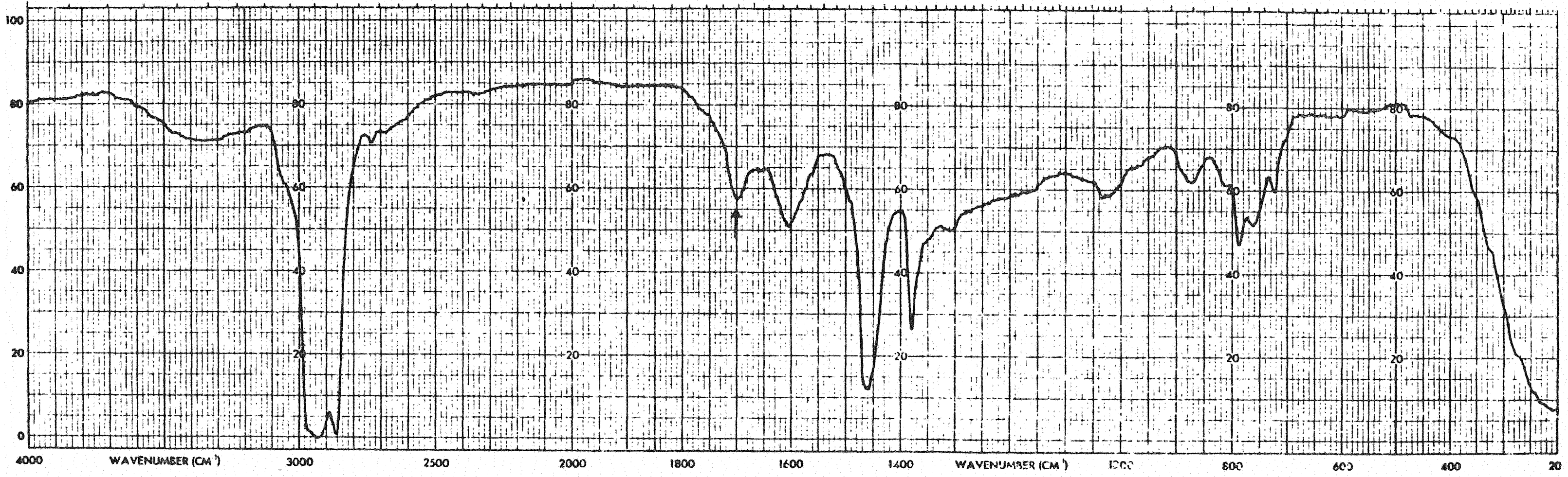


FIG.13: Unknown Pure Batch Asphalt. The presence of Chem-crete was questioned in this asphalt sample. For a pure batch asphalt, no absorption at 1700 cm^{-1} should be present unless Chem-crete has been added. From the IR spectra of this sample, it appears to contain Chem-crete.

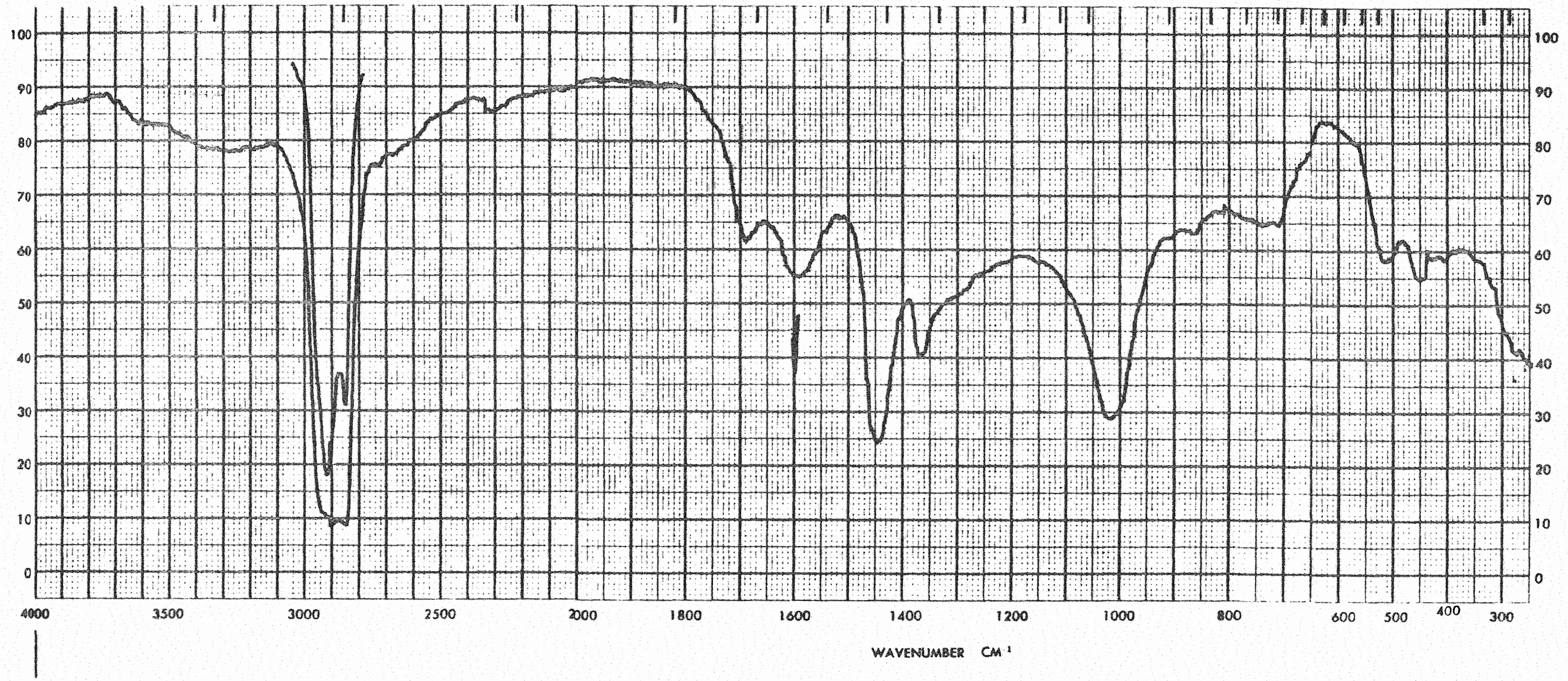


Figure 14a: Beaver County Road Core Asphalt No. 401-01

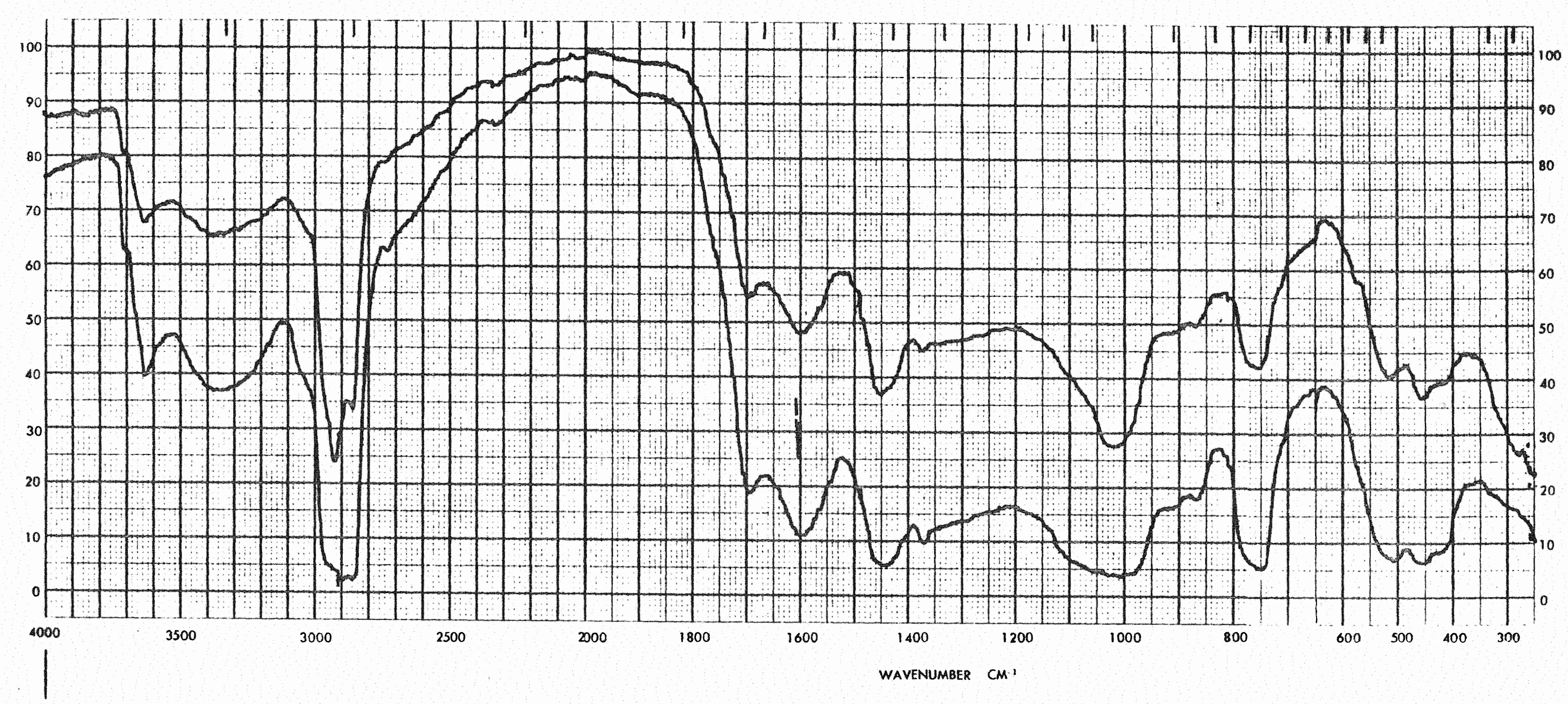


Figure 14b: Beaver County Road Core Asphalt Asphaltenes Fraction 401-02

Figure 14c: Beaver County Road Core Asphalt Resins Fraction 401-03

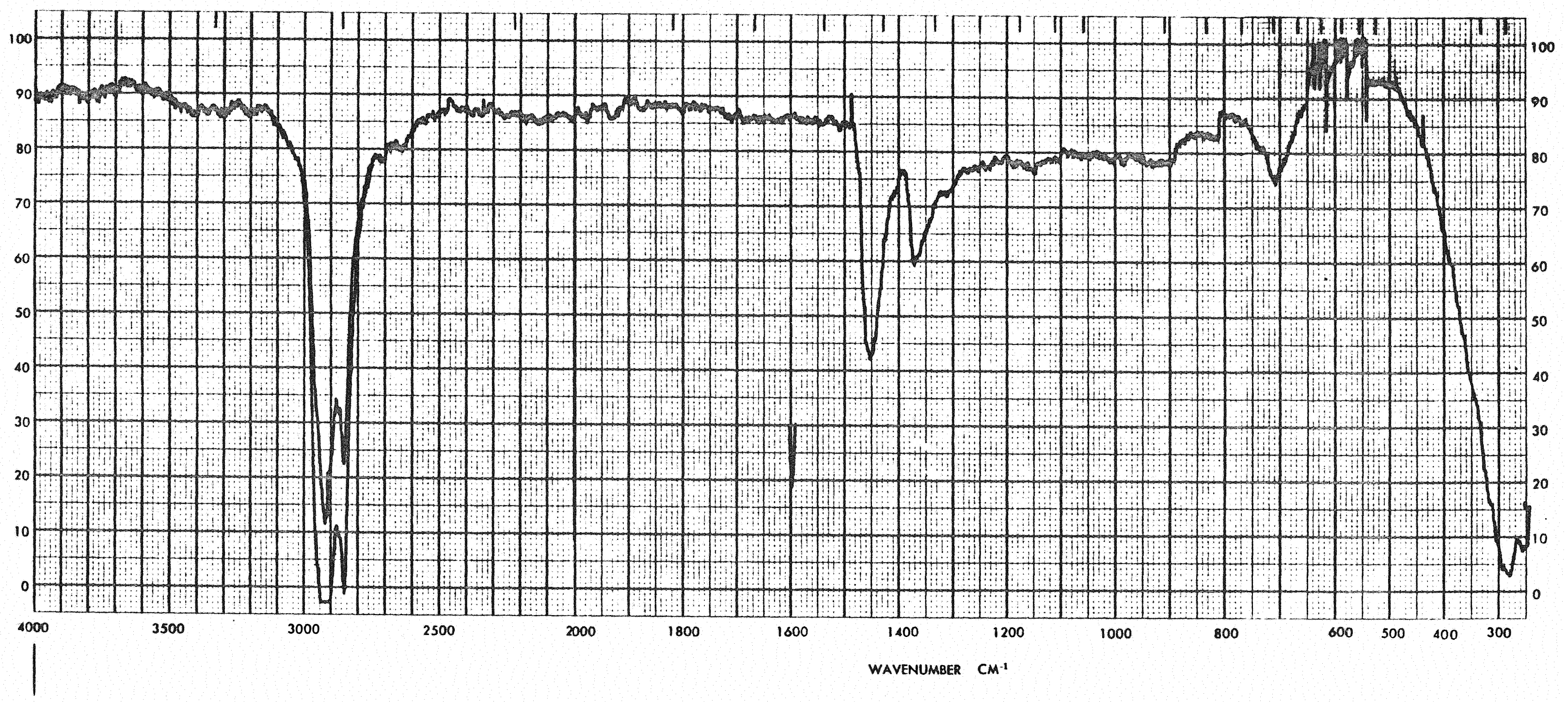


Figure 14d: Beaver County Road Core Asphalt Oils Fraction 401-04

be used for "direct" fingerprinting of the asphalt. For example, the June Core taken 6-12-82 from US-81, near Enid, Oklahoma, is known to have been laid 3-2-82 with a 3-inch base (409 Q) of Big Springs, Texas asphalt/ Chem-crete (BSTa-124) and a 5-inch surface layer (408 P) of Sun Oil/Chem-crete (SCCa-121). Quality control samples of the batch asphalts were obtained at the time the road was laid. One can see that infrared spectra for the core samples and their corresponding control samples match exactly (Figures 15 & 16).

Further verification can be obtained from nuclear magnetic resonance analysis. From the branchiness index data (Table 5, page 29), a direct match between the branchiness index of the June core samples and their corresponding control samples is observed. The "branchiness index" for batch asphalts and road cores also reveals some unique differences. The pure batch asphalts (AC-3, AC-3A, and AC-4) all appear to have a low branchiness index of ∿0.25 while the asphalt cutbacks (MC-300, MC-800, and MC-30) branchiness index is in the 30 percent range. One might note that the recycled section of the Beaver County road project, samples 2A and 3, is also around 0.25, while the control section samples 1 and 2 are around 0.34. Rubber asphalt and the surface horizon of the Styrelf road (411 and 412) have branchiness indices distinctly different from the other samples.

It is apparent from this initial research that spectroscopic differences among the asphalts analyzed can be seen. The importance of obtaining specific road samples along with their road history and physical properties, as well as quality control samples of the asphalt used on these same roads cannot be over-emphasized. These samples must be obtained for this research to continue in a productive and controlled manner. The importance and usefulness of fingerprinting asphalts will only be evident when a library of spectral information of known asphalts used on Oklahoma roads and their control samples is compiled and related to road performance.

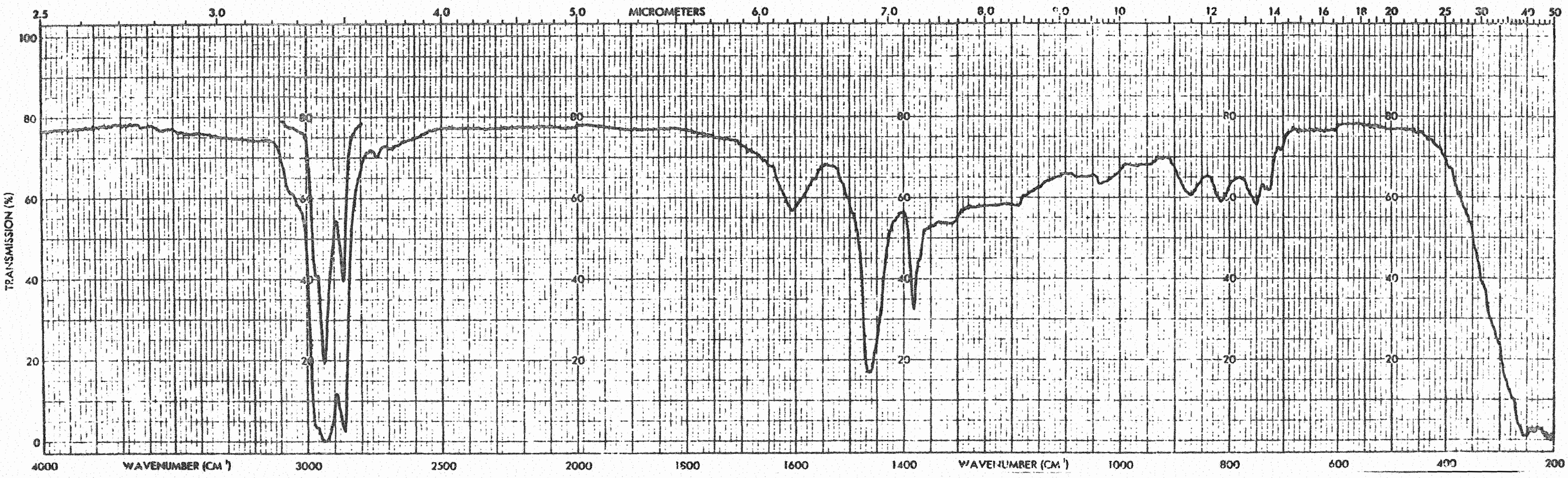


Figure: 15a. BST-123 Big Springs Texas Asphalt

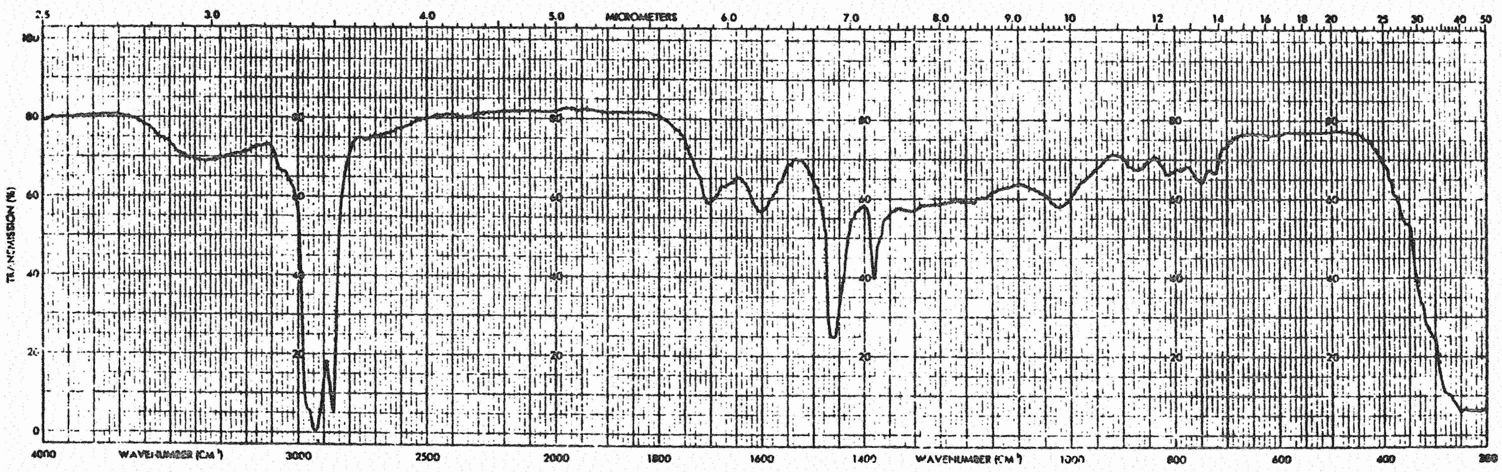


Figure 15b. BSTa-124 Big Springs Texas Asphalt with Chem-crete added.

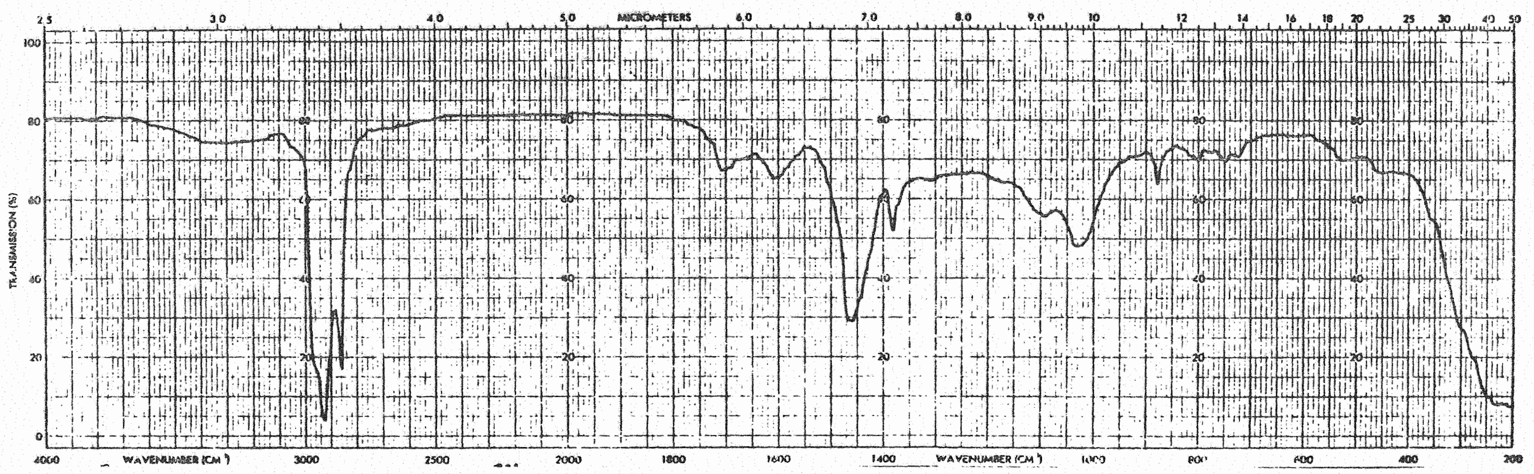


Figure: 15c. June Q - 409, 3 inch base of Big Springs Texas Asphalt with Chem-crete.

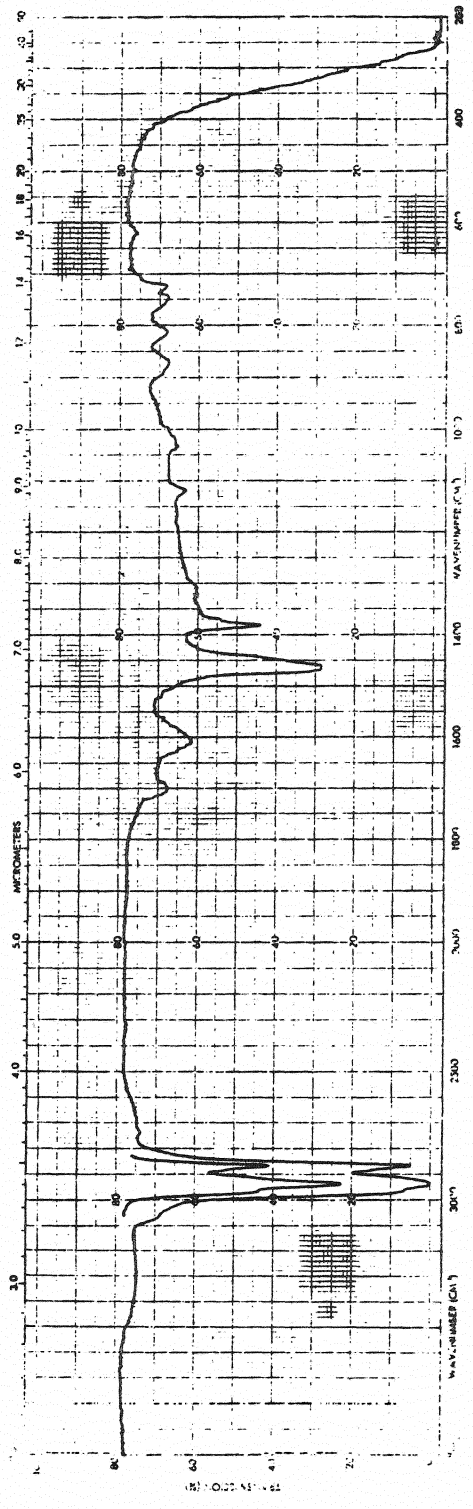


Figure: 16a. SOX-120 Sun Oil Asphalt

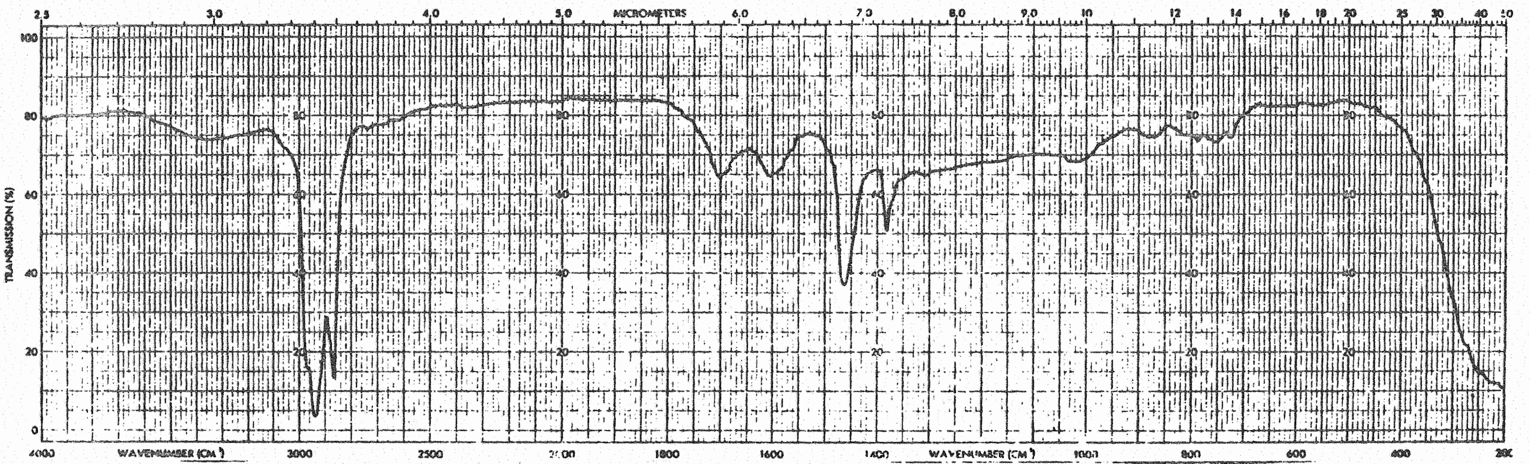


Figure: 16b. SCCa-121 Sun Oil Asphalt with Chem-crete added.

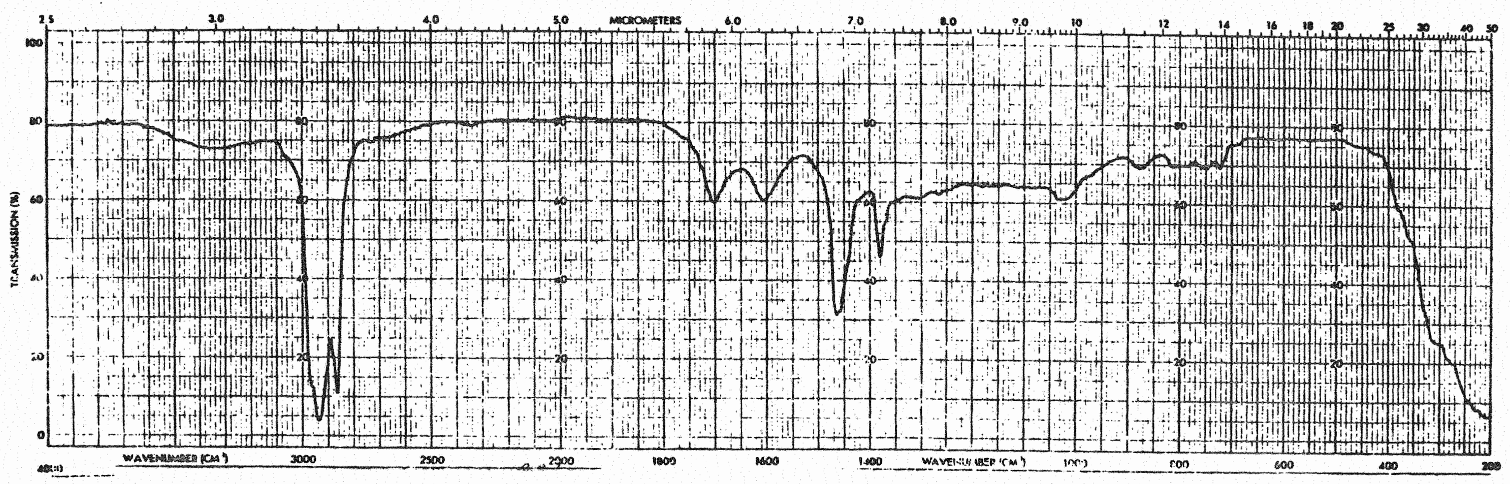


Figure: 16c. June P - 408, 5 inch surface layer of Sun Oil Asphalt with Chem-crete.

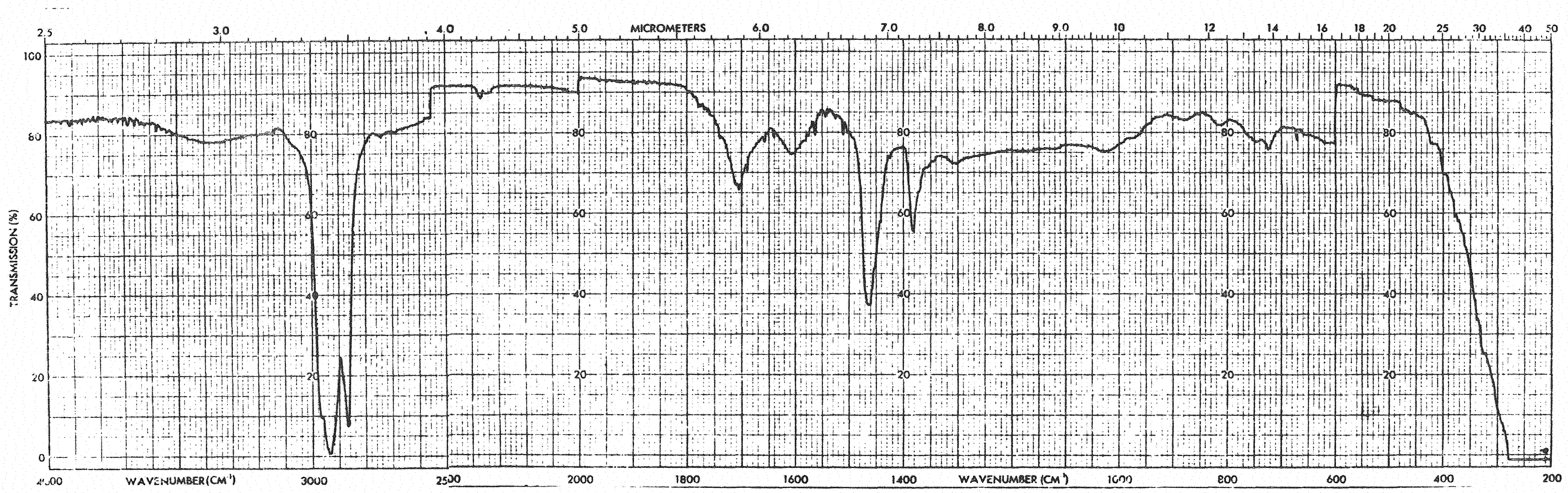


Figure:17 : Unknown asphalt taken from a road laying project. By comparing the Infrared spectra of this asphalt with others in our IR spectra library it appears to match quite well with the IR of Sun Oil/Chem-crete (SCCb-122) asphalt.

II. THE CONVERSION OF WASTE COAL INTO THE SYNTHESIS OF AN ASPHALT EXTENDER

A. Introduction

Since the late 1800's coal liquefaction techniques have been known (64). The first processes were inefficient; however, with minor changes, they did provide liquid fuels for Germany during World War II. In the 1930's and 1940's, a small U.S. effort directed towards the manufacture of synthetic oils led to the construction of two small liquefaction plants. This U.S. program ended in 1955 when readily available Middle East oil made coal liquefaction uneconomical.

In response to the Middle East oil embargo and the dependence of the U.S. on expensive, as well as unreliable sources of imported crude oil, renewed efforts to obtain coal liquefaction products have been made. The Federal Highway Administration has recognized the need for new sources of highway binder materials by sponsoring projects to examine asphalt extenders produced from cellulosic wastes (65), lignin, and sulfur. This project has been undertaken to rapidly determine if Oklahoma waste coal of high sulfur content has the possibility of being utilized as a raw material for the synthesis of an asphalt extender or as an asphalt replacement.

There is no difficulty in converting the Oklahoma waste coal into a liquid material when it is combined with hydrogen, hydrogen and asphalt, hydrogen and animal fat, or hydrogen and linseed oil. The conversion reaction readily takes place at temperatures in the range of 250-350°C, and at hydrogen pressures of 2600-3000 psi with reasonable coal conversions. The product material has excellent initial miscibility with petroleum asphalt; however, after 2-4 weeks separation occurs. Solution solubility measurements show the similarities and differences between petroleum asphalt and the coal-derived asphalt (CDA) synthesized in this project.

B. Thermal Decomposition of Coal

Thermal degradation is well-established as a process for the liquefaction of coal. Coal tars have been used as jet fuel, fungicides, and wood preservation, as well as for road tar. The chemical composition of the liquefaction product will resemble that of the coal and it will be different than petroleum asphalt due to the basic coal structure. Because of the differing structures, coal tar, in itself, would not be expected to be completely miscible with petroleum asphalt, therefore, its use as an additive could not be feasible.

Thermodynamically, coal should react at low temperatures to form smaller molecules (Figure 1). The development of low temperature conversion processes should therefore, be feasible; if the rates of reaction are reasonable. Table 1 summarizes the thermal decomposition parameters examined in this study. Lower temperatures appear to produce the highest yields of CS_2 soluble material.

C. Chemical Degradation

The action of water, ammonia, caustic and acids will cause the chemical communition of coal. The coal product often will contain reduced sulfur and ash contents. An examination of the action of several inorganic reagents upon the Oklahoma Waste Coal is summarized in Tables 2-5. In each case a CS_2 soluble material is obtained; however, the yield is low.

The CS_2 soluble material is partially soluble in AC-3; however, after several days separation occurs. It is important to note that trifluoroacetic acid (CF_3CO_2H) extracts the sulfur rich materials from the coal (66,67). Conditions are noted where the hydrogen content of the CS_2 soluble material increases, this increase parallels the yield of CS_2 soluble material associated with thermal decomposition.

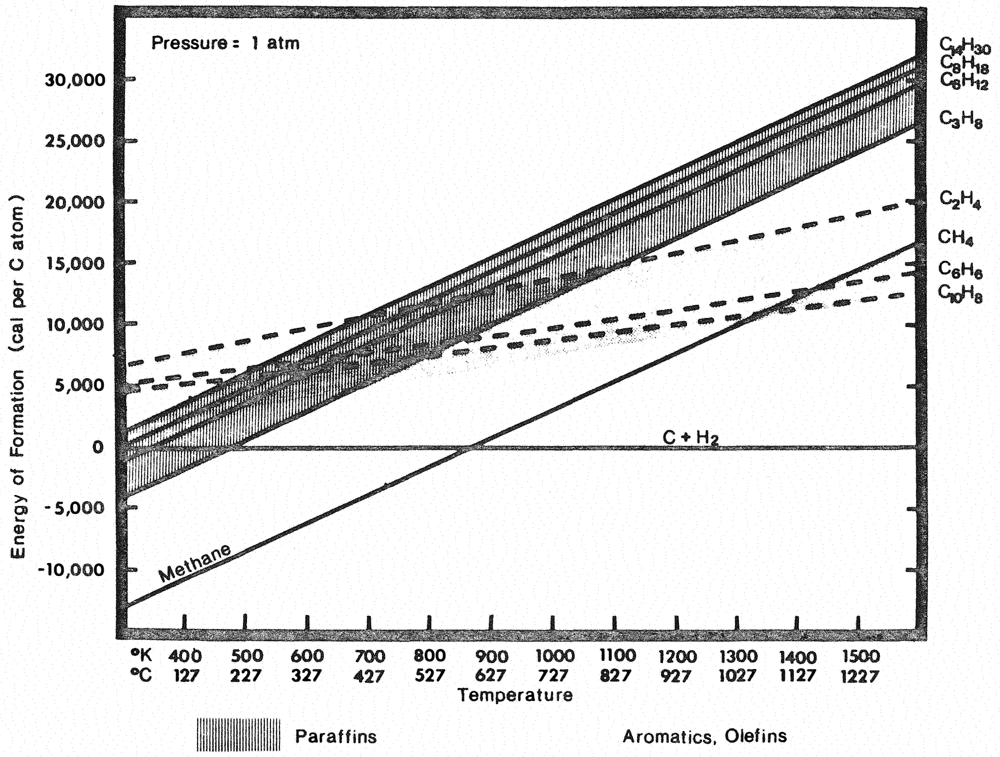


Figure 1: Thermodynamic Parameters

TABLE 1

Thermal Decomposition of Oklahoma Waste Coal

Sample	Temperature/Time °C.	Hrs.	Composition of CS_2 Soluble Material Wt %, Ash Free C	H	N	O	S	CH Ratio	% Soluble in CS_2
Coal*	Initial Material		80.6	5.3	1.8	3.7	8.6	$C_{100}H_{79}$	3%
AC-3	Standard		86.2	10.9	0.7	0.7	1.5	$C_{100}H_{151}$	100%
T-1	250	40							4%
T-2	300	40							6%
T-3	350	40	81.2	4.7	1.2	9.8	3.1	$C_{100}H_{69}$	12%
T-4	400	40							12%
T-5	450	40							12%
T-6	500	40							10%
T-7	600	40							8%
T-8	700	40	79.5	4.3	1.2	13.4	1.6	$C_{100}H_{65}$	5%
T-9	250	60							8%
T-10	300	60							1 %
T-11	350	60	83.0	5.9	1.8	6.5	2.8	$C_{100}H_{71}$	14%
T-12	250	80	83.1	6.1	1.6	7.4	1.8	$C_{100}H_{88}$	12%

*Composition of Coal

TABLE 2

Reaction of Water with Oklahoma Waste Coal

Sample	Temperature/Time/Pressure			Composition of CS_2 Soluble Material Wt%, Ash Free					CH Ratio	% Soluble in CS_2
	°C	Hrs.	Psi	C	H	N	O	S		
Coal*	-	-	---	80.6	5.3	1.8	3.7	8.6	$C_{100}H_{79}$	3%
AC-3	-	-	---	86.2	10.9	0.7	0.7	1.5	$C_{100}H_{151}$	100%
W-1	350	40	20,500	81.2	5.4	0.7	9.5	3.2	$C_{100}H_{79}$	15%
W-2	350	40	28,000	81.8	6.4	0.8	7.7	3.3	$C_{100}H_{95}$	22%
W-3	350	40	28,000	81.9	6.4	0.8	7.7	3.2	$C_{100}H_{94}$	22%
W-4	400	40	28,000	82.3	6.7	0.9	7.30	2.6	$C_{100}H_{98}$	24%
W-5	500	40	28,000	82.1	6.7	0.8	7.8	2.6	$C_{100}H_{98}$	18%
W-6	600	40	28,000	80.4	5.0	0.9	11.1	2.6	$C_{100}H_{75}$	15%
W-7	350	60	28,000	82.0	6.7	1.1	8.4	1.8	$C_{100}H_{98}$	32%
W-8	350	80	28,000	82.0	7.1	1.1	8.1	1.7	$C_{100}H_{103}$	35%
W-9	350	80	1,000	80.8	5.4	1.8	7.8	4.2	$C_{100}H_{80}$	40%
W-10	250	80	28,000	81.0	5.5	1.8	7.2	4.5	$C_{100}H_{81}$	4%

*Composition of Coal

TABLE 3

Reaction of 10% Aqueous NaOH with Oklahoma Waste Coal

Sample	Temperature/Time/Pressure			Composition of CS_2 Soluble Material Wt%, Ash Free					CH Ratio	% Soluble in CS_2
	°C	Hrs.	Psi	C	H	N	O	S		
Coal*	-	-	---	80.6	5.3	1.8	3.7	8.6	$C_{100}H_{79}$	3%
AC-3	—	-	---	86.2	10.9	0.7	0.7	1.5	$C_{100}H_{151}$	100%
C-1	350	40	5,000	81.4	5.8	0.8	10.2	1.8	$C_{100}H_{86}$	18%
C-2	350	40	28,000	83.3	7.8	0.8	6.6	1.5	$C_{100}H_{112}$	28%
C-3	400	40	28,000	82.3	7.1	0.8	8.3	1.5	$C_{100}H_{103}$	25%
C-4	350	60	28,000	84.4	8.2	0.6	5.5	1.3	$C_{100}H_{116}$	28%
C-5	250	40	28,000	81.6	5.9	0.8	10.0	1.7	$C_{100}H_{87}$	4%

*Composition of Coal

TABLE 4

Reaction of 20% Aqueous H_2SO_4 with Oklahoma Waste Coal

Sample	Temperature/Time/Pressure			Composition of CS_2 Soluble Material Wt%, Ash Free					CH Ratio	% Soluble in CS_2
	°C	Hrs.	Psi	C	H	N	O	S		
Coal*	-	-	---	80.6	5.3	1.8	3.7	8.6	$C_{100}H_{79}$	3%
AC-3	-	-	---	86.2	10.9	0.7	0.7	1.5	$C_{100}H_{151}$	100%
H-1	350	40	5,000	82.6	5.9	0.9	9.0	1.6	$C_{100}H_{86}$	17%
H-2	350	40	28,000	85.2	8.1	0.7	4.7	1.3	$C_{100}H_{114}$	25%
H-3	400	40	28,000	86.2	8.7	0.6	3.4	1.1	$C_{100}H_{121}$	23%
H-4	350	60	28,000	86.2	8.9	0.7	3.0	1.2	$C_{100}H_{123}$	31%
H-5	250	40	28,000	82.7	6.2	0.9	8.5	1.7	$C_{100}H_{90}$	10%

*Composition of Coal

TABLE 5

Reaction of 80% Aqueous CF_3CO_2H with Oklahoma Waste Coal

Sample	Temperature/Time/Pressure °C	Hrs.	Psi	Composition of CS_2 Soluble Material Wt%, Ash Free C	H	N	O	S	CH Ratio	% Soluble in CS_2
Coal*	-	-	---	80.6	5.3	1.8	3.7	8.6	$C_{100}H_{79}$	3%
AC-3	-	-	---	86.2	10.9	0.7	0.7	1.5	$C_{100}H_{151}$	100%
F-1	350	40	5,000	82.7	5.9	0.9	3.8	6.7	$C_{100}H_{86}$	20%
F-2	350	40	28,000	82.7	6.2	0.8	3.2	7.1	$C_{100}H_{90}$	26%
F-3	350	60	28,000	83.0	7.1	0.9	2.2	6.8	$C_{100}H_{102}$	31%
F-4	400	40	28,000	82.8	6.3	0.8	3.1	7.0	$C_{100}H_{91}$	27%
F-5	250	80	28,000	82.6	5.9	0.9	3.5	7.1	$C_{100}H_{86}$	14%

*Composition of Coal

D. Hydrogenation Reactions

1. Introduction

The constitution of petroleum and coal-derived asphaltenes was the topic of a major American Chemical Society held in 1979 (68-70). The structural differences between these asphaltenes has been well described by T.F. Yen (68). "In general, coal-derived asphaltenes have higher aromaticity than petroleum-based asphaltenes. Another major characteristic difference is that coal asphaltenes contain more hydroxyl and pyrrolic groups in addition to ether-oxygen or basic nitrogen functions than to petroleum asphaltene." These differences are important when one tries to mix coal-derived asphalt with the petroleum material. This topic is discussed in Section E.

Tables 6-8 present typical experimental results for this brief investigation and Table 9 compares several different conversion processes.

2. The Syntheses

Tables 6-10 summarize the amount of coal conversion as a function of temperature and pressure. Reasonable yields of liquid product are obtained wehn the coal is simply combined with hydrogen gas (Table 6); however, the material has only short-term (1-4 days) miscibility with commercial petroleum asphalt.

In order to prepare a material with long term miscibility, the interaction of the coal with hydrogen in the presence of asphalt, animal fat, and linseed oil was examined. It is important to note that the last two represent renewable resources. Indeed, animal fat is a waste material in this region; new uses for it could have economic importance.

Table 7 and Figure 2 summarize the experimental effort when asphalt is added to the reaction mixture. The addition of the asphalt improves the maltene/asphaltene ratio as would be anticipated. It is important to note

TABLE 6

Conversion of Oklahoma Coal into Asphaltic Bitumen

Reaction of Coal with Hydrogen Gas

Number	CDA-1	CDA-2	CDA-3	CDA-4	CDA-5	CDA-6	CDA-7	CDA-8
Weight in grams of coal:	50.0	100.9	50.9	50.0	1.11	0.77	0.80	1.03
Conditions:								
Temperature °C	250	250	490	180	350	350	350	350
Pressure psi (initial)	4000	4000	2000	4000	2000	2000	2000	2000
Pressure psi (final)	7200	7000	4800	6250	2840	2900	2900	2900
Time of Rxn (hrs)	60	64	13	18	66	30	4	65
Yields:								
% Total Yield	44.4	44.0	19.1	1.6	51.0	19.5	16.3	53.0
% Coal Conversion	44.4	44.0	19.1	1.6	51.0	19.5	16.3	53.0

that little change occurs in the AC-3 upon hydrogenation and that 40-45% conversions occur in the coal samples.

Table 8 summarized the experiments with anmial fat. The high temperature experiment (CDA-24) provides a product with reasonable maltene/asphaltene and C/H ratios. The linseed oil experiments (Table 9) provide high conversion yields.

The synthetic asphalts obtained in this study qualitatively demonstrated a wide range of penetrations, viscosities, ductilities, and general handling properties. The product made from coal/linseed oil/H_2 (CDA-41) had the most asphalt-like properties. It had an AASHTO penetration of 20; however, its ductility was only 3.

TABLE 7

Conversion of Oklahoma Coal into Asphaltic Bitumen
Reaction of Coal/Asphalt Mixtures[1] with Hydrogen Gas

Sample	CDA-10	CDA-11	CDA-12	CDA-13	CDA-14	CDA-15	CDA-16	CDA-17	CDA-18	CDA-19	CDA-61	CDA-62	CDA-63	CDA-64	CDA-65	CDA-66	CDA-67	CDA-68	CDA-69
Weight in grams	16.0	1.26	1.34	0.91	2.58	1.14	1.12	1.69	1.46	26.7	114.7	0.90	1.69	1.46	1.46	1.64	1.12	2.92	1.94
Conditions:																			
Temp. (°C)	280	250	250	250	250	250	300	300	300	300	300	350	350	350	350	350	400	400	400
Pressure Psi (initial)	2000	2000	2000	2000	2000	2000	2000	2000	2000	2000	2000	2000	2000	2000	2000	2000	2000	2000	2000
(final)	3800	2650	2680	2700	2700	2700	2820	2880	2800	3900	3600	2920	2900	2890	2900	2910	3000	2900	2900
Time of Rxn (hrs)	66	4	8	18	60	84	4	8	18	60	84	4	18	30	60	84	4	18	30
Yields:																			
% Total Yield	96.9	53.2	56.2	56.0	60.9	71.9	53.6	54.4	57.5	70.4	72.7	55.6	58.6	58.2	83.6	75.6	28.6	28.4	22.1
% Loss as volatile materials	3.1	2.4	1.5	3.3	0.4	.9	1.8	7.1	2.1	6.4	11.5	2.2	4.1	1.4	3.4	2.4	--	--	--
% Net Yield (coal converted)	--	6.3	12.3	12.1	21.7	43.9	7.1	8.9	15.1	40.8	45.4	11.1	17.2	16.4	64.1	51.2	Loss of CS_2 Soluble Material		

[1] Equal weight of each condensed material

[2] Asphalt and hydrogen gas

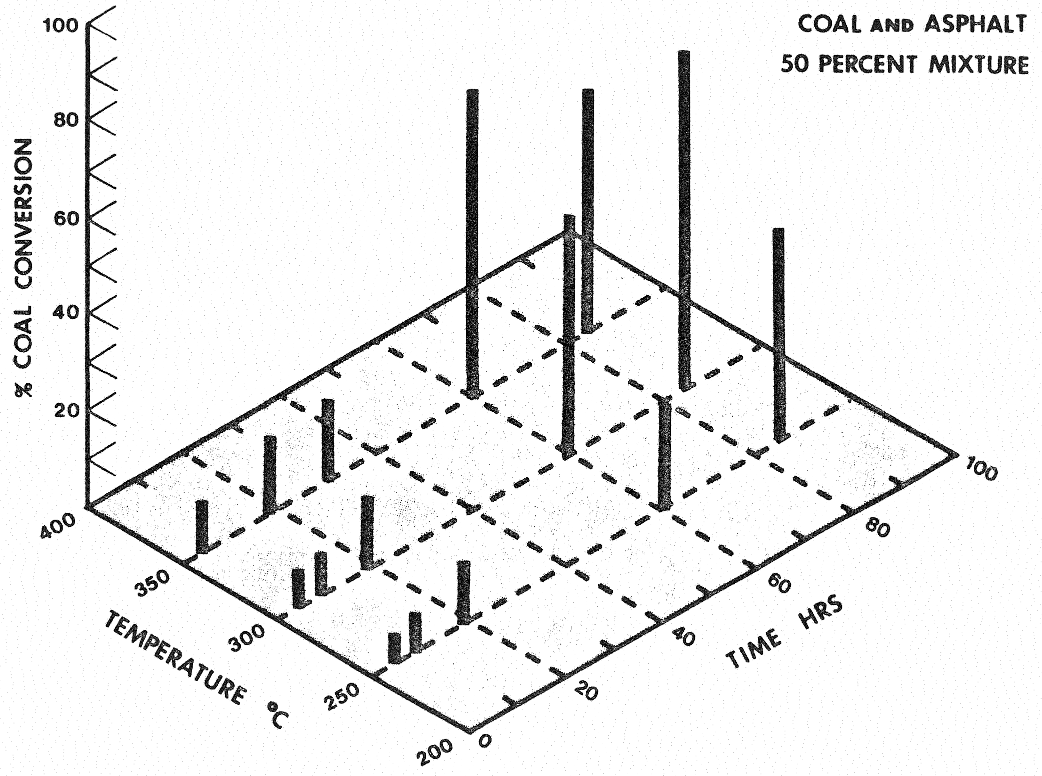


Figure 2: Yields for the Reaction of Hydrogen with Coal in the Presence of Asphalt.

TABLE 8

Conversion of Oklahoma Coal into Asphaltic Bitumen

Reaction of Coal with Hydrogen Gas Using Animal Fat[1] as a Hydrogen Carrier

Number	CDA-20[2]	CDA-21	CDA-22	CDA-23	CDA-24
Weight in Grams	20.0	49.9	58.4	59.4	29.5
Conditions:					
Temperature °C	250	290	300	300	375
Pressure Psi (initial)	2000	2020	2000	2000	2000
Pressure Psi (Final)	3800	3900	3500	3880	3900
Time of Rxn (hrs)	65	60	90	95	8
Yields:					
% Total Yield	82.5	61.1	77.4	76.6	67.8
% Loss as Volatile Material	17.5	18.0	5.5	10.1	12.5
% Net Yield (coal converted)	--	22.2	54.8	53.2	35.6

[1] Equal weights of each condensed material

[2] Animal fat and hydrogen gas

TABLE 9

Conversion of Oklahoma Coal into Asphaltic Bitumen
Reaction of Coal with Hydrogen Gas Using Linseed Oil as a Hydrogen Carrier

Number	CDA-40[2]	CDA-41	CDA-42
Weight in grams	30.0	56.8	197.7
Conditions:			
Temperature (°C)	250	250	260
Pressure Psi (initial)	2000	2000	2000
Pressure Psi (final)	3600	3600	3400
Time of Rxn (hrs)	90	96	94
Yields:			
% Total Yield	98.4	71.7	69.4
% Loss of Volatiles	1.6	3.0	7.5
% Net Yield (coal converted)	---	43.3	38.8

[1] Equal weights of each condensed material

[2] Linseed oil and hydrogen gas

TABLE 10

Conversion of Oklahoma Coal into an Asphalt Product
Comparison of Charge Used*

Charge	Coal/H_2	Coal/ Asphalt/ H_2	Coal/ Fat/H_2	Coal/H_2/ Stearic Acid	Coal/H_2 Linseed Oil	Coal/CO	Fat	Asphalt
Number	(CDA-5)	(CDA-69)	(CDA-21)	(CDA-31)	(CDA-42)	(CDA-80)	(CDA-20)	(CDA-10)
Weight in grams	1.1	1.46	49.9	20.0	197.7	25.0	20.0	16.0
Conditions:								
Temp. °C	350	350	290	250	260	350	250	280
Pressure psi (initial)	2000	2000	2000	2000	2000	1000	2000	2000
Pressure psi (final)	2900	2800	3900	3600	3400	2700	3800	3800
Time of Rxn (hrs.)	66	60	60	65	94	63	65	66
Yields:								
% Weight of Yield	51.0	82.2	61.1	49.5	69.4	<0.1	82.5	96.9
% of Coal Conversion	51.0	64.0	22.2	0	38.8	<0.1	--	--

*Equal weights of coal and condensed reagent to form total weight of sample.

3. Elemental Analyses

Hydrogenation of the coal is essential to synthesize a road asphalt. Table 11 confirms that hydrogen will indeed react with the Oklahoma waste coal; however, the amount of conversion is not sufficient to make it comparable to asphalt. The hydrogenation of coal/asphalt mixtures should result in the formation of a material which has asphalt properties (Table 12). It is important to note that the AC-3 does not hydrogenate at these conditions and the coal conversions are sufficient so that the analyses are not biased by asphalt. Tables 13 and 14 describe similar reactions. In each case a product can be obtained which raises the C/H ratio to an acceptable level, as well as reducing the heteroatom (N and S) level to a reasonable level for an asphalt.

TABLE 11

Elemental Analyses

Reaction of Coal with Hydrogen Gas

			Composition Wt. %, Ash Free					Ratios Wt. %/Wt. %			Average Molecular Formula Per 100 Carbon Atoms				
Sample	Temp	Hrs	C	H	N	O	S	$\frac{C}{H}$	$\frac{C}{O}$	$\frac{C}{N+O+S}$	C	H	N	O	S
Coal	Control		80.6	5.3	1.8	3.7	8.6	15.1	21.7	5.7	100	79.3	1.89	3.45	3.97
AC-3	Control		86.2	10.9	0.7	0.7	1.5	7.9	123	29.3	100	151	0.71	0.61	0.67
Coal/H_2															
CDA-1	250	60	86.9	7.1	1.7	2.9	1.6	12.3	30.5	14.3	100	97.4	1.65	2.46	0.67
CDA-2	250	64	87.0	7.3	1.2	2.8	1.8	12.0	31.3	15.1	100	100	1.18	2.40	0.78
CDA-3	490	13	87.1	7.2	1.0	0.3	4.4	12.1	300	15.25	100	99.2	0.97	0.25	1.91

TABLE 12

Elemental Analyses

Reaction of Coal/Asphalt Mixture with Hydrogen Gas

			Composition Wt. %, Ash Free					Ratios Wt. %/Wt. %			Average Molecular Formula Per 100 Carbon Atoms				
Sample	Temp	Hrs	C	H	N	O	S	$\frac{C}{H}$	$\frac{C}{O}$	$\frac{C}{N+O+S}$	C	H	N	O	S
Coal	Control		80.6	5.3	1.8	3.7	8.6	15.1	21.7	5.7	100	79.3	1.89	3.45	3.97
AC-3	Control		86.2	10.9	0.7	0.7	1.5	7.9	151	29.3	100	151	0.71	0.61	0.67
AC-3/Coal	Mixture		86.0	8.5	1.3	0.2	4.0	10.1	453	15.7	100	118	1.25	0.17	1.76
AC-3/H_2	280	70	87.0	11.1	0.5	0.6	0.7	7.8	138	10.8	100	153	0.53	0.54	0.29
Coal/Asphalt/H_2															
CDA-11	250	4	85.6	10.6	0.7	1.4	1.7	8.1	59.9	22.7	100	149	0.7	1.25	0.72
CDA-62	350	4	82.9	9.4	0.8	5.4	1.5	8.8	15.5	10.8	100	136	0.81	4.85	0.68
CDA 19	300	60	86.6	10.0	0.7	0.8	1.9	8.7	104	25.3	100	138	0.73	0.72	0.80
CDA-61	300	84	86.8	8.4	1.2	0.5	3.1	10.3	161	18.1	100	117	1.15	0.47	1.33
CDA-67	400	4	87.9	10.0	1.4	0.3	1.4	8.8	266	41.1	100	137	0.37	0.28	0.61
CDA-68	400	18	87.0	10.2	0.6	<0.1	2.9	8.5	-	25.3	100	142	0.56	<0.1	1.23
CDA-69	400	30	88.5	9.1	0.6	0.6	1.2	9.7	147	36.7	100	124	0.59	0.51	0.51

TABLE 13

Elemental Analyses

Reaction of Coal with Hydrogen Gas Using Animal Fat as a Hydrogen Carrier

			Composition Wt. %, Ash Free					Ratios Wt. %/Wt. %			Average Molecular Formula Per 100 Carbon Atoms				
Sample	Temp.	Hrs	C	H	N	O	S	$\frac{C}{H}$	$\frac{C}{O}$	$\frac{C}{N+O+S}$	C	H	N	O	S
Coal	Control		80.6	5.3	1.8	3.7	8.6	15.1	21.7	5.7	100	79.3	1.89	3.45	3.97
AC-3	Control		86.2	10.9	0.7	0.7	1.5	7.9	123	29.3	100	151	0.71	0.61	0.67
Animal Fat	Control		76.7	12.2	0.0	11.1	0.1	6.3	6.9	6.9	100	190	0.03	10.8	0.05
Fat/H_2	250	65	85.0	14.3	0.1	0.3	0.3	5.9	293	121	100	202	0.12	0.26	0.13
Coal/Fat/H_2															
CDA-21	290	60	84.5	9.2	1.1	3.9	1.2	9.2	21.5	13.4	100	130	1.16	3.49	0.55
CDA-22	300	90	81.0	9.9	0.9	6.5	1.7	8.2	12.4	8.9	100	147	0.93	6.03	0.78
CDA-23	300	95	86.5	8.2	1.3	2.4	1.5	10.5	36.7	16.5	100	114	1.33	2.05	0.67
CDA-24	375	8	85.6	8.7	1.4	2.9	1.3	9.8	29.2	15.1	100	123	1.41	2.57	0.59

TABLE 14

Elemental Analyses

Reaction of Coal with Hydrogen Gas Using Linseed Oil as Hydrogen Carrier

Sample	Temp	Hrs	Composition Wt. %, Ash Free					Ratios Wt. %/Wt. %			Average Molecular Formula Per 100 Carbon Atoms				
			C	H	N	O	S	$\frac{C}{H}$	$\frac{C}{O}$	$\frac{C}{N+O+S}$	C	H	N	O	S
Coal	Control		80.6	5.3	1.8	3.7	8.6	15.1	21.7	5.7	100	79.3	1.89	3.45	3.97
AC-3	Control		86.2	10.9	0.7	0.7	1.5	7.9	123	29.3	100	151	0.71	0.61	0.67
Linseed Oil	Control		76.9	10.9	0.2	11.9	0.1	7.0	6.5	6.4	100	170	0.23	11.6	0.02
Coal/Linseed Oil/H_2															
CDA-41	250	95	81.0	9.9	0.7	7.2	1.3	8.2	11.3	8.8	100	147	0.75	6.65	0.59

4. Bitumen Analyses

Tables 15-18 summarize the maltene and asphaltene yield for each process. Each table describes the reaction yield, the yield of semi-solid and the percentage of maltenes and asphaltenes in the semi-solid. The reaction of coal with hydrogen produces a product which has a poor maltene/asphaltene ratio; however, when asphalt, animal fat, or linseed oil is added to the reaction mixture a better maltene/asphaltene ratio os obtained. The calculations are described in the experimental section of this report.

Figure 3 shows the excellent correlation between the weight-% of hydrogen in the sample and its pentane solubility. Weight-% hydrogen is therefore directly proportional to the percentage of maltenes in the sample.

TABLE 15

Bitumen Analyses
Reaction of Coal with Hydrogen Gas

				CS$_2$ Soluble Material			
					Semi-Solid		
Sample	Temp (°C)	Time (hr)	Psi	Yield %	Yield %	% Maltenes	% Asphaltenes
Coal	Control			1.5	0	--	--
AC-3	Control			100	100	79	21
CDA-1	250	60	7200	44	44	21	79
CDA-2	250	64	7000	44	44	45	55
CDA-3	490	13	4800	19	13	30	60

TABLE 16

Bitumen Analyses

Reaction of Coal/Asphalt Mixtures with Hydrogen Gas

				CS_2 Soluble Material			
					Semi-Solid		
Sample	Temp (°C)	Time (hr)	Psi	Yield %	Yield %	% Maltenes	% Asphaltenes
Coal	Control			1.5	0	--	--
AC-3	Control			100	100	79	21
AC-3/H_2	280	66	3800	97	97	78	22
CDA-19	300	60	3900	70	70	67	33
CDA-61	300	84	3600	73	73	52	48

TABLE 17

Bitumen Analyses

Reaction of Coal with Hydrogen Gas Using Animal Fat as a Hydrogen Carrier

				CS$_2$ Soluble Material			
					Semi-Solid		
Sample	Temp (°C)	Time (hr)	Psi	Yield %	Yield %	% Maltenes	% Asphaltenes
Coal	Control			1.5	0	--	--
AC-3	Control			100	100	79	21
Animal Fat	250	65	3800	100	0	--	--
CDA-21	290	60	3900	80	60	47	53
CDA-22	300	90	3500	77	77	51	49
CDA-23	300	95	3880	78	58	29	71
CDA-24	375	8	3900	68	64	60	38

TABLE 18

Bitumen Analyses

Reaction of Coal with Hydrogen Gas Using Linseed Oil as Hydrogen Carrier

				CS$_2$ Soluble Material			
					Semi-Solid		
Sample	**Temp (°C)**	**Time (hr)**	**Psi**	**Yield %**	**Yield %**	**% Maltenes**	**% Asphaltenes**
Coal	Control			1.5	0	--	21
AC-3	Control			100	100	79	21
Linseed Oil	250	90	3600	98	98	98	0
CDA-41	250	96	3600	72	72	64	36
CDA-42	260	94	3400	70	46	60	40

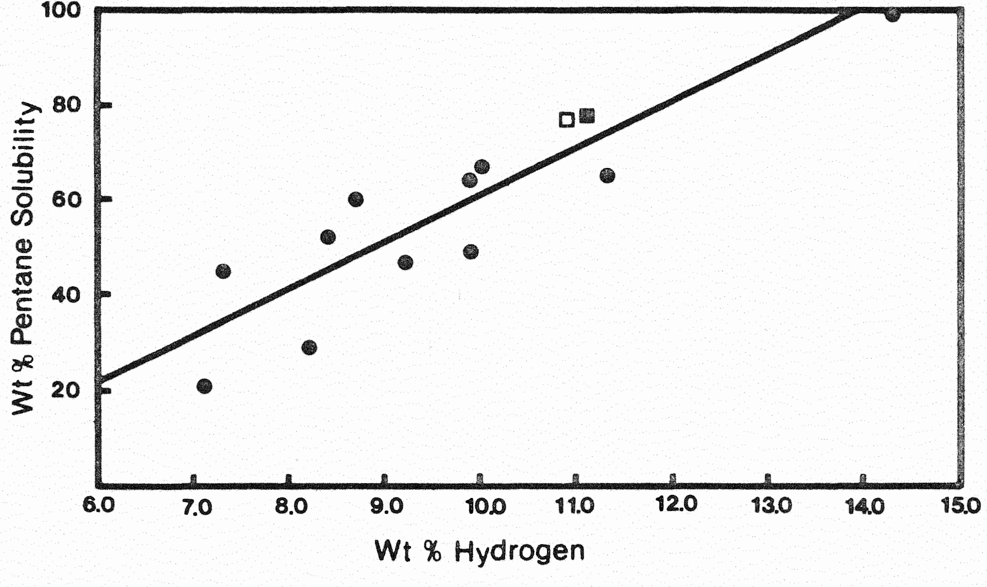


Figure 3: Relationship between Pentane Solubility and wt% Hydrogen

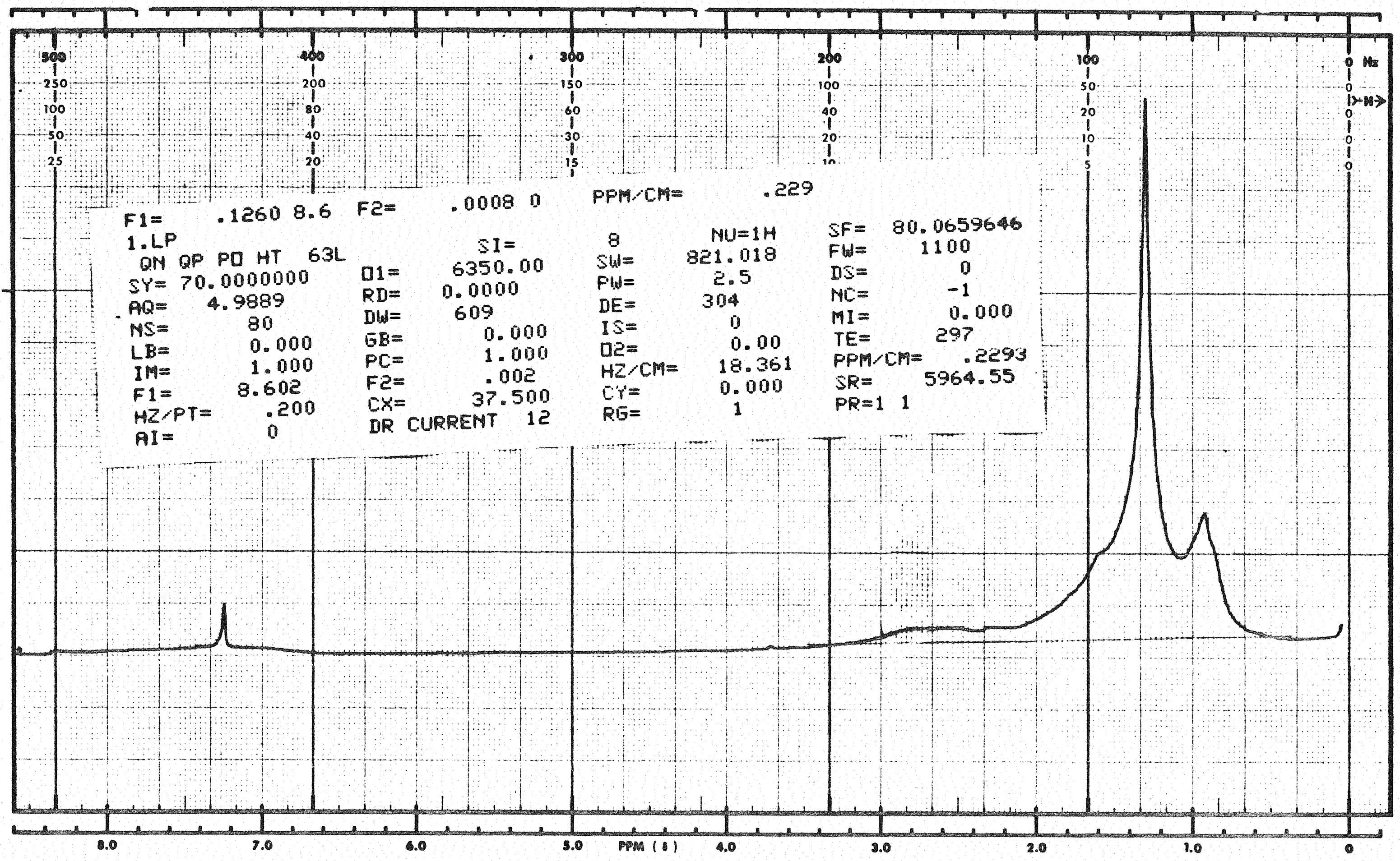
5. Nuclear Magnetic Resonance Spectra

This section contains a complete collection of representative nuclear magnetic resonance spectra. Figure 4 is the spectrum for commercial AC-3. The presentation is a sum of 80 scans, the lack of any aromatic protons is reasonable for this material. Figure 5 confirms that the asphalt is little changed upon treatment with hydrogen (Table 8). The simple hydrogenation of coal produces a material which is rich in aromatic protons (6.9-8.0δ); at coking conditions (500°C) aromatic protons dominate the spectrum, at 250°C some aliphatic groups are noted (Figures 6 and 7).

The reaction product of coal/asphalt with hydrogen is well described in Figures 8-13. The 300°C product changes with increased reaction time; after 60 hours some aromatic protons remain; however, after 84 hours the trace of aromatic protons is reasonable for asphalt and a rich variety of aliphatic protons are noted (Figures 8 and 9).

The product from the runs at 350°C to 400°C is shown in Figures 10-13. It is worth noting that these spectra parallel the conversion yields given in Table 7, since the 400°C runs show a breakdown of the simple aliphatic groupings into more complex moieties (2.0-3.0δ) as the reaction time increases. The nuclear magnetic resonance data supports the observation (Tables 7,12,16) that low reaction times (250°C-300°C) and a contact time of 60 hours gives the best reaction product.

The spectrum of the product from the fat/H_2 reaction (Figure 14) shows the anticipated spectrum of hydrogenated fat. The spectra (Figures 15-17), appear to be the same; however, the chemical shifts are now in the region anticipated for asphalt (Figure 4).



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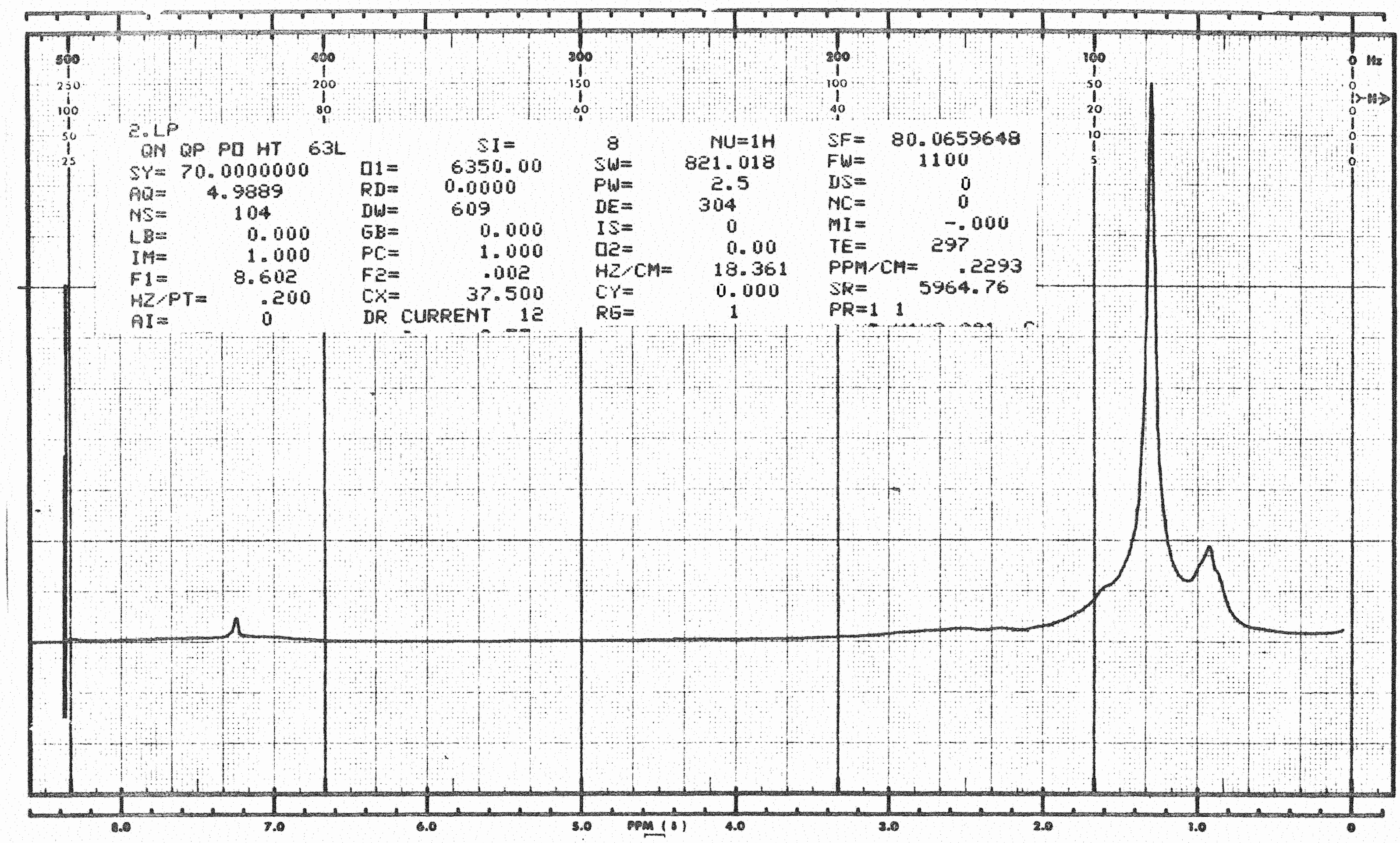
1.LP
 QN QP PO HT  63L             SI=         8         NU=1H       SF=  80.0659646
SY= 70.0000000      O1=     6350.00      SW=     821.018       FW=    1100
AQ=    4.9889       RD=    0.0000        PW=        2.5        DS=       0
NS=        80       DW=      609         DE=       304         NC=      -1
LB=     0.000       GB=        0.000     IS=         0         MI=      0.000
IM=     1.000       PC=        1.000     O2=        0.00       TE=     297
F1=     8.602       F2=         .002     HZ/CM=   18.361       PPM/CM=    .2293
HZ/PT=   .200       CX=       37.500     CY=       0.000       SR=    5964.55
AI=         0       DR CURRENT    12     RG=         1         PR=1 1
```

Figure 4. Nuclear Magnetic Resonance Spectrum of commercial AC-3. peak at 7.2δ is $CHCl_3$ in the $CDCl_3$.)



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2.LP
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SY= 70.0000000   D1=     6350.00    SW=    821.018     FW=     1100
AQ=    4.9889    RD=    0.0000      PW=      2.5       DS=        0
NS=      104     DW=     609        DE=     304        NC=        0
LB=      0.000   GB=       0.000    IS=       0        MI=      -.000
IM=      1.000   PC=       1.000    D2=       0.00     TE=      297
F1=      8.602   F2=        .002    HZ/CM=   18.361    PPM/CM=   .2293
HZ/PT=    .200   CX=      37.500    CY=       0.000    SR=    5964.76
AI=      0       DR CURRENT  12     RG=       1        PR=1 1
```
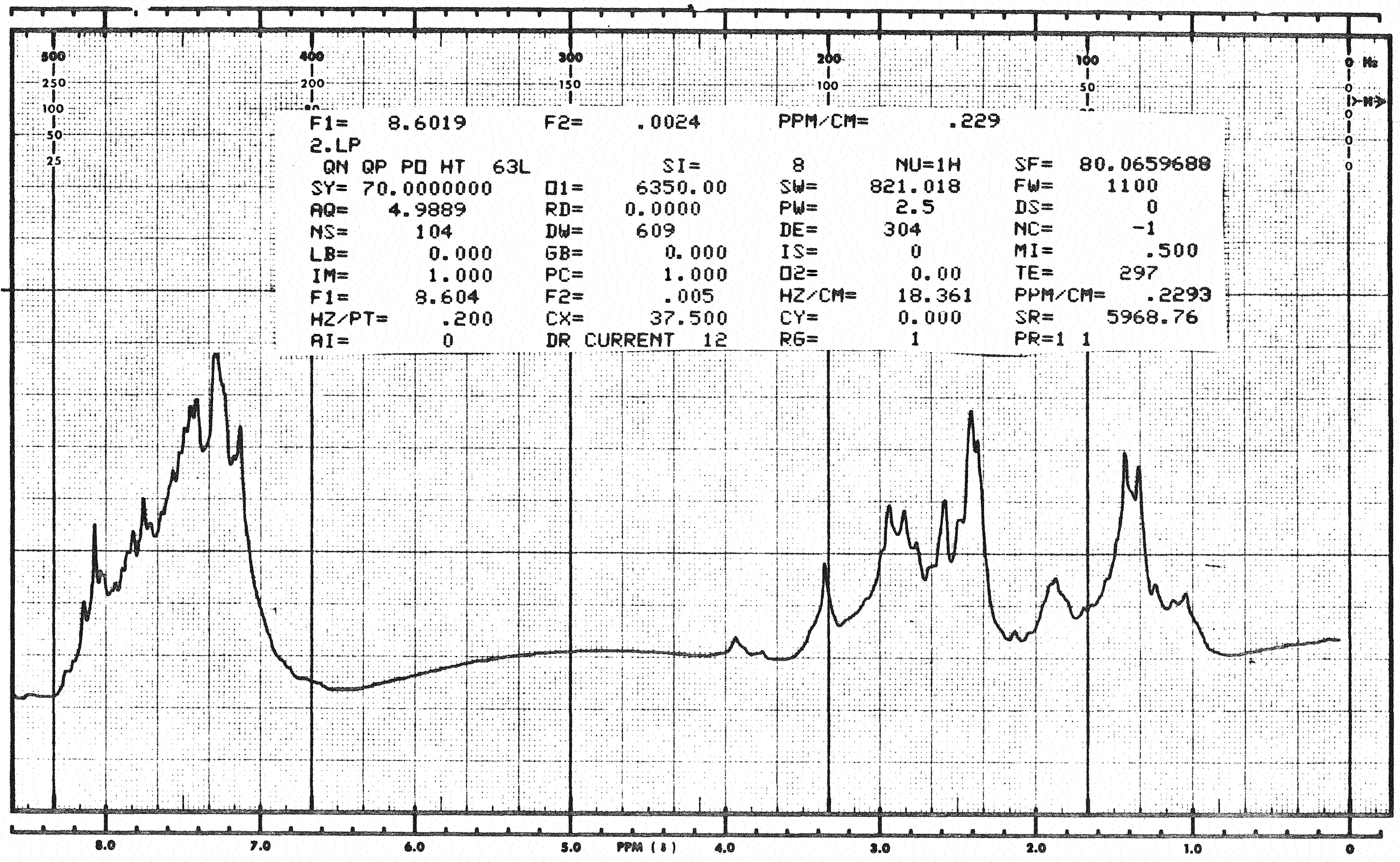

Figure 5. Nuclear Magnetic Resonance Spectrum of CDA-10 reaction of commercial AC-3 asphalt with hydrogen gas at 280°C for 66 hours. (15% in $CDCl_3$; peak at 7.2δ is $CHCl_3$ in $CDCl_3$.)



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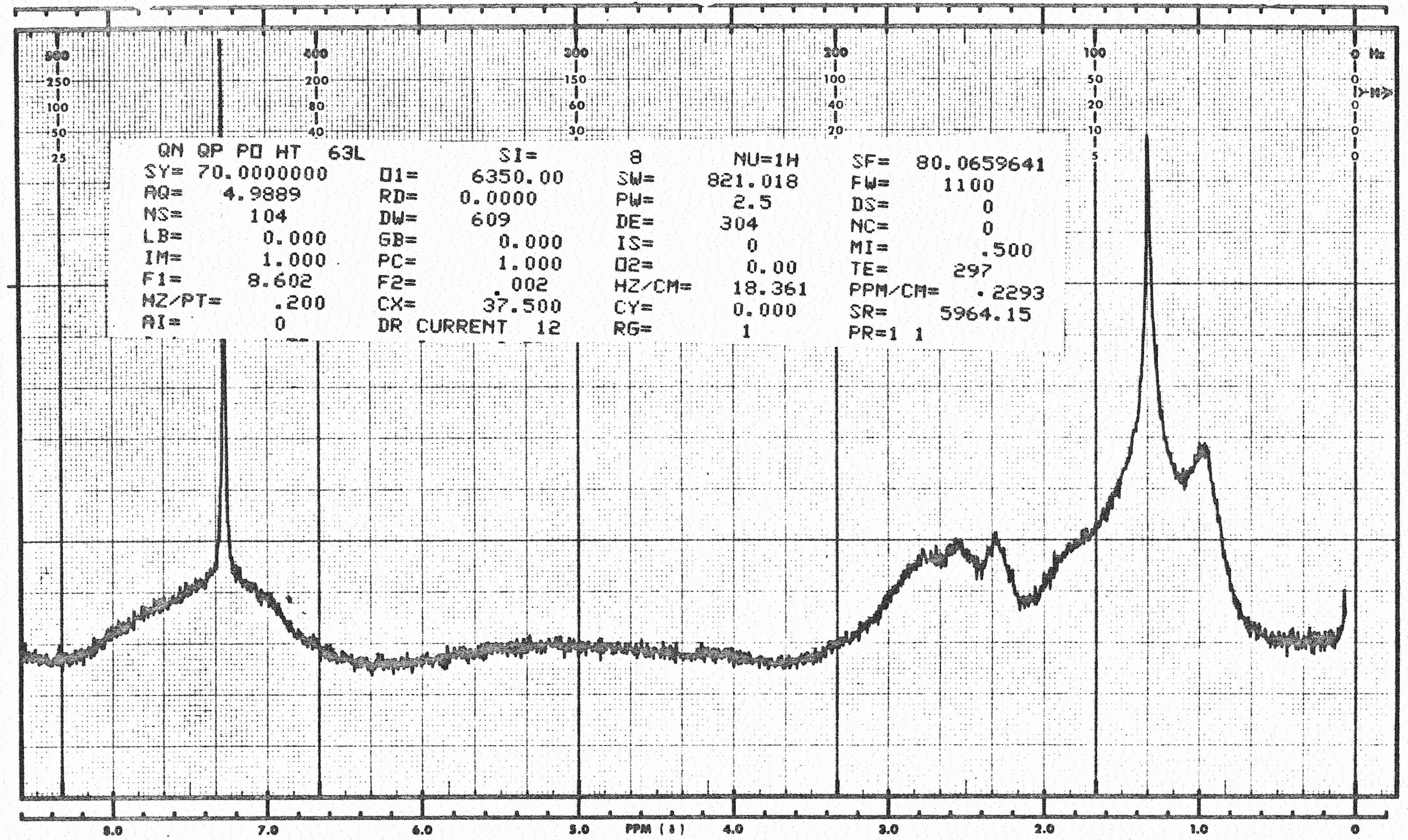
SY= 70.0000000      O1=     6350.00     SW=    821.018       FW=     1100
AQ=    4.9889       RD=    0.0000       PW=      2.5         DS=        0
NS=      104        DW=     609         DE=     304          NC=       -1
LB=        0.000    GB=        0.000    IS=        0         MI=      .500
IM=        1.000    PC=        1.000    O2=        0.00      TE=     297
F1=      8.604      F2=        .005     HZ/CM=   18.361      PPM/CM=   .2293
HZ/PT=      .200    CX=       37.500    CY=        0.000     SR=    5968.76
AI=        0        DR CURRENT  12      RG=        1         PR=1 1
```

Figure 6. Nuclear Magnetic Resonance Spectrum of CDA-3 reaction of coal with hydrogen gas at 490°C for 13 hours. (15 % in $CDCl_3$; peak at 7.2δ is $CHCl_3$ in $CDCl_3$.)



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  QN QP PD HT   63L           SI=        8        NU=1H      SF=  80.0659641
SY= 70.0000000      D1=     6350.00    SW=     821.018    FW=      1100
AQ=    4.9889       RD=    0.0000      PW=       2.5      DS=        0
NS=      104        DW=     609        DE=     304        NC=        0
LB=        0.000    GB=        0.000   IS=        0       MI=         .500
IM=        1.000    PC=        1.000   D2=         0.00   TE=      297
F1=      8.602      F2=       .002     HZ/CM=    18.361   PPM/CM=   .2293
HZ/PT=      .200    CX=       37.500   CY=       0.000    SR=     5964.15
AI=        0        DR CURRENT   12    RG=        1       PR=1  1
```
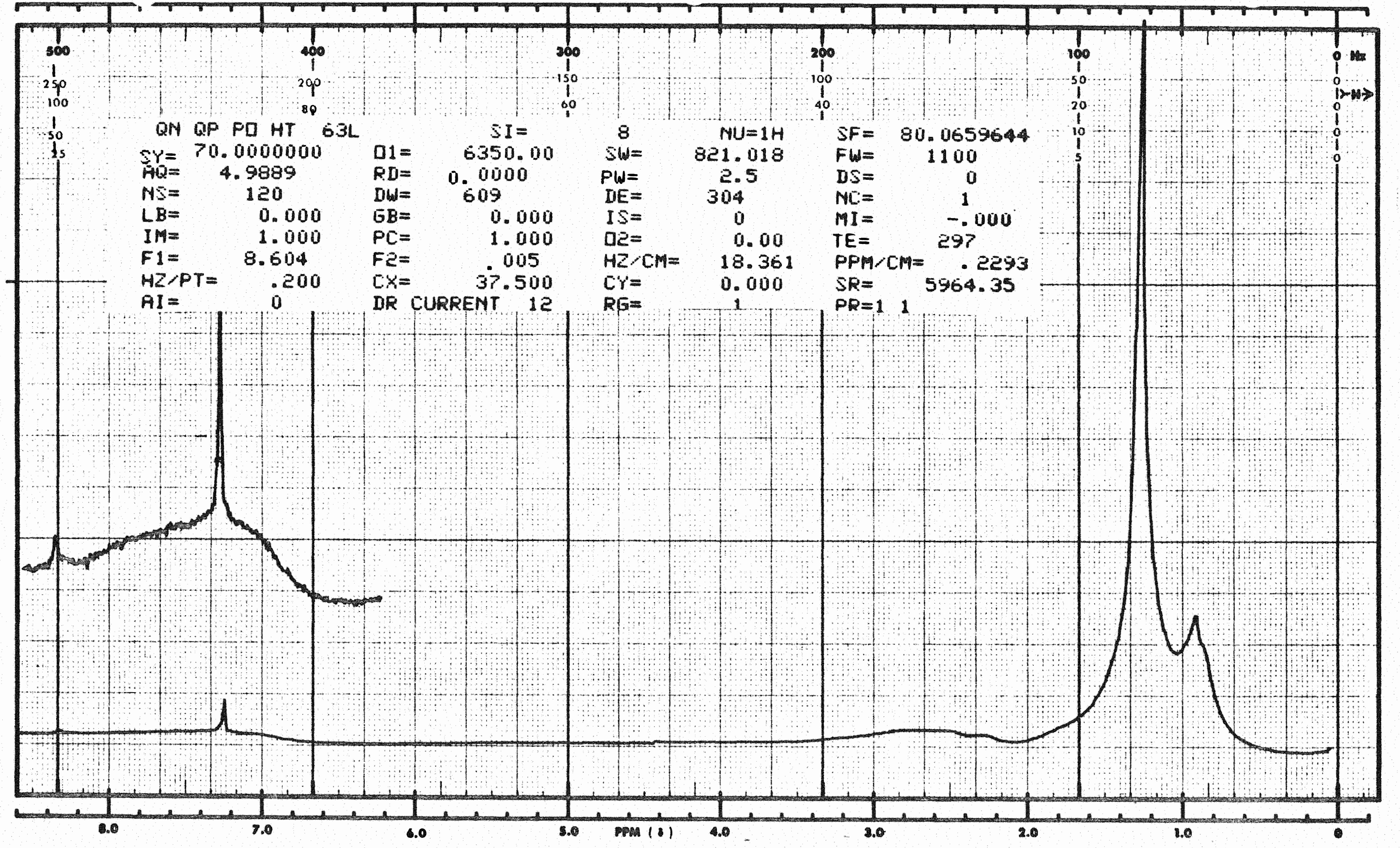

Figure 7. Nuclear Magnetic Resonance Spectrum of CDA-2 reaction of coal with hydrogen gas at 250°C for 64 hours. (15% in $CDCl_3$; peak at 7.2δ is $CHCl_3$ in $CDCl_3$).



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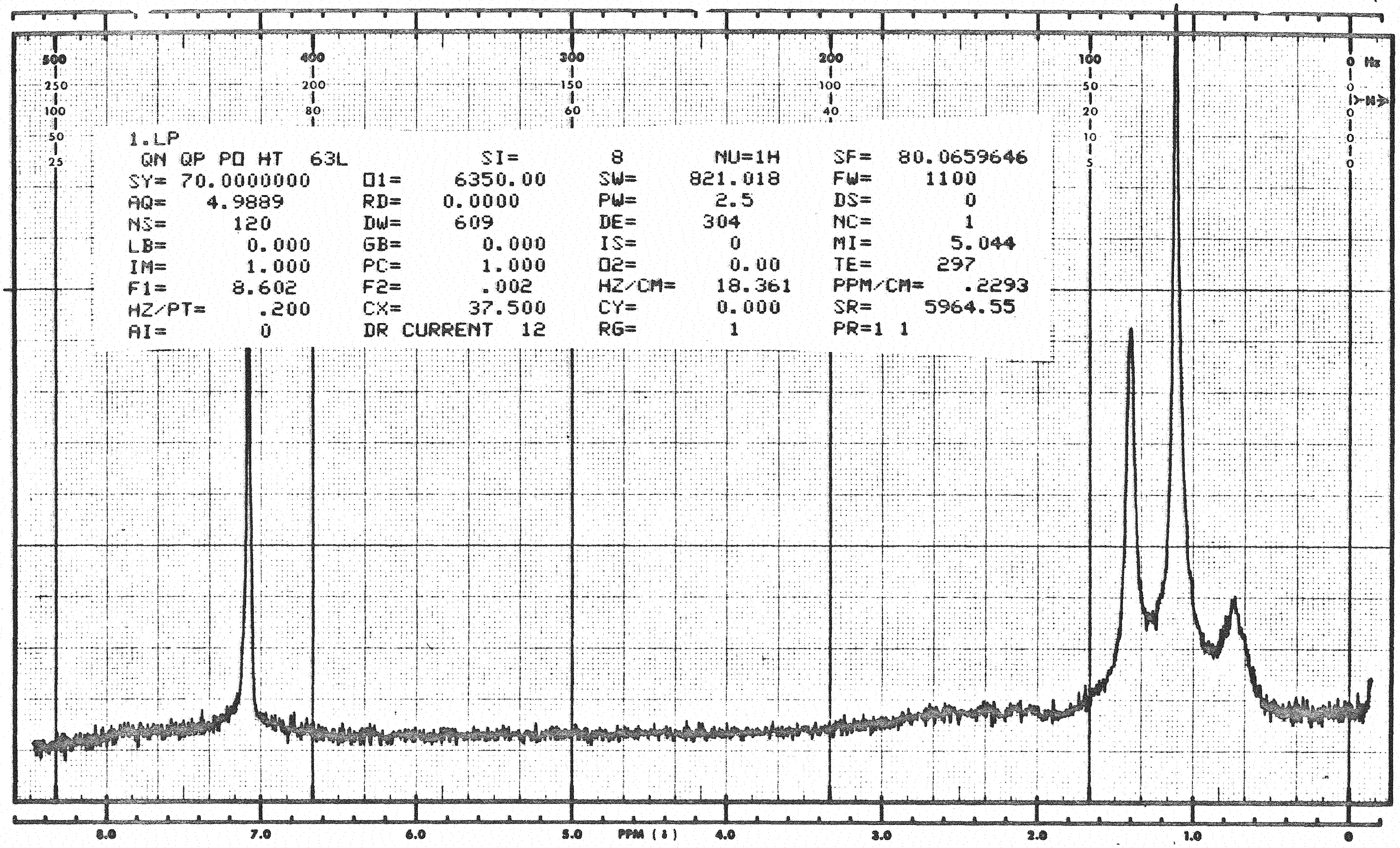
SY= 70.0000000    O1=     6350.00    SW=      821.018   FW=     1100
AQ=    4.9889     RD=   0.0000       PW=        2.5     DS=        0
NS=      120      DW=      609       DE=      304       NC=        1
LB=       0.000   GB=        0.000   IS=        0       MI=       -.000
IM=       1.000   PC=        1.000   O2=        0.00    TE=      297
F1=      8.604    F2=         .005   HZ/CM=    18.361   PPM/CM=   .2293
HZ/PT=     .200   CX=       37.500   CY=        0.000   SR=     5964.35
AI=        0      DR CURRENT   12    RG=        1       PR=1  1
```

Figure 8. Nuclear Magnetic Resonance Spectrum of CDA-19 reaction of coal with commercial AC-3 asphalt and hydrogen gas at 300°C for 60 hours. (15% in $CDCl_3$; peak at 7.2δ is $CHCl_3$ in $CDCl_3$.)



```
1.LP
 QN QP PO HT  63L          SI=        8        NU=1H       SF=  80.0659646
SY= 70.0000000    O1=      6350.00   SW=      821.018     FW=      1100
AQ=    4.9889     RD=    0.0000      PW=        2.5       DS=         0
NS=      120      DW=      609       DE=      304         NC=         1
LB=        0.000  GB=        0.000   IS=         0        MI=         5.044
IM=        1.000  PC=        1.000   O2=          0.00    TE=       297
F1=      8.602    F2=         .002   HZ/CM=     18.361    PPM/CM=    .2293
HZ/PT=      .200  CX=       37.500   CY=         0.000    SR=      5964.55
AI=          0    DR CURRENT    12   RG=         1        PR=1 1
```

Figure 9. Nuclear Magnetic Resonance Spectrum of CDA-61 reaction of coal with commercial AC-3 asphalt and hydrogen gas at 300°C for 84 hours. (15% in $CDCl_3$; peak at 7.2δ is $CHCl_3$ in $CDCl_3$.)

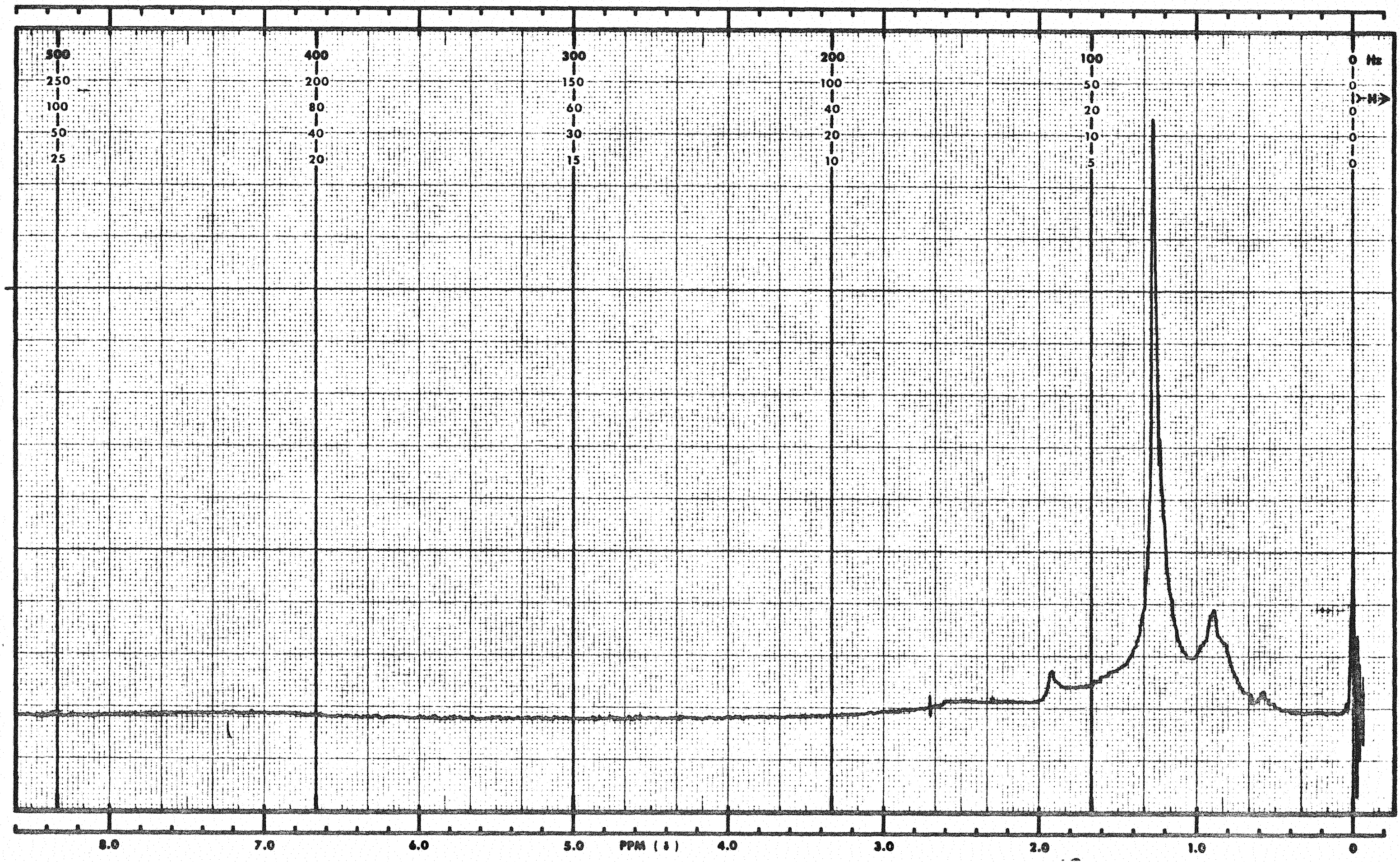
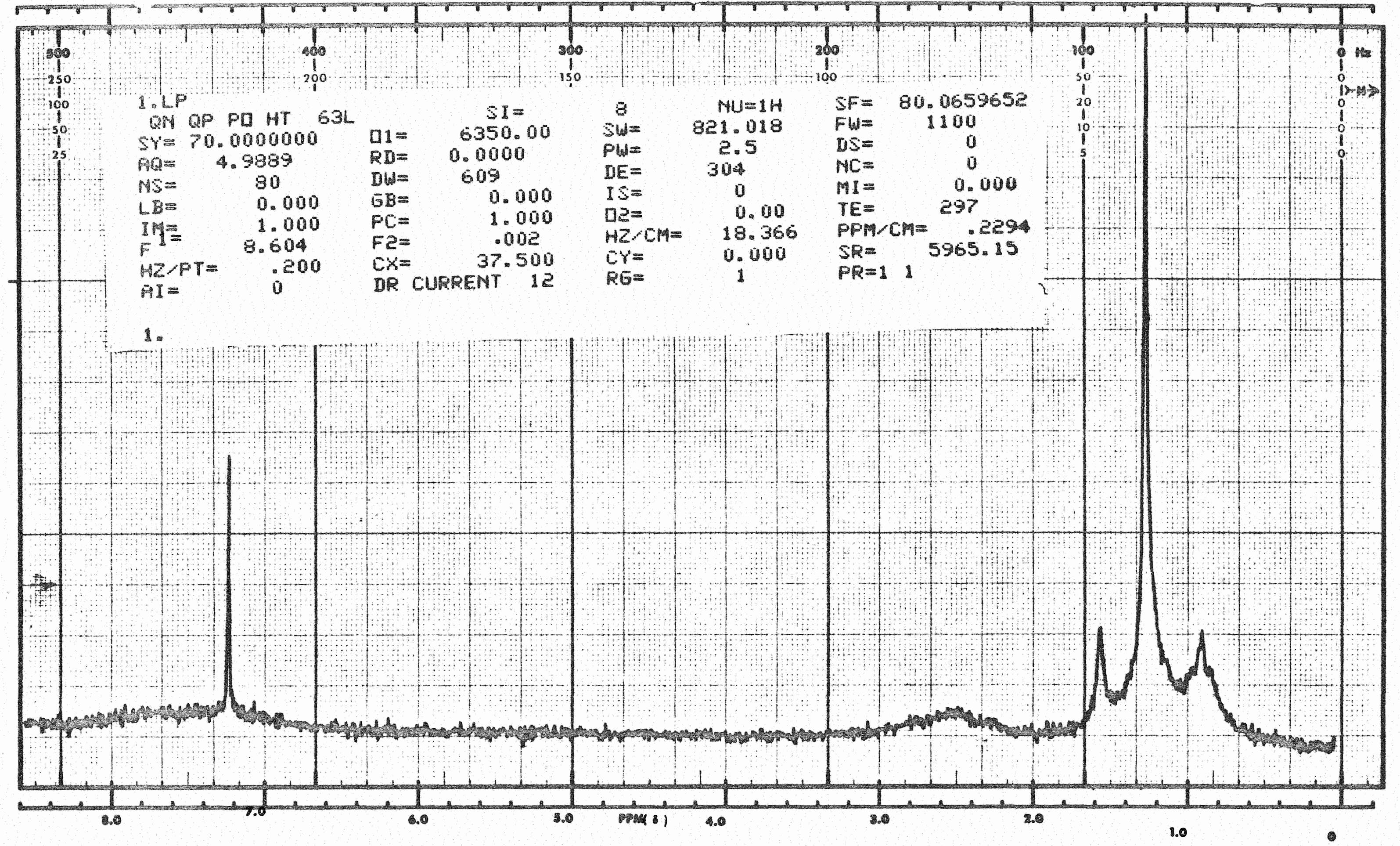


Figure 10. Nuclear Magnetic Resonance Spectrum of CDA-62 reaction of coal with commercial AC-3 asphalt and hydrogen gas at 350°C for 4 hours. (15% in $CDCl_3$; peak at 7.2δ is $CHCl_3$ in $CDCl_3$.)



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AQ=    4.9889       RD=    0.0000     PW=       2.5       DS=        0
NS=        80       DW=      609      DE=      304        NC=        0
LB=     0.000       GB=        0.000  IS=        0        MI=        0.000
IM=     1.000       PC=        1.000  D2=        0.00     TE=      297
F1=    8.604        F2=        .002   HZ/CM=    18.366    PPM/CM=    .2294
HZ/PT=     .200     CX=       37.500  CY=       0.000     SR=     5965.15
AI=        0        DR CURRENT   12   RG=        1        PR=1  1

1.
```
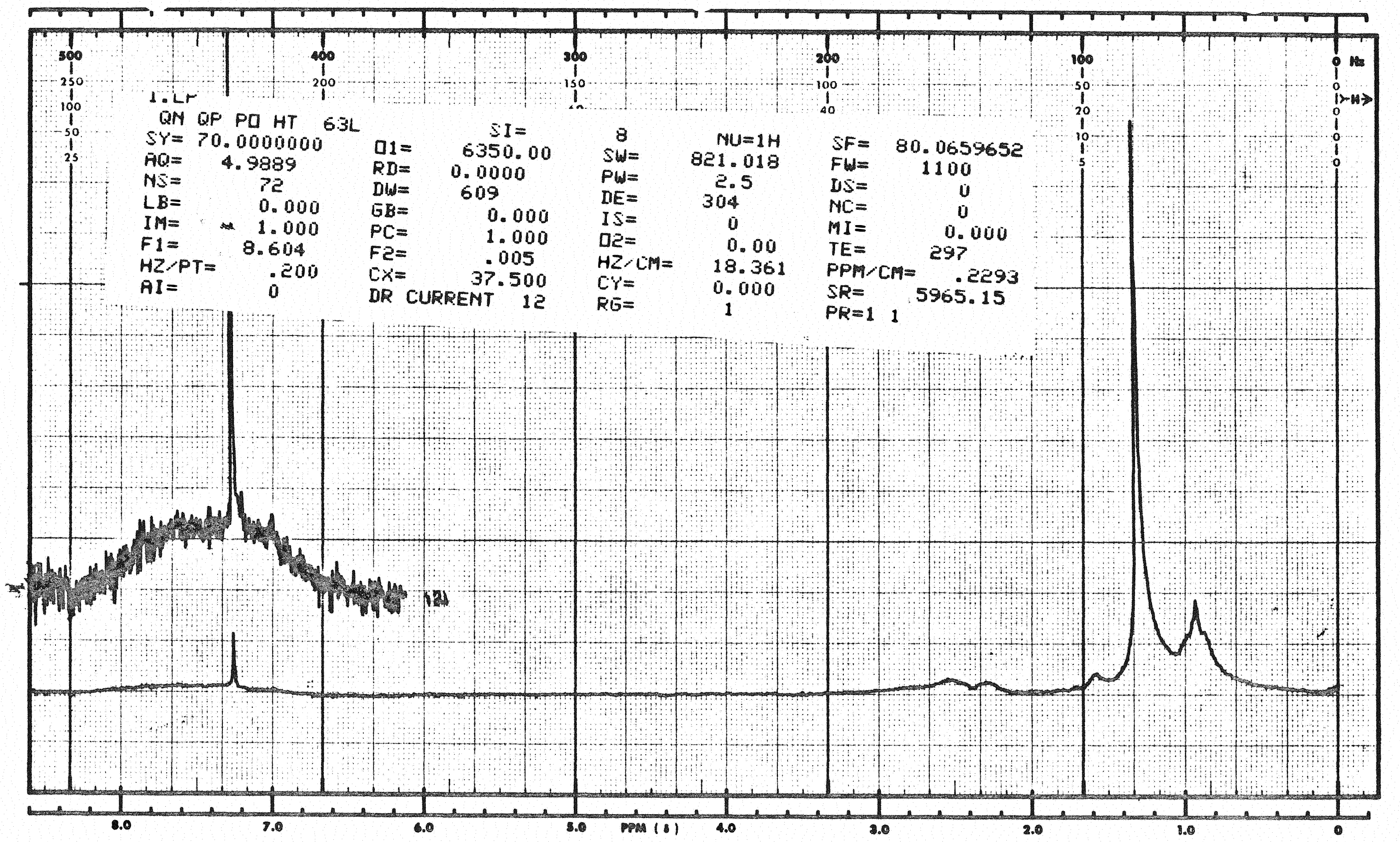

Figure 11. Nuclear Magnetic Resonance Spectrum of CDA-67 reaction of coal with commercial AC-3 asphalt and hydrogen gas at 400°C for 4 hours. (15% in $CDCl_3$; peak at 7.2δ is $CHCl_3$ in $CDCl_3$.)



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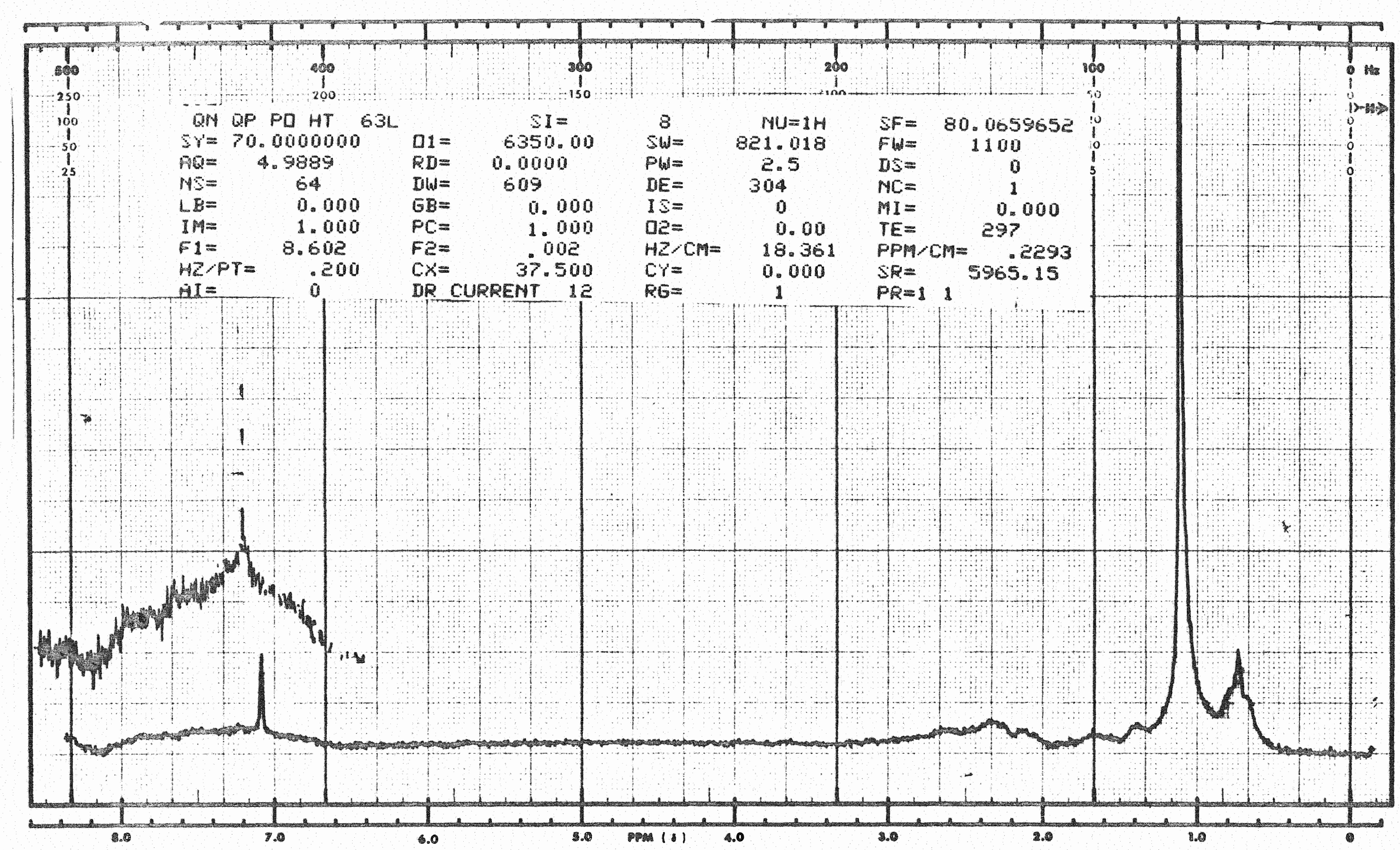
AQ=     4.9889     O1=      6350.00   SW=        NU=1H      SF=  80.0659652
NS=         72     RD=    0.0000      PW=      821.018      FW=      1100
LB=      0.000     DW=      609       DE=          2.5      DS=         0
IM=      1.000     GB=        0.000   IS=        304        NC=         0
F1=     8.604      PC=        1.000   O2=          0        MI=     0.000
HZ/PT=    .200     F2=         .005   HZ/CM=       0.00     TE=       297
AI=         0      CX=       37.500   CY=       18.361      PPM/CM=   .2293
                   DR CURRENT   12    RG=        0.000      SR=    5965.15
                                                 1          PR=1  1
```

Figure 12. Nuclear Magnetic Resonance Spectrum of CDA-68 reaction of coal with commercial AC-3 asphalt and hydrogen gas at 400°C for 18 hours. (15% in $CDCl_3$; peak at 7.2δ is $CHCl_3$ in $CDCl_3$.)



```
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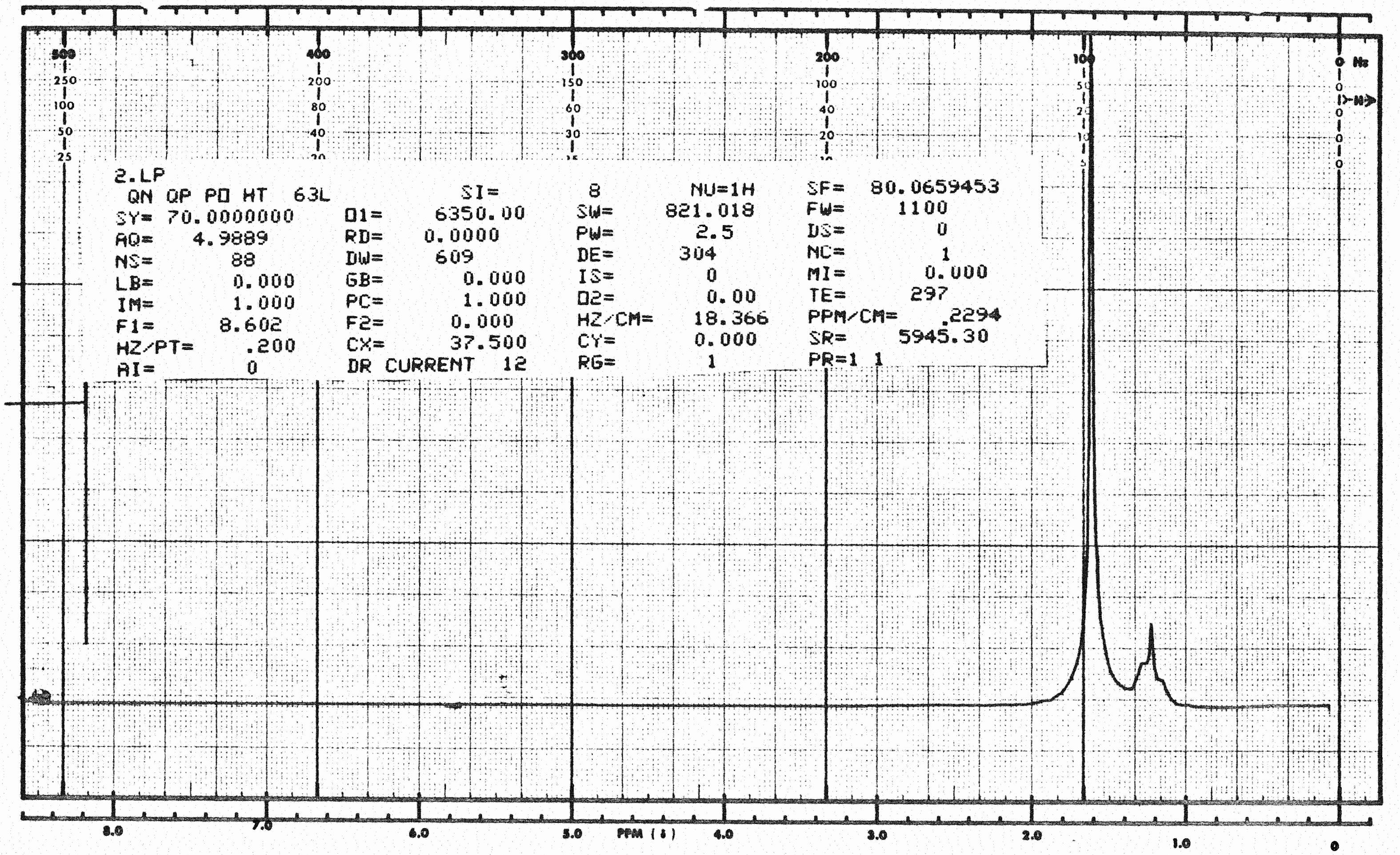
AQ=    4.9889      RD=     0.0000       PW=       2.5         DS=          0
NS=        64      DW=     609          DE=      304          NC=          1
LB=     0.000      GB=        0.000     IS=        0          MI=      0.000
IM=     1.000      PC=        1.000     D2=        0.00       TE=       297
F1=     8.602      F2=        .002      HZ/CM=   18.361       PPM/CM=   .2293
HZ/PT=   .200      CX=       37.500     CY=       0.000       SR=    5965.15
AI=         0      DR CURRENT   12      RG=        1          PR=1  1
```

Figure 13. Nuclear Magnetic Resonance Spectrum of CDA-69 reaction of coal with commercial AC-3 asphalt and hydrogen gas at 400°C for 30 hours. (15% in $CDCl_3$; peak at 7.2δ is $CHCl_3$ in $CDCl_3$.)



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AQ=    4.9889     RD=    0.0000     PW=        2.5       DS=        0
NS=        88     DW=     609       DE=       304        NC=          1
LB=     0.000     GB=       0.000   IS=          0       MI=        0.000
IM=     1.000     PC=       1.000   D2=         0.00     TE=      297
F1=    8.602      F2=      0.000    HZ/CM=    18.366     PPM/CM=    .2294
HZ/PT=    .200    CX=      37.500   CY=       0.000      SR=    5945.30
AI=        0      DR CURRENT  12    RG=          1       PR=1 1
```

Figure 14. Nuclear Magnetic Resonance Spectrum of CDA-20 reaction of animal fat and hydrogen at 250°C for 65 hours. (15% in $CDCl_3$; peak at 7.2δ is $CHCl_3$ in $CDCl_3$.)

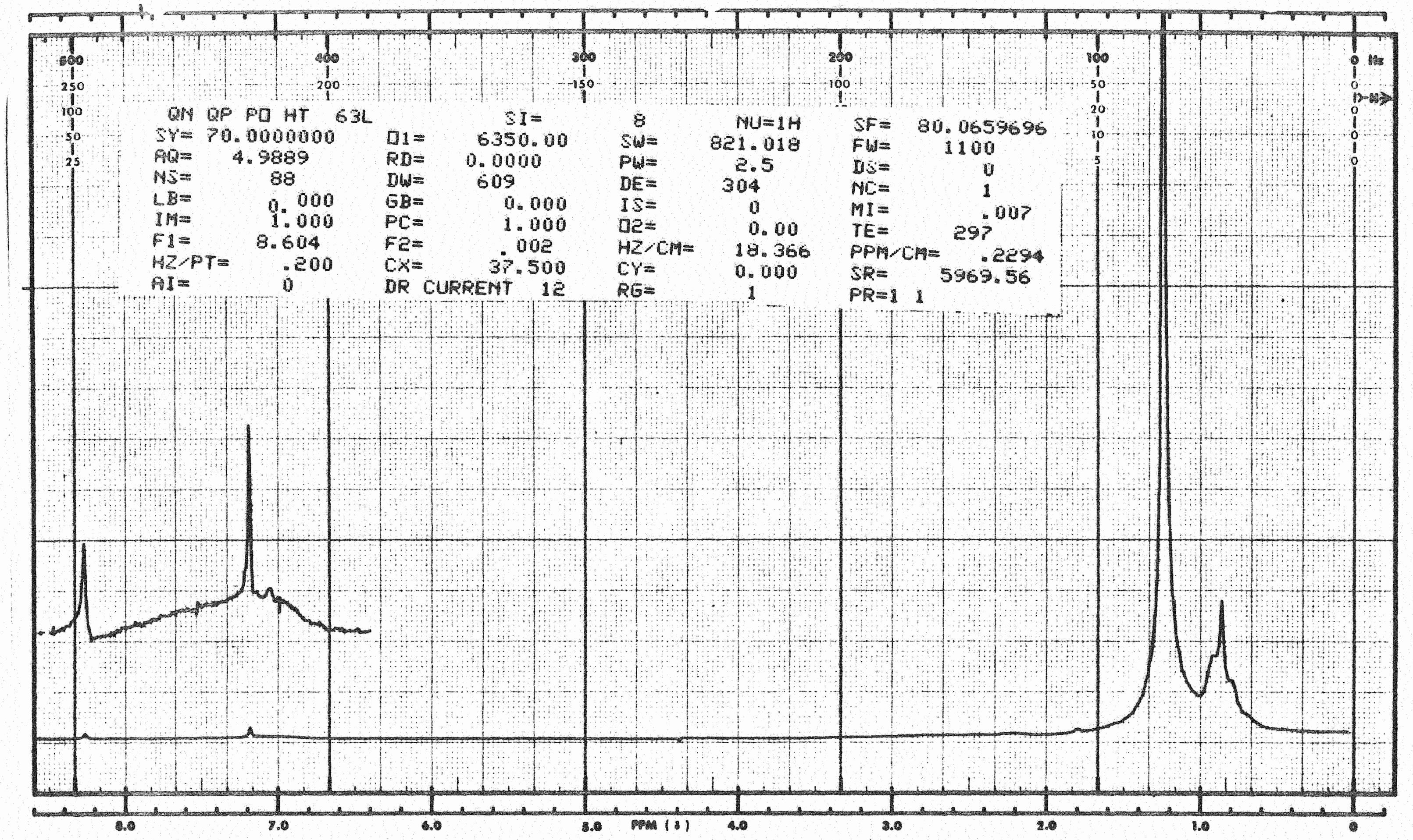
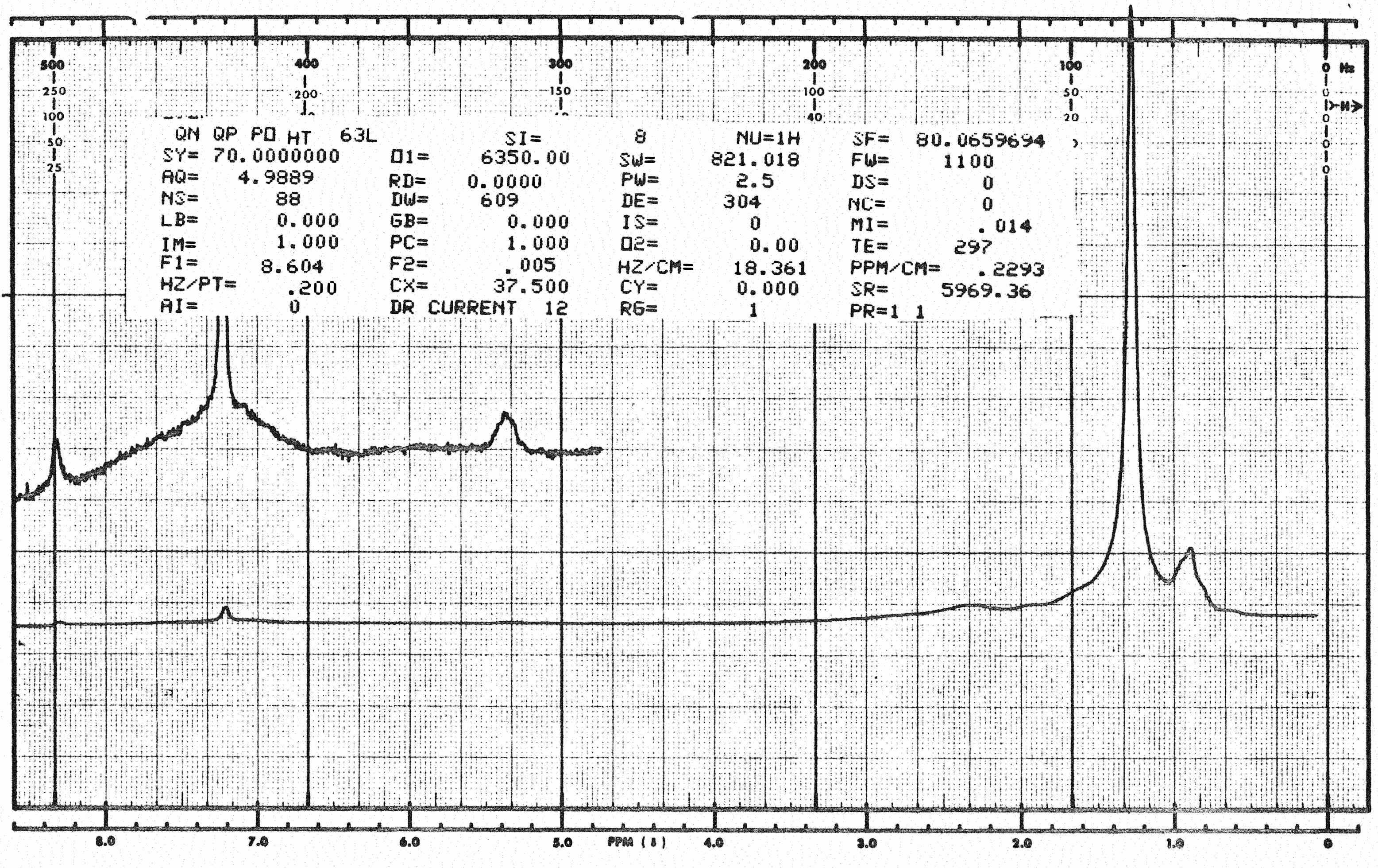


Figure 15. Nuclear Magnetic Resonance Spectrum of CDA-21 reaction of coal with animal fat and hydrogen gas at 300°C for 60 hours. (15% in $CDCl_3$; peak at 7.2δ is $CHCl_3$ in $CDCl_3$.)



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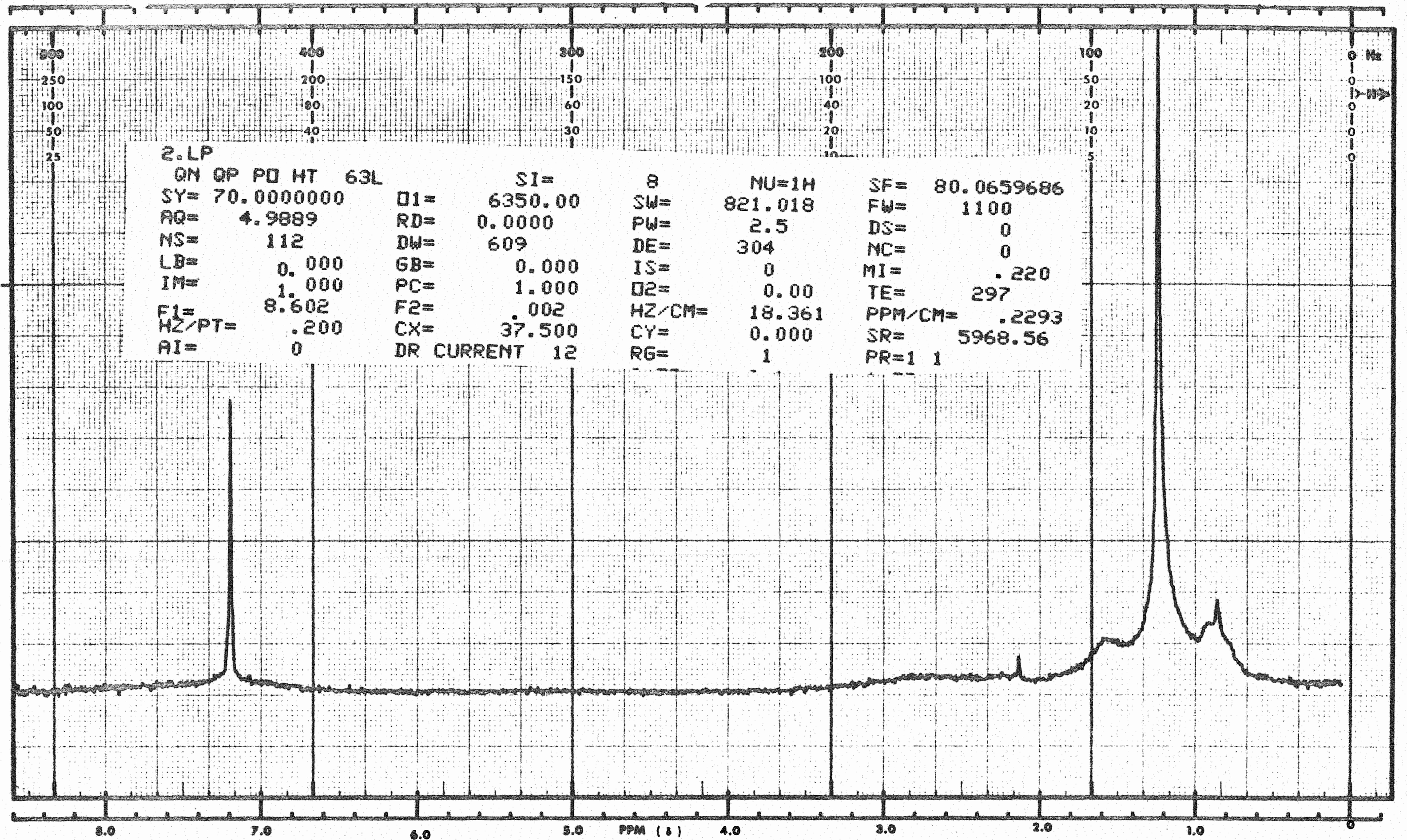
AQ=    4.9889     RD=    0.0000      PW=       2.5          DS=         0
NS=       88      DW=      609       DE=      304           NC=         0
LB=      0.000    GB=        0.000   IS=        0           MI=        .014
IM=      1.000    PC=        1.000   O2=        0.00        TE=      297
F1=    8.604      F2=        .005    HZ/CM=   18.361        PPM/CM=   .2293
HZ/PT=    .200    CX=       37.500   CY=      0.000         SR=     5969.36
AI=        0      DR CURRENT   12    RG=        1           PR=1  1
```

Figure 16. Nuclear Magnetic Resonance Spectrum of CDA-22 reaction of coal with animal fat and hydrogen gas at 300°C for 90 hours. (15% in $CDCl_3$; peak at 7.2δ is $CHCl_3$ in $CDCl_3$.)



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AQ=   4.9889        RD=    0.0000      PW=      2.5        DS=       0
NS=     112         DW=     609        DE=     304         NC=       0
LB=       0. 000    GB=       0.000    IS=       0         MI=        . 220
IM=       1. 000    PC=       1.000    D2=       0.00      TE=     297
F1=     8.602       F2=        . 002   HZ/CM=   18.361     PPM/CM=    .2293
HZ/PT=     .200     CX=      37.500    CY=      0.000      SR=    5968.56
AI=        0        DR CURRENT  12     RG=       1         PR=1 1
```
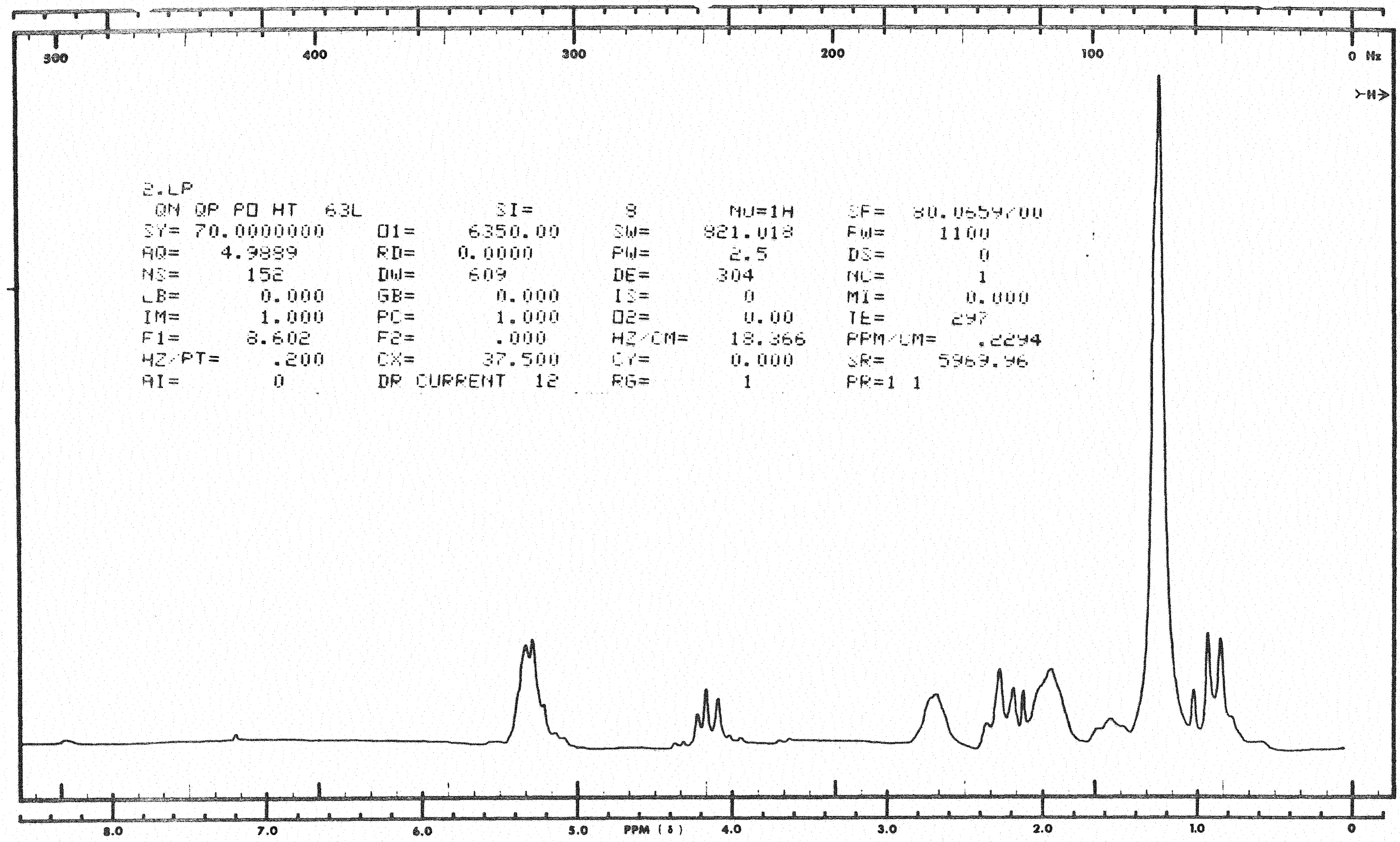

Figure 17. Nuclear Magnetic Resonance Spectrum of CDA-23 reaction of coal with animal fat and hydrogen gas at 300°C for 95 hours. (15% in $CDCl_3$; peak at 7.2δ is $CHCl_3$ in $CDCl_3$.)

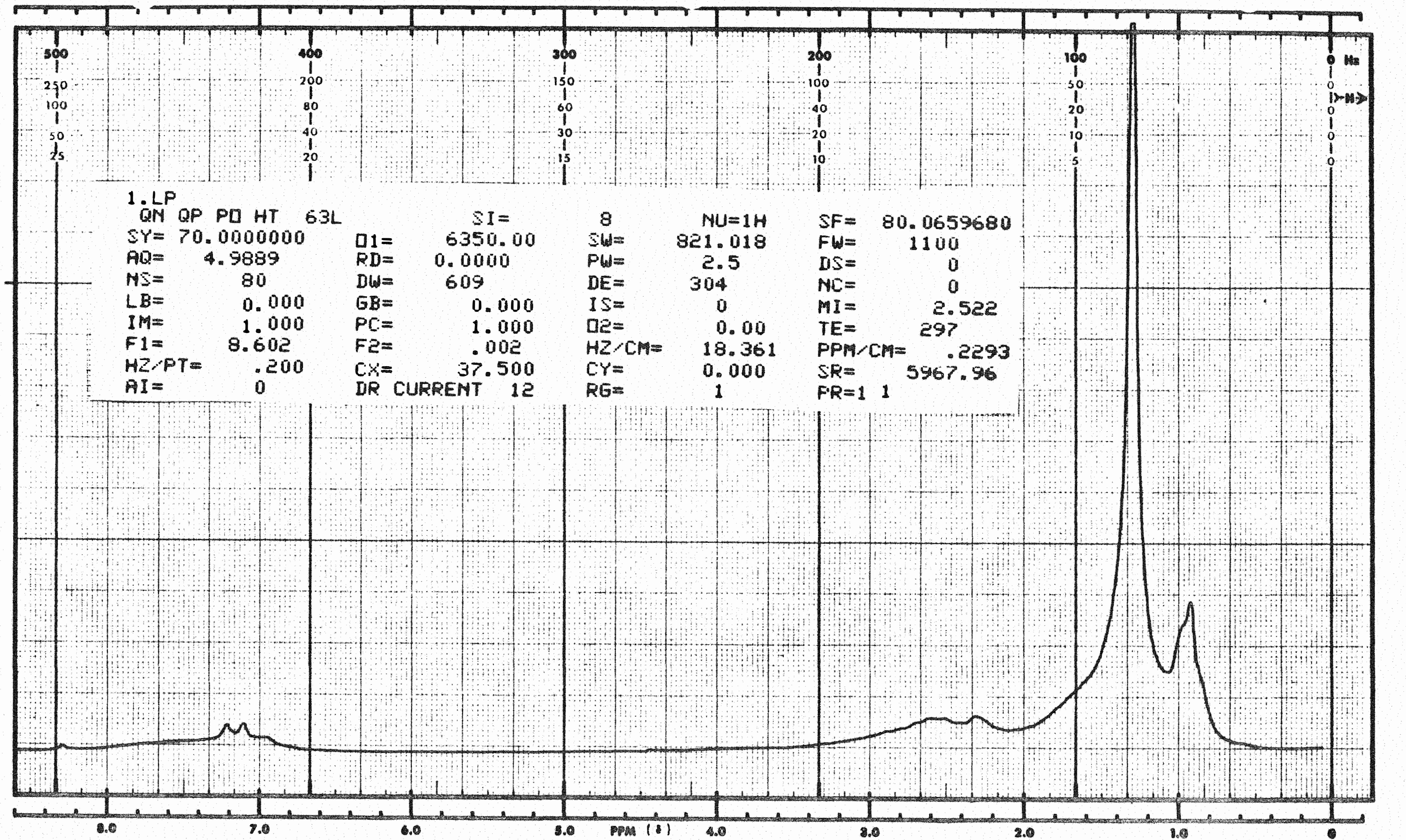
The product from the linseed oil effort has a nuclear magnetic resonance spectrum much like that of AC-3 (c.f. Figures 4, 18, and 19); however, the complex nature of the linseed oil is apparent (2-3δ).

Extensive ^{13}C nuclear magnetic resonance studies which were not a part of this effort are now underway to better describe the carbon environments in the synthetic asphalts.



```
2.LP
 QN QP PD HT  63L          SI=         8        NU=1H        SF=  80.0659700
SY= 70.0000000     O1=     6350.00     SW=     821.018      FW=     1100
AQ=   4.9889       RD=    0.0000       PW=       2.5        DS=        0
NS=      152       DW=     609         DE=      304         NC=        1
LB=      0.000     GB=        0.000    IS=        0         MI=       0.000
IM=      1.000     PC=        1.000    D2=        0.00      TE=      297
F1=      8.602     F2=         .000    HZ/CM=    18.366     PPM/CM=    .2294
HZ/PT=    .200     CX=       37.500    CY=        0.000     SR=     5969.96
AI=        0       DR CURRENT   12     RG=        1         PR=1 1
```

Figure 18. Nuclear Magnetic Resonance Spectrum of CDA-40 reaction of linseed oil and hydrogen gas at 250°C for 90 hours. (15% in $CDCl_3$; peak at 7.2δ is $CHCl_3$ in $CDCl_3$.)



```
1.LP
 QN QP PO HT  63L           SI=       8        NU=1H      SF=  80.0659680
SY= 70.0000000   O1=     6350.00   SW=     821.018   FW=     1100
AQ=    4.9889    RD=    0.0000     PW=      2.5      DS=       0
NS=       80     DW=     609       DE=     304       NC=       0
LB=      0.000   GB=        0.000  IS=       0       MI=       2.522
IM=      1.000   PC=        1.000  O2=        0.00   TE=     297
F1=     8.602    F2=         .002  HZ/CM=   18.361   PPM/CM=    .2293
HZ/PT=    .200   CX=       37.500  CY=       0.000   SR=     5967.96
AI=       0      DR CURRENT   12   RG=       1       PR=1  1
```

Figure 19. Nuclear Magnetic Resonance Spectrum of CDA-42 reaction of coal with linseed oil and hydrogen gas at 260°C for 94 hours. (15% in $CDCl_3$; peak at 7.2δ is $CHCl_3$ in $CDCl_3$.)

6. Infrared Spectra

Infrared spectra were recorded for all of the samples noted in Figures 4-19; however, only selected spectra are presented here, since within a series, they are similar. Figure 20 is of AC-3. The particular sample shows some oxidation; however, the scan is typical. Infrared spectra are excellent for fingerprinting or for making broad generalizations about complex mixtures; however, due to the different extinction coefficients of functional groups and of molecular substances one must be very careful not to overinterpret the data. All of the infrared spectra (Figures 20-24) are reasonable for asphalt; however, the nuclear magnetic resonance spectra and solubility profiles (Section E) clearly show that these materials are not road asphalt. The importance of using several techniques to characterize materials is clearly illustrated in this effort.

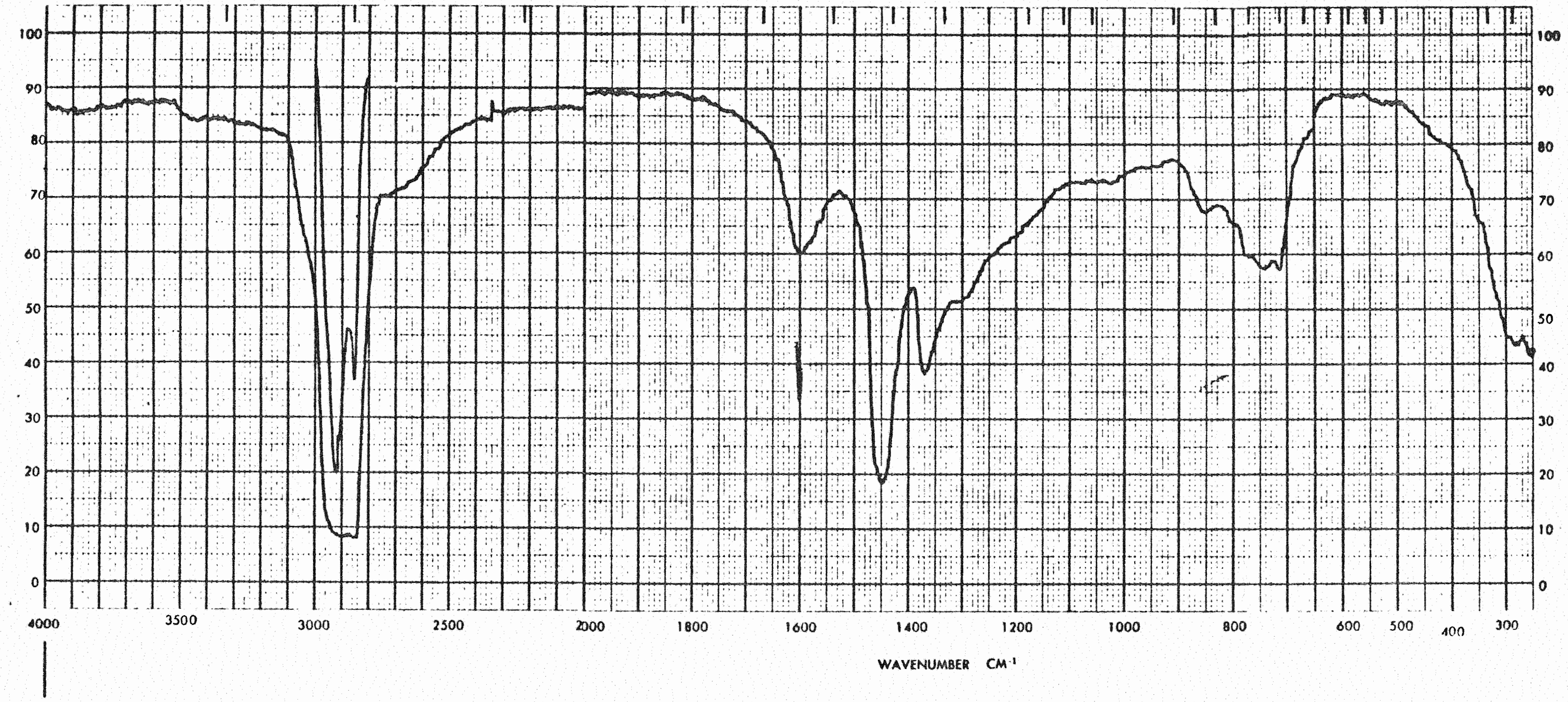


Figure 20. Infrared Spectrum of commercial AC-3 asphalt (Thin film, KBr disk)

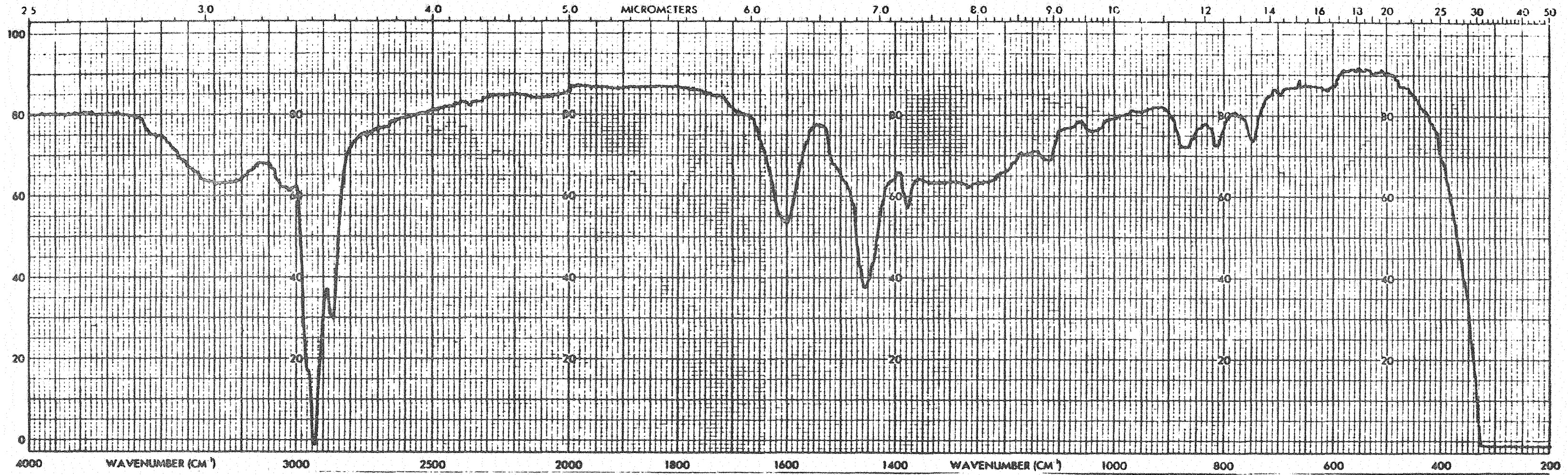


Figure 21. Infrared Spectrum of CDA-2 reaction of coal with hydrogen gas at 250°C for 60 hours. (Thin film, KBr disk)

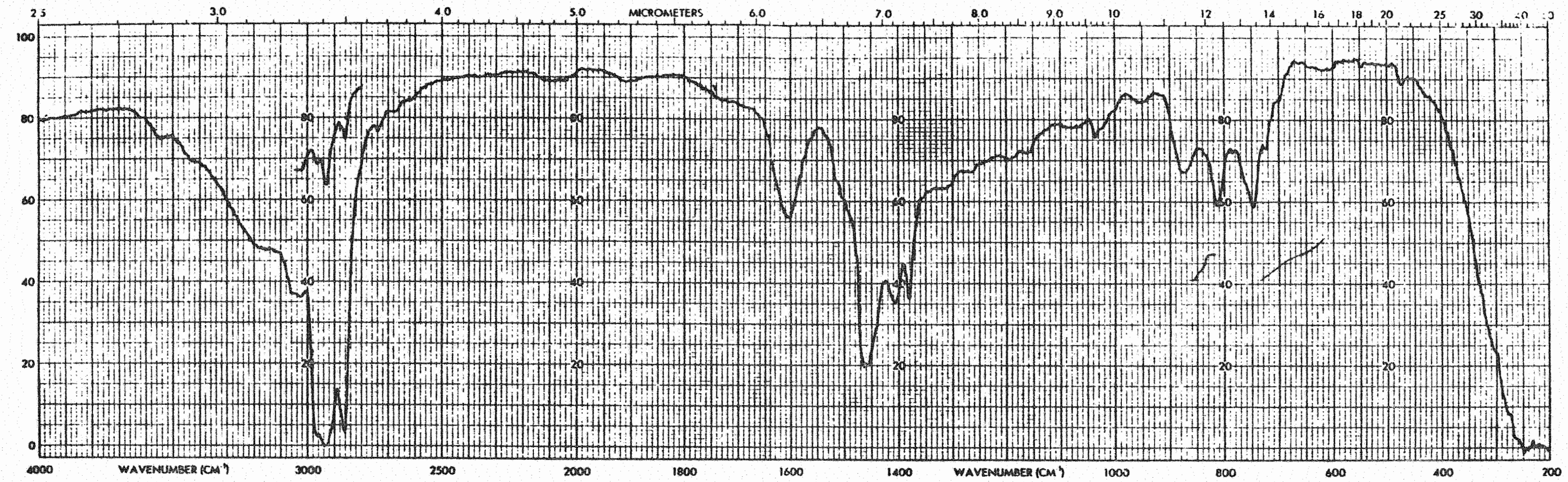


Figure 22. Infrared Analysis of CDA-67 reaction of coal with commercial AC-3 asphalt and hydrogen gas at 400°C for 4 hours. (Thin film, KBr disk)

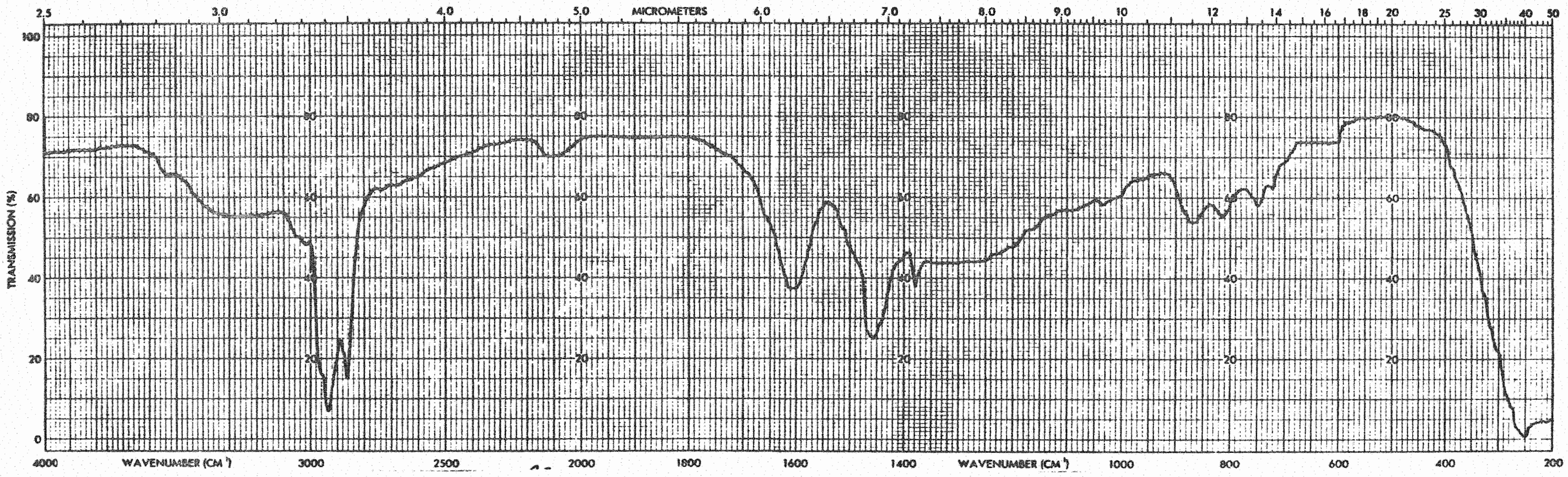


Figure 23. Infrared Analysis of CDA-23 reaction of coal with animal fat and hydrogen gas at 300°C for 95 hours. (Thin film, KBr disk)

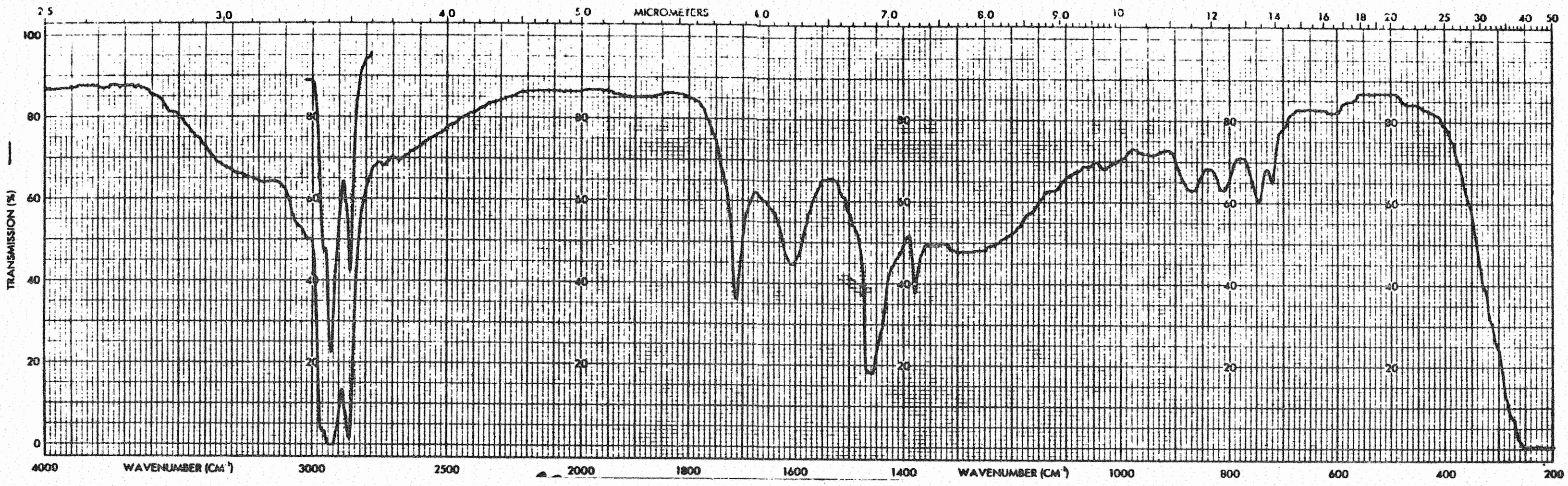


Figure 24. Infrared Analysis of CDA-42 reaction of coal with linseed oil and hydrogen gas at 260°C for 94 hours. (Thin film, KBr disk)

E. Solubility and Compatibility

1. Introduction

Whether one works with a synthetic asphalt or with a petroleum distillate one of the problems which must be addressed is that of mutual solubility or miscibility of the materials which are blended to form the roadway binder. The design of a suitable test procedure for developing a solubility profile of the bitumen material is therefore, of primary importance. The model described in this section appears to meet all of the required criteria for a solubility profile which will allow the prediction of mutual solubility.

A familiar application of modeling is drawing the best fitting line through data points to indicate a fundamental relationship between useful road life and traffic load. One would want a trend line or a mathematical model that would accurately describe data already collected with the objective of predicting the life or roads in use or yet to be be laid. If the line were drawn by means of an accepted statistical regression formula, one could not only be assured of obtaining the best possible fit of that model to that particular set of data, but one could also obtain a number representing a statistical correlation of the data to the line or proposed trend. This correlation would indicate how close the relationship truly is, or how appropriate the proposed line. Fitting the data to a curved line, such as a logarithmic, or hyperbolic line may yield an improved correlation. On the other hand, a low correlation of the data to any proposed line may simply indicate inadequate data or the lack of a true relationship between the parameters in question. But in any case, the higher the correlation of the data to the model, the more assured one usually is that the model had predictive value.

It must be pointed out that such modeling does not necessarily show the dependency of one parameter on the other. It only shows that there is a relationship in the way the parameters vary together. The parameters may vary according to a different controlling parameter.

During the course of the project, a mathematical model has been developed that appears to accurately describe some relationships between solubility, compatibility, and possibly, performance of asphaltic materials.

The model consistently has a very high statistical correlation with large amounts of data. This high correlation indicates that the model is descriptive and predictive, given our current level of understanding. Fortunately, the model is also intuitively sensible. It may be some time, however, before solubility theory can fully explain the reasons for the relationships suggested by the model.

2. The Hildebrand Solubility Parameter

Asphalt is a homogenous, self-compatible mixture consisting of a variety of molecular species that are mutually dissolved or dispersed. It has long been known that a rule-of-thumb in predicting the compatibility of mixtures is the maxim, *similia similibus solvuntur*, or, "like dissolves like." A freer translation states that a compound is most readily dissolved in a substance that is similar to it. The thrust of solubility and compatibility theory has been to determine the factors that affect compatibility and to quantify those parameters.

One of the early attempts to quantify solubility characteristics was proposed by Hildebrand and involves the use of indices called Solubility Parameters (71). It has been shown that the solubility characteristics of a substance are closely related to its energy of vaporization. Hildebrand showed that solubility characteristics are best related to a parameter which is the square root of the energy of vaporization per cubic centimeter. This is also the square root of the cohesive energy density, or the square root of the internal pressure. This solubility parameter is unique for a given substance and is easily determined experimentally. Hildebrand chose the designation δ to represent the solubility parameter but since there are several scales for the solubility parameter, all of which are designated by the symbol δ, and also the use of δ as a mathematical operation; SP will be used in this discussion in order to avoid confusion later.

The range of solubility parameters for most organic compounds is from around 6.5 to about 14.0 (the units use $cal^{1/2}\ cm^{-3/2}$, called the "Hildebrand;" however, they are often omitted). Within certain constraints, substances whose parameters are numerically the same or only slightly different are more miscible than substances whose parameters are grossly different. As a rule, solvents whose solubility parameters differ by no more than two units ($|SP_1 - SP_2|$ is less than 2), are miscible in all proportions. A larger difference is predictive of immiscibility or incompatibility.

The solubility parameters of pure substances such as the common organic solvents are fairly easily calculated from published empirical data (72,73,74). The solubility parameters for more complex or more exotic substances are usually determined by comparisons to the simpler, more common ones. For example, a frequently used method for determining the solubility parameter of a complex substance, such as a high polymer, is to determine its solubility in a number of solvents with known parameters, obtaining a solubility profile, as depicted in Figure 25. The effective SP of the substance is the median of the solubility distribution, or usually, median SP's of those compounds in which it is extremely soluble. The effective SP for the hypothetical substance in figure 25 is about 9.5. The effective solubility parameter could also be thought of as the "center of solubility" for the substance.

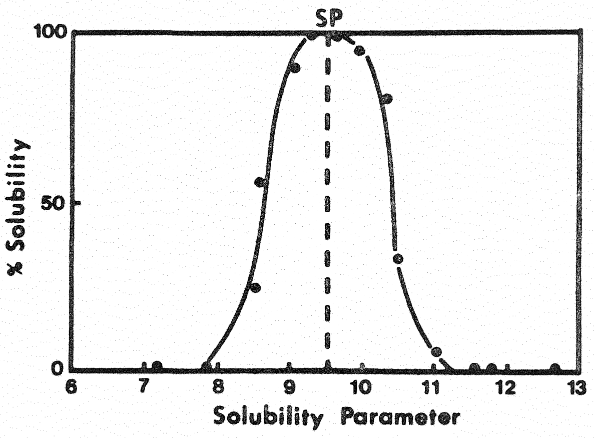


Figure 25: Typical Profile Using the Hildebrand Parameter

It follows, then, that two substances A and D whose solubility profiles are related to each other as in Figure 26a should be immiscible.

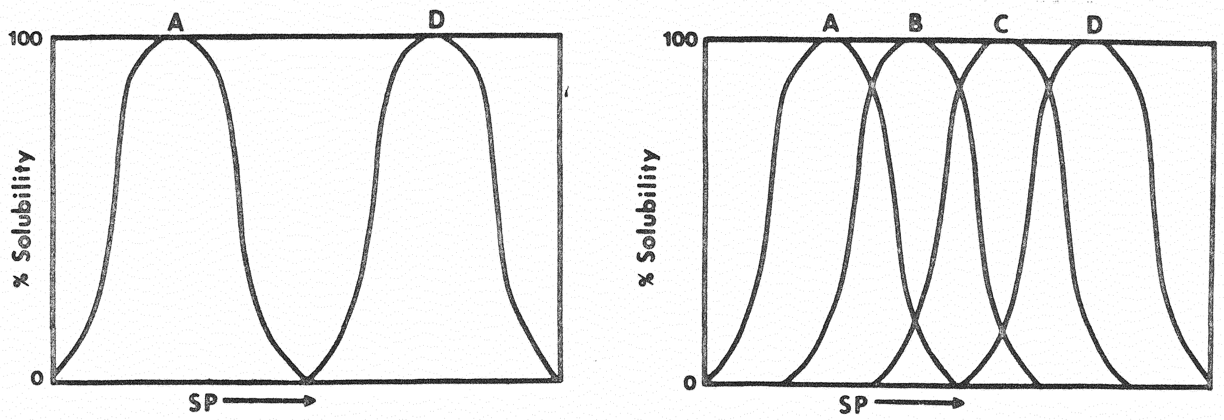


Figure 26a

Figure 26b

Figure 26: Relationship Between SP and Compatibility

However, a mixture containing compounds A,B,C, and D that are related as in Figure 26b should be homogenous and phase stable if mixed in the proper proportions. Although A and D differ considerably in SP and solubility profile, the four compounds together constitute a chain of compatibility, each substance being miscible with its neighboring subtance. Substances B and C. then, could act as emulsifying agents for dispersing A into D, in a fashion similar to the emulsifying action of soap with oil and water.

As has been well established by many groups studying compatibility of various fractional components of asphalt, individual components appear to be related to one another in much the same way as compounds A, B. C. and D. When various fractions are isolated and mixed with other isolated fractions, some combinations are quite incompatible. But when taken as a group, as in whole asphalt, they form an homogenous mixture.

There is another observation that can be advanced from the Solubility Parameter theory. If the fractional components of asphalt (or, by analogy, compounds A,B,C, and D) were mixed and treated as a single substance in determining the solubility profile, a profile such as the one shown in Figure 27 would be expected. The region of 100 percent solubility would be much broader and the SP or center of solubility less definite. This is precisely the type of profile exhibited by whole asphalt.

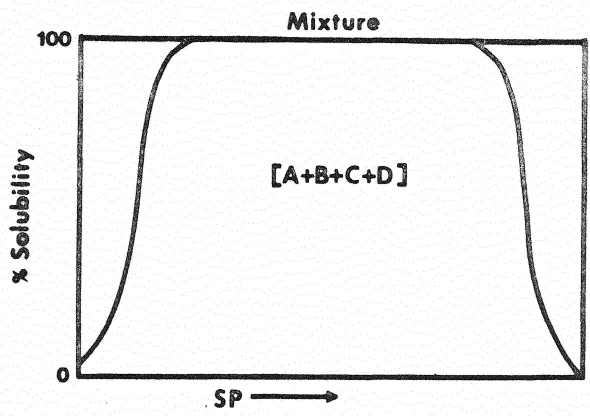


Figure 27: Profile of a Complex Mixture

3. Theory vs. Application

Although the Hildebrand solubility parameter is useful in predicting the compatibility of many mixtures, it was also true that there were in practice many departures from the theory. Taking into account only the SP, there are many compatible mixtures that should be incompatible, and vice versa. There are also factors, such as chemical reactions, which are not accounted for by the SP.

It was recognized by Hildebrand and others that the observed energy of vaporization is the result of a number of contributing factors, each of which has an individual effect on solubility. These contributing factors include, but are not limited to: molecular vibrational and rotational energies, dipole vector quantities, and hydrogen bonding parameters. One or more of these factors may be disproportionately large or small and may have a great bearing on the solubility of a compound, while making only a small contribution to the magniture of SP. Therefore, as might be expected, the Hildebrand solubility parameter is of most value when applied to groups of substances that are similar in the factors contributing to SP.

Ironically, these are the groups which can usually be assumed, from general experience, to be most similar, and therefore, most likely to be compatible. One is left, in many cases, with little advantage over the alchemist who stated that "like dissolves like." A good example of how simple SP theory often relies heavily on common sense is that of the solubility of asphalt in acetone. The SP of acetone is about 9.7. This is well inside the predicted range of 100 percent solubility of asphalt. However, asphalt is not very soluble in acetone, since asphalt is a relatively non-polar mixture, while acetone is relatively polar. Since the Hildebrand SP does not directly differentiate on the basis of the polarity of substances, it is apparent why, in this case, SP is not very predictive of compatibility.

4. Use of Expanded Concepts of Solubility in Asphalt Technology

Most of the refinements of the SP concept have been methods of describing substances in terms of multiple parameters rather than the SP alone. The parameters used are, by and large, varying mathematical arrangements of those parameters that contribute to SP. One of the simplest and most useful methods of this type is that proposed by Bagley (72). It has been observed by Hildebrand and others that many of the deviations from the SP model are exhibited by compounds that tend to form hydrogen bonds or that are extremely polar. For this and other reasons, Bagley proposes that two parameters, δr and δV be defined, such that:

$$SP^2 = \delta r^2 + \delta V^2$$

Where δr is primarily the hydrogen bonding constituent of SP and δV includes the other constituent effects, of which molecular dipole effects are a prominent factor.

In Figure 28 a number of solvents have been placed on their δV, δr coordinates (73). As in the linear plot of SP, closeness is indicative of similarity and compatibility. In the SP plot, however, distance was defined as $[SP_2 - SP_1]$, whereas, in this system,

$$(\text{distance})^2 = (\delta V_1-\delta V_2)^2 + (\delta r_1-\delta r_2)^2.$$

This is mathematically more complicated, but much more precise in expressing the relationships between the solvents.

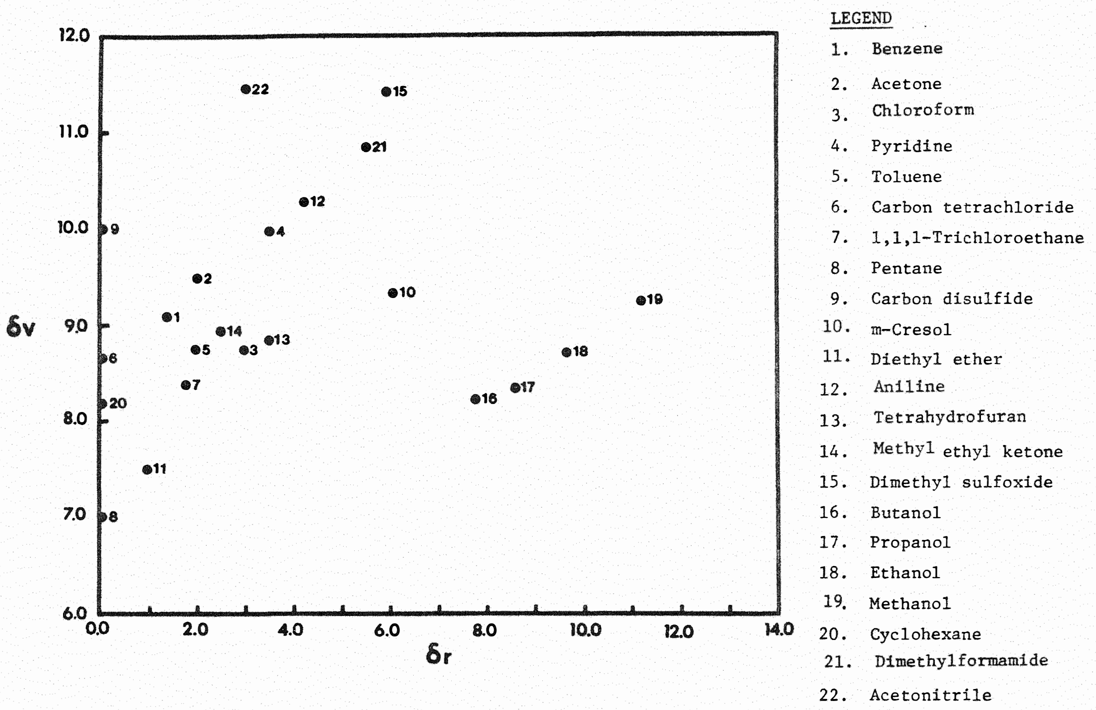
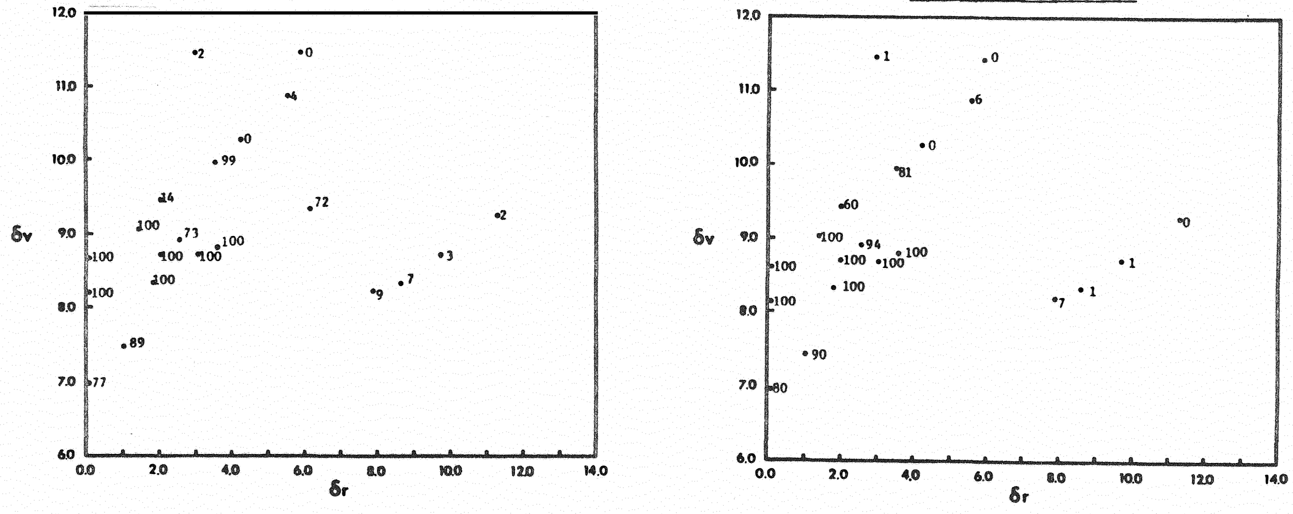


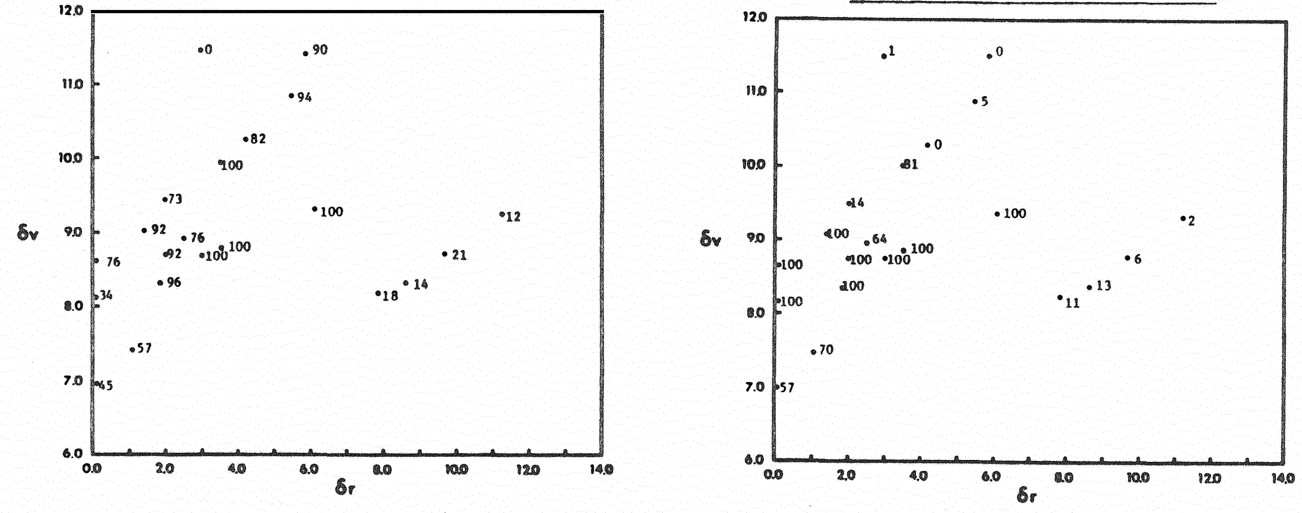
Figure 28: Solubility Relationships of Some Common Solvents

In the following set of figures, the solubility profiles of a number of asphaltic compounds are presented. This data in each profile was obtained by determining the percent solubility of the sample in each of the solvents mapped in Figure 28 according to ASTM 2042-76. Each percent solubility is, in turn, mapped according to the coordinates of the corresponding solvent.



29a ASPHALT - AC-3

29b ASPHALT - AC-4



29c HYDROGENATED COAL

29d STYRELf A - CORE SAMPLE

Figure 29: Solubility Maps of Three Asphalts and a Coal Derivative

In the above diagrams, areas or regions of high solubility are suggested. On closer inspection, one finds that a center of solubility is suggested, from which, as distance increases, solubility decreases. (The profile for hydrogenated coal has special features which will be discussed later.) The general pattern suggested is, in fact, nothing more than a three dimensional homology to the two dimensional Hildebrand solubility profile. The similarity is shown in Figure 30. The pattern suggested by the solubility diagrams in Figure 29 is similar to those depicted in Figure 30c. In three dimensions, the two dimensional Hildebrand distribution is analogous to a cone, which is, in turn, mapped as a family of circles on the δV vs. δr coordinates. One of the results of this project has been to define the general form of the cone mathematically, and then to fit that form to individual sets of data by regression analysis, thereby generating the best fitting regular solubility profile for each asphalt.

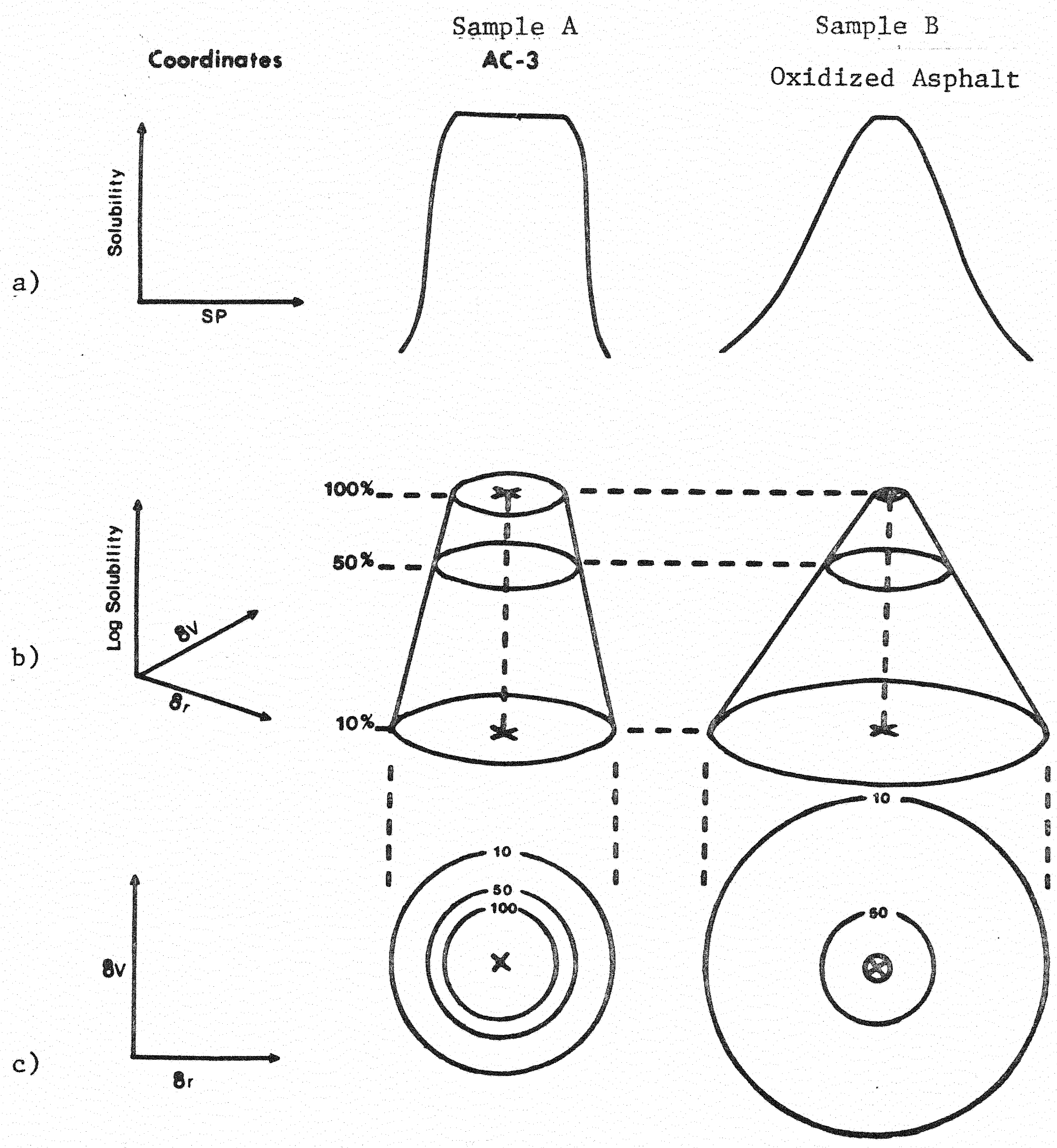


Figure 30: Relationship of the Complex Model to the Hildebrand Profile

The cone giving the best fit to the data is actually elliptical rather than circular. The equation is a variant of the general form for an elliptical cone, and is as follows:

$$[(\delta r - \delta rc)^2 + (\delta V - \delta Vc)^2]\ [\phi^2 \cos^2 (\psi - \theta) + \sin^2 (\psi - \theta)] - \left[\frac{(\ln Sol) - I}{m}\right]^2 = 0$$

where, Sol is the percent solubility of the sample in a given solvent; δr and δV are δr and δV of the solvent; δrc and δVc are δr and δV of the center of the ellipse; I is the ln on the solubility axis of the vertex of the cone; m is the slope of the sides of the cone; ϕ is an eccentricity constant (the eccentricity equals $\sqrt{1 - \phi^2}$); θ is the angle between the δr axis and the elliptic axis; and ψ is the angle, such that $\tan\psi = \dfrac{\delta V - \delta Vc}{\delta r - \delta rc}$.

The equation is a combination of the polar equation of an ellipse and the rectangular equation of a cone. The reason for choosing this form is that it can easily be written as a linear transformation as follows:

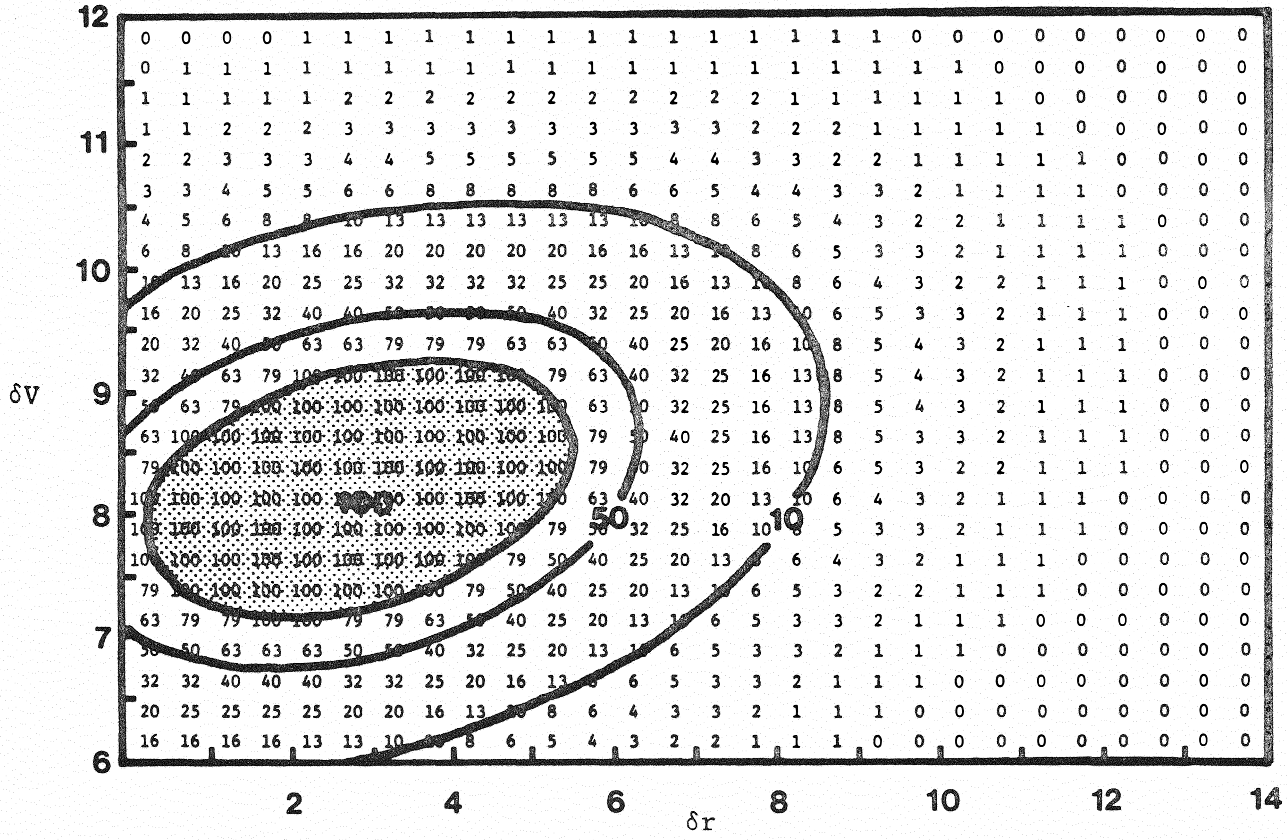
$$\ln Sol = m[(\delta r - \delta rc)^2 + (\delta V - \delta Vc)^2][\phi^2 \cos^2(\psi - \theta) + \sin^2(\psi - \theta)]^{1/2} + I$$

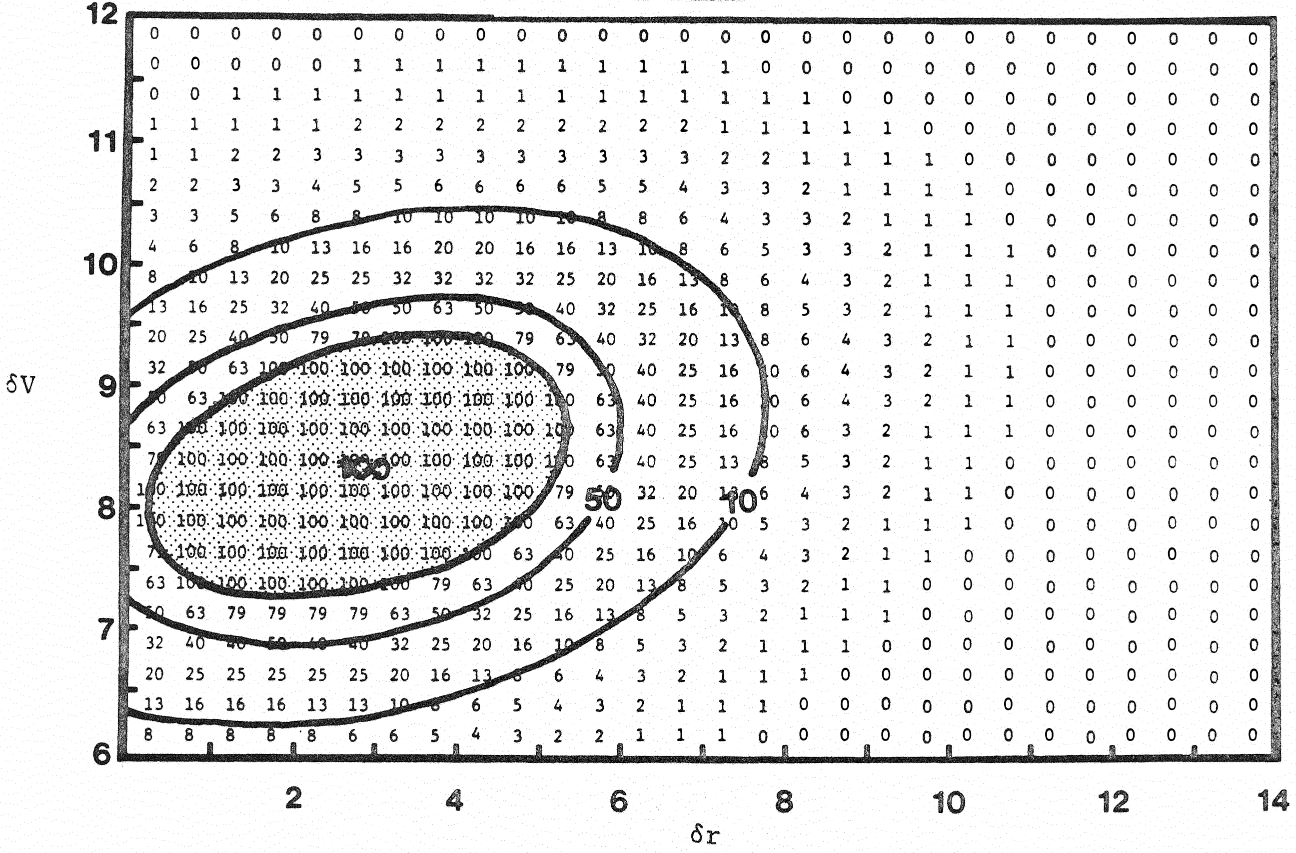
This equation is in the form: $y = mX + b$; the general form of a straight line.

There are six variables to be determined for each profile: δrc, δVc, θ, ϕ, m, and I. A simple computer or a programmable calculator can be used to determine δrc, δVc, θ, and ϕ by an iterative search. Linear regression in conjunction with the search can generate m, I, and the statistical correlation with the data. The iterative search is for the maximum correlation.

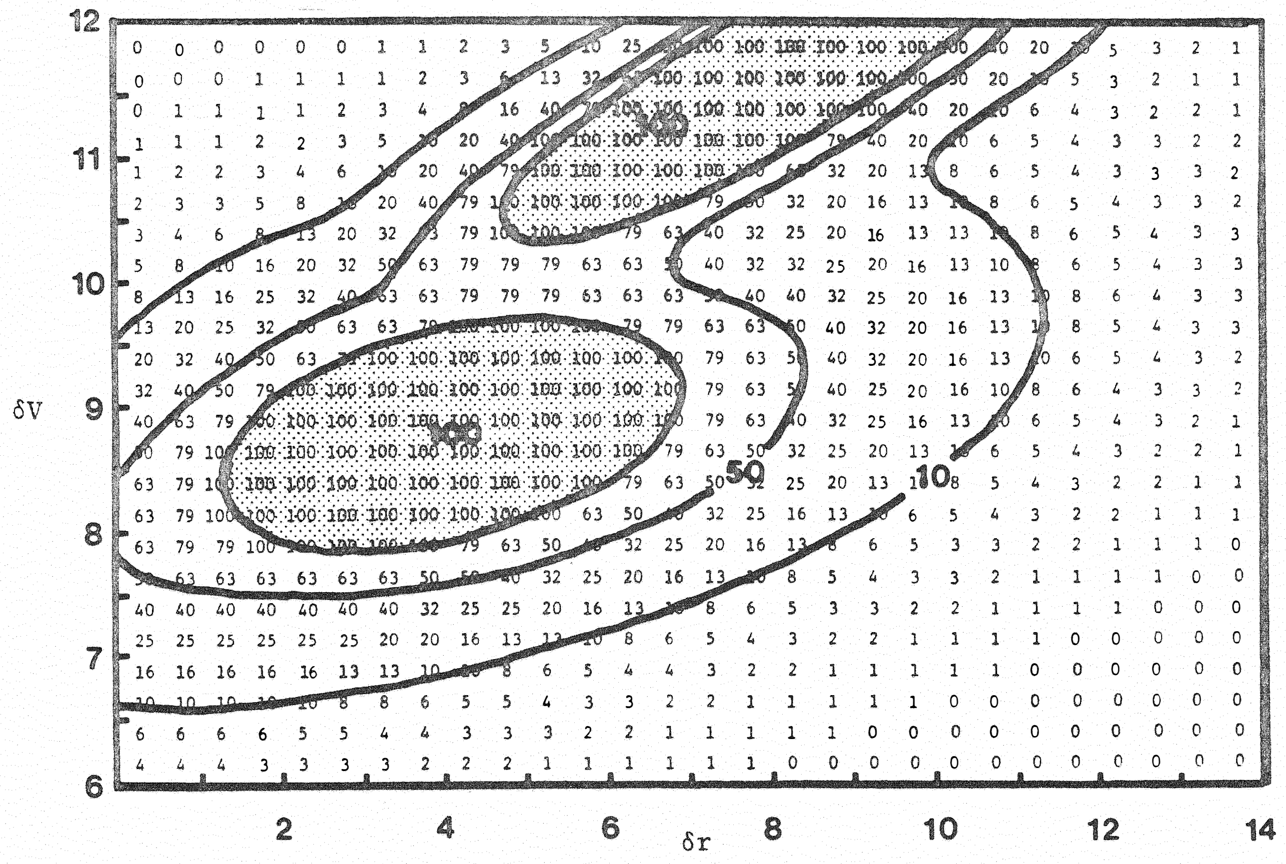
Figure 31 shows the regression-generated profiles of the samples presented in Figure 29. It should be noted that hydrogenated coal (Figures 29c and 31c) is best described in terms of two overlapping populations, rather than one. This model lends itself well to complicated analysis of that type. Furthermore, if two or more populations are known, or suspected to

Figure 31: Regression-generated Profiles

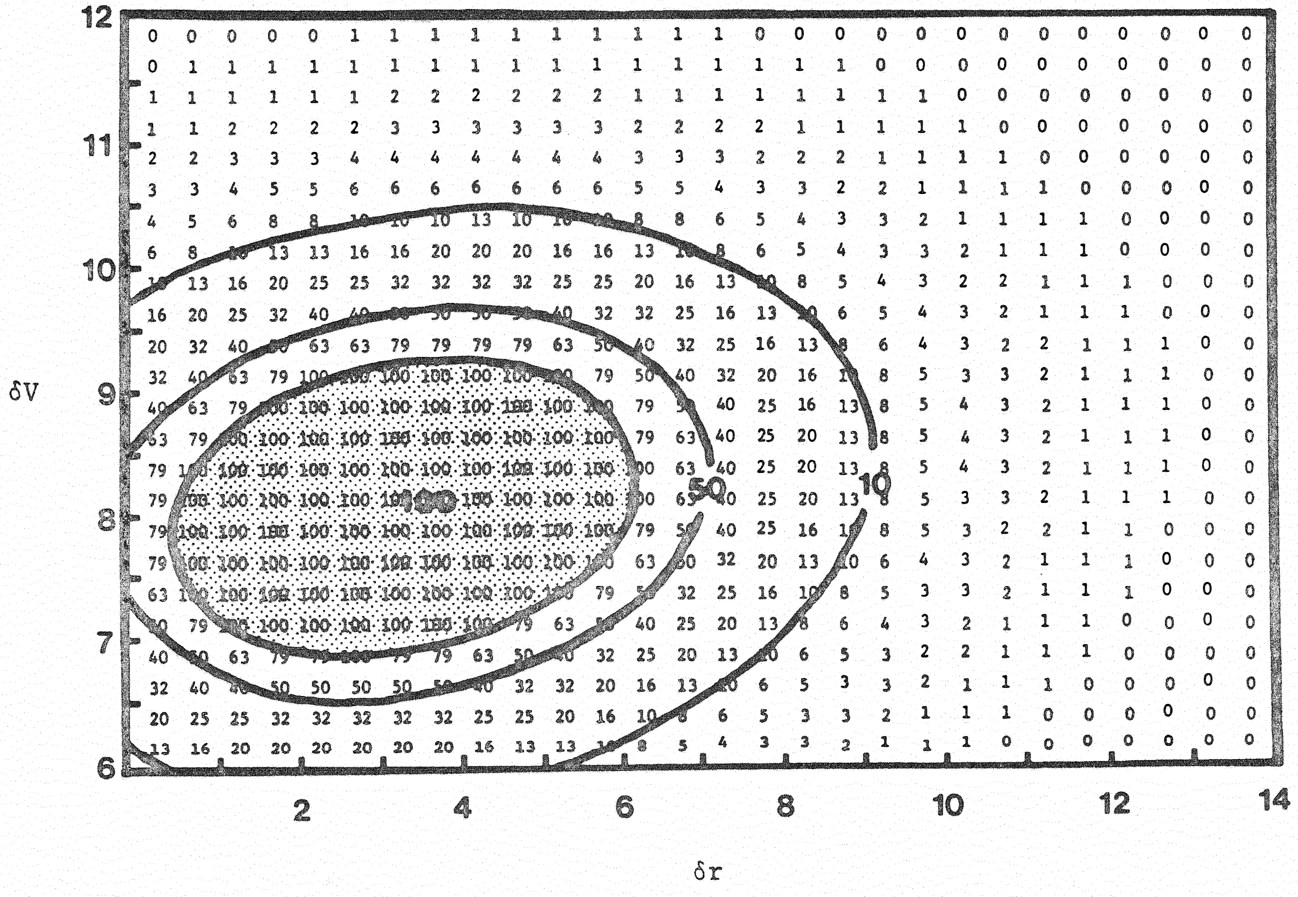

ASPHALT - AC-3


ASPHALT - AC-4

HYDROGENATED COAL - CS_2 SOLUBLE FRACTION



STYRELF A - CORE SAMPLE



be present (as in the case of asphalt with an additive) the profile of a known population can be mathematically subtracted out, and a regression performed on the remainder.

A minimum of six points describes the cone, just as a minimum of two points describes a straight line. The detail with which one wishes to map is theoretically limited only the the amount of well distributed solubility data collected.

5. Uses for Solubility Data

Such characterization of asphalt and asphalt-like materials has several advantages over other methods, and especially methods involving fractionation. Fractionation schemes are inherently non-commutative, that is, the way fractions are defined is very much dependent upon the order in which they are removed. For example, one may first remove the asphaltenes, then the resins, and then the oils, or first the asphaltenes, followed by the nitrogen bases, then the acidaffins, and so forth. However, a comparison of fractionation schemes reveals that changing the order of the fractionation can result in the reclassification of whole populations of molecules. If, for example, a molecule has both asphaltene and resin-like properties, it would be classified as an asphaltene in most schemes, but as a resin if the separation order were reversed. Classification as one or the other is arbitrary, since the effect of the molecule on the asphalt mixture is as both an asphaltene and a resin, and may, in fact, depend upon its dual nature, as is the case with a detergent molecule.

Consider, for example, the profile of hydrogenated coal in Figure 31c. There are two distinct regions of very high solubility. This together with what is known about the chemistry of hydrogenated coal, strongly suggests that two functionalities or moieties exist on the same group of molecules. This is one explanation for its incompatibility with asphalt in mixture, and may also explain why, historically, attempts to separate suitable asphalt material from other hydrogenated coal products have been generally unsuccessful. These are features that are not so clearly revealed by traditional fractionation schemes (68,69,70).

It is normal when using the rule "like dissolves like" to predict solubility to note only the functional groupings on substances. The concepts presented here go beyond this first approximation to include dynamic properties of materials. This is important since the structure of asphalt is not fully known. For example, isopropylnitrile, $(H_3C)_2CHCN$, and bis(m-hyenoxyphenyl)ether, $(HOC_6H_4)_2O$, do not have similar structures; however, they have the same δr, δV coordinates (2.5,9.7) and they are miscible in all proportions (73).

Solubility profiles should, therefore, provide great insight into the nature of asphalts, without the need for specific functional group determinations. These diagrams could be used to describe the aging of asphalt. The Styrelf A core diagram shown in Figure 31 is displaced towards greater δr; this is reasonable since oxidized substances have increased values of δr. A typical trend is shown by the values of δr, δV for the n-propyl grouping $(H_3CCH_2CH_2-)$ as the attached functional groupings are changed from $-CH_3$ (0,6.9), -C(O)H (3.4,7.7), -C(O)OH (5.2,7.6), to -OH (8.5,8.5) (73).

Other applications of this method can include the comparison of asphalts that perform poorly with those that perform well, as well as the observation of changes that occur in roadway material as the highway ages. The goal of both these applications is, of course, to be able to predict well in advance, the suitability and expected performance of an asphalt before highway construction begins (73).

F. Experimental

1. Apparatus

a. Pressure

High pressures were generated and contained using commercial apparatus.

i. Reactors

The 800 mL reactors were constructed of 316 stainless steel by High Pressure Equipment Company, Inc. (Erie, PA). They are rated by the manufacturer at 8,400 psi at 650°F. The 12 mL reactors were constructed by Tem-Pres Research (State College, PA) and are rated 60,000 psi at 800°C.

ii. Intensifiers

High water pressures were generated using a Hydraulic Engineering Corp. (Los Angeles, CA) pump 10-600-30 rated at 30,000 psi. The unit was attached to a high-pressure hydrothermal research unit (HB-1B-4, Tem-Pres) for gauging and temperature control. Increased hydrogen pressures were obtained with an AMINCO (Silver Spring, MD) gas booster pump rated at 6,000 psi (406-135LA).

b. Instruments

i. Infrared Spectra

Infrared spectra were recorded using a Perkin-Elmer Model 283-B Infrared Spectrophotometer. The abscissa calibration was confirmed using polystyrene.

ii. Nuclear Magnetic Resonance Spectra

Proton nuclear magnetic resonance spectra were obtained with an IBM NR-80 Fourier Transform Multinuclear NMR Spectrometer. The spectra as presented in this report are time averaged for 100-200 scans to enhance the intensity of low abundance groupings.

2. Procedures - Asphalt Syntheses

a. High Pressure Reactions

The same general procedure was used with the large or small high pressure reactors. The coal and any solid or liquid reagent is weighed in a glass liner and then placed into the reactor. It is then sealed and then the gaseous reactant (e.g. H_2) is compressed into the reactor. The reaction is heated and the reaction temperature, pressure, and time recorded. The system is then cooled to room temperature and the pressure released in the fume hood. The material in the bomb was physically collected and then the chamber was washed with CS_2 until the CS_2 remained colorless. The solid was dried and then weighed. The CS_2 was then evaporated and the yield of soluble material obtained.

b. Yield Calculations

Since the solubility of asphalt, linseed oil, and animal fat in CS_2 is unchanged after the hydrogenation, the coal conversion can be calculated from the loss of solid and confirmed by the gain in CS_2 soluble material. Tables 6-10 present yield data.

Yields were calculated using these expressions:

$$\% \text{ Soluble Yield} = \frac{\text{Total weight of } CS_2 \text{ soluble material}}{\text{Weight Charge}} \times 100\%$$

$$\% \text{ Semi-Solid} = \frac{\text{Weight of solid and semi-solid material}}{\text{Weight Charge}} \times 100\%$$

$$\% \text{ Asphaltenes} = \frac{\text{Weight of pentane insoluble semi-solid}}{\text{Weight of semi-solid}} \times 100\%$$

$$\% \text{ Maltenes} = \frac{\text{Weight of pentane soluble semi-solid}}{\text{Weight of semi-solid}} \times 100\%$$

$$\% \text{ Coal Conversion} = \frac{\begin{array}{l}\text{Charge weight of coal} \\ \text{minus } CS_2 \text{ insoluble material}\end{array}}{\text{Charge weight of coal}} \times 100\%$$

(Assumption: Only coal gave rise to CS_2 insoluble material)

$$\% \text{ Loss} = \frac{\text{Weight Charge minus Weight treated charge}}{\text{Weight Charge}}$$

(Assumption: Loss is in volatile materials. Neglects weight increase due to H_2 reactions.)

c. Separation Scheme

Figure 32 shows the general separation scheme. The amount of material termed soluble yield is determined by removal of the CS_2. The material is often a mixture of two phases. Since the liquid is not miscible with the semi-solid, it is decanted from the semi-solid. Infrared spectra confirm this oil as being a mixture of fatty acids, fatty alcohols, and glycerol. The semi-solid is washed with 100 times its volume to separate the maltenes from the asphaltenes. Tables 15-18 summarize the results.

d. Definitions

Charge - refers to the material placed in the reaction bomb. The weight of the Charge is the total weight of that material (excluding hydrogen) before the reaction.

Treated Charge - the total charge after hydrogenation.

Soluble Yield - refers to that portion of the total bomb contents after reaction that are soluble in carbon disulfide. The consistency of this method ranges from oily to brittle solid.

Semi-solid - refers to the solid and semi-solid portion of the soluble yield. This definition is particularly necessary in those cases where light oils separate and are decanted from the heavier weight asphaltic bitumens.

Asphaltenes and Maltenes - refer to the defined fractions of the semi-solid material only asphaltenes are the pentane insoluble materials, while maltenes are the pentane soluble fraction.

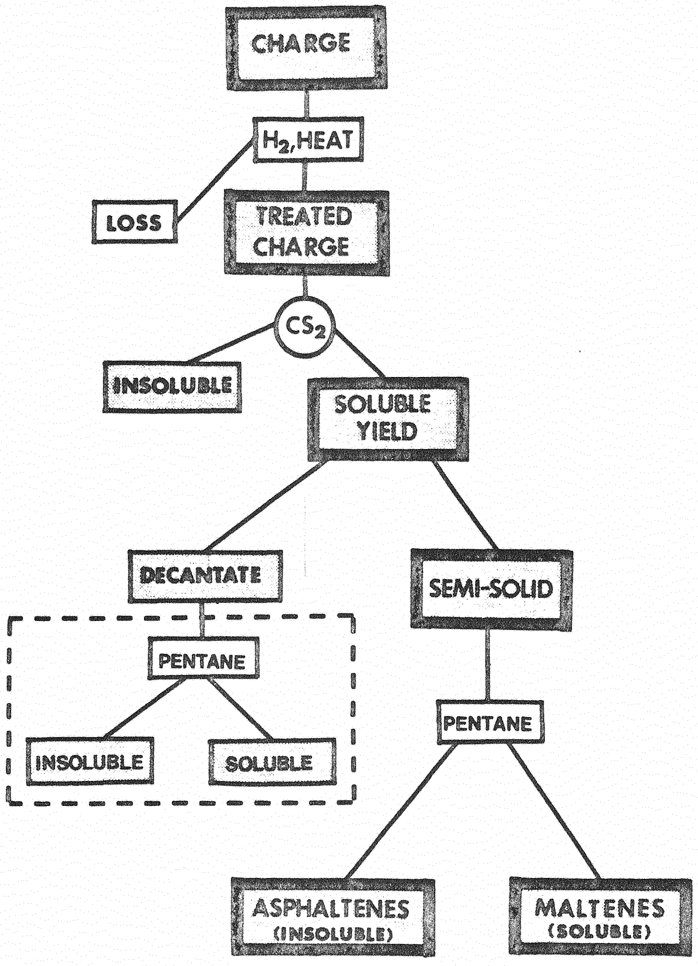


Figure 32: Separation Scheme for Treated Charge

3. Procedure - Solvent Solubility

Summary of Method - The described procedure is for determination of the percent (w/w) solubility of sample material in a variety of solvents. This is accomplished by first dispersing the material in the solvent or exposing it to the solvent in a thin film, then filtering the suspended material. The percent solubility is calculated from the weight of either the portion of sample dissolved in the filtrate or that portion not passing the filter.

The method used is adapted from ASTM 2042-76: Standard Method Test for Solubility of Asphalt Materials in Trichloroethylene. The significant variations from the ASTM method are a substitution in the method of filtration and the addition of a thin film technique for maximizing contact between the sample material and solvents in which it is not fully dispersed. These variations are described in the following pages.

Sample Materials - The whole asphalts, AC-3 and AC-4, are commercial asphalts of Phillips Petroleum Company and were supplied in bulk by the Oklahoma Department of Transportation (OkDOT). Styrelf A is asphalt extracted from a road core sample obtained in the course of an asphalt recycling project and supplied by OkDOT. The hydrogenated coal is the carbon disulfide soluble portion of Oklahoma coal that was pulverized and ground to 60 mesh powder, then treated with hydrogen gas at 6000 psi at 300°C for 60 hours. The coal used is from the Secor coal near Enterprise, Oklahoma. It was sampled from a strip mine on the Wistoff Brothers lease.

Solvents - All solvents, except 1,1,1 - trichloroethane, were anhydrous and of reagent grade or better. Trichloroethane was purchased as industrial grade, but was redistilled before use. Solvents were purchased from the following companies: benzene, acetone, chloroform, pyridine, toluene, m-cresol, diethyl ether, tetrahydrofuran, propanol, methanol, and dimethylformamide from J.T. Baker Chemical Company; carbon tetrachloride, pentane, methlethylketone, dimethyl sulfoxide, and acetonitrile from Fischer-Scientific Company; carbon disulfide and butanol from Aldrich Chemical Company; 1,1,1 - trichloroethane from Cone Solvents, Inc.; aniline from Matheson, Coleman, and Bell; tetrahydrofuran and cyclohexane from Mallinckrodt, Inc.; and ethanol from AAPER Alcohol and Chemicals.

Solvation Methods - Approximately 0.5 g of the sample was required for each solubility determination. These portions were accurately weighed in clean, preweighed Erlenmeyer flasks (250 ml cap.), using a Mettler single pan balance. The appropriate amount of solvent was added to each to yield a 1:100 (w/v) suspension or solution. The suspensions were then stirred for a sufficient period of time (six hours or longer) to allow the soluble portion to be extracted into solution.

For solvents not fully dispersing the sample (solubility less than 10 or 20 percent), a thin film of the sample was prepared for contact with the solvent. A 0.5 g portion was weighed, as above, in an erlenmeyer flask. Then, an amount of carbon disulfide was added that was just sufficient to dissolve the sample. The carbon disulfide was then allowed to evaporate from the sample at 250°C in a fume hood until the weight of the sample was constant at its originally measured weight. This provided a thin film of sample in the flask to which a hundredfold amount (w/v) of solvent was added. The preparation was then covered and allowed to stand a minimum of eighteen hours before filtration.

Filtration Methods - Although future applications of this procedure may demand more rigorous measurement of solubility, reproducibility adequate for solubility profiles was obtained by filtration of solvent suspensions by gravity flow through paper filters (See discussion of method).

Filters allowing rapid, reproducible measurements were of a grade that retains fine crystalline precipitate (Whatman No. 5 or equivalent). Filters were fluted and preweighed and placed in suitable funnels without wetting. For samples showing appreciable (greater than 20 percent) solubility, the solvent suspension was poured into the filter and allowed to drain by gravity flow. The filter and retentate were air dried, then oven dried by 70°C and weighed. The weight of the rententate was taken as the weight of the insoluble material. For samples showing little solubility (especially thin film samples), the filtrate was collected in a pre-weighed round bottom flask and flash evaporated to a constant weight on a Büchler Instruments flash evaporator. The weight of the residue was taken as the weight of the soluble portion of the sample.

Calculations - Percent solubility of the sample in the given solvent was calculated as follows:

Percent Solubility = (A/S) x 100% or 100% - [(B/S) x 100]

where, A = weight of the soluble portion in the filtrate
B = weight of the insoluble retentate
S = weight of the sample

There was found to be good agreement (± 2%) between the two methods of calculation when applied to the same sample.

Discussion of Method - There are several reasons for using the rapid filtration techniques instead of the more stringent procedure outlined in the ASTM Standard Method. Among rheologically similar asphalts, there can be a great deal of variation in their solubilities in an individual solvent. The purpose of the solubility profile is to show solubility patterns or trends that are consistent, while allowing for these variations. For examples, it is typical that one asphalt may be 30% soluble in pentane, while a second is 60% soluble, The same two asphalts may be almost identical in rheology and in road performance. Since there are solubility patterns that show this similarity and still allow for a 30 percent variation in pentane solubility, the necessity for solubility measurement to a precision of 0.035% as called for in the ASTM method was not indicated. The method used allows for the rapid collection of data for a large number of solvents, while allowing reproducibility within 3% for samples of high solubility and within 1% for thin film samples of low solubility. This precision is quite sufficient for reproducible profiles of high statistical correlations. A more rigorous methodology should be necessary only if extremely detailed profiles are shown to be valid and useful.

COMMERCIAL POTENTIAL

The basic technical knowledge for the liquefaction of coal has been known for more than 100 years.[1] Summaries of current technological advances have had extensive coverage in the scientific news press, in government reports, as well as in scientific and engineering journals.

In a summary of the current status of the Exxon Donor Solvent (EDS) process the two general procedures for liquefaction are defined:[12] "Indirect liquefaction involves and then synthesizing hydrocarbons from the gas. Direct liquefaction involves the direct hydrogenation of coal to produce liquids," For asphalt use it would appear to be reasonable to use a direct liquefaction procedure since a higher heteroatom content can be tolerated for road work as compared to a fuel. The processes are often described by acronyms which may or may not convey technical meaning. A good basic summary of the acronyms has been assembled by P.C. White and M.B. Neuworth in a report which contains quarterly summaries from several major liquefaction efforts.[13] In the Solvent-Refined Coal (SRC) process high-sulfur, high-ash coals are converted to low-sulfur, low-ash liquid fuel. The coal is first pulverized and mixed with a coal-derived solvent in a slurry mix tank and then hydrogenated.[13,14] Variations of this scheme include the use of catalysts and temperature-pressure variations.

It would appear reasonable to examine commercial liquefaction products as asphalt extenders.

CONCLUSIONS

1. Infrared and nuclear magnetic resonance spectra can be used to fingerprint asphalt.
2. Coal when hydrogenated in the presence of asphalt, linseed oil, or animal fat, forms a material with short term miscibility with petroleum asphalt.
3. Solubility profiles can be used to determine the general constitution of impurities in synthetic asphalt which may lead to immiscibility with petroleum asphalt.
4. An asphaltic material can be prepared from coal which has reasonable heteroatom and carbon/hydrogen contents.

RECOMMENDATIONS

This effort was designed as a rapid survey to develop possible areas for future work.

1. The Oklahoma waste coal should be hydrogenated in the presence of additional renewable resources, e.g., corn oil, fish oil, soybean oil.
2. The synthetic asphalt should be blended with petroleum asphalt and tested for long term miscibility and rheological properties.
3. Large scale synthesis (2-5 pound) procedures for synthetic asphalt should be developed.
4. The products from current coal liquefaction processes should be examined for potential use as road asphalt.
5. Solubility profiles should be obtained for a wide range of petroleum asphalt and synthetic asphalts. These profiles should be correlated with rheological, chemical, and spectroscopic properties of the profiled materials.
6. The OkDOT should establish a library of spectral data for commercial asphalts, as well as for asphalts from road surfaces for the correlation with road performance.

APPENDIX A

List of Asphalt Samples

Sample	No.	Description
AC-4	101	Pure Batch Asphalt Penetration Range 200-300
AC-3	102	Pure Batch Asphalt Penetration Range 85-100
AC-3A	103	Pure Batch Asphalt Penetration Range 120-150
MC-3000	104	Asphalt Cutback with Petroleum Solvent (Naptha) Viscosity 5212
MC-800	105	Asphalt Cutback with Petroleum Solvent (Naptha) Viscosity 1339
MC-30	106	Asphalt Cutback with Petroleum Solvent Viscosity 49
CMS-1	110	Emulsified Asphalt Medium Setting Viscosity 100+
CMS-2	111	Emulsified Asphalt Medium Setting Viscosity 100+
CRS-2	112	Emulsified Asphalt Rapid Setting Viscosity 75-400
Emulsion SS-1	114	Emulsified Asphalt Slow Setting Viscosity 20-100
CCM	119	Unknown Asphalt possibly containing 1 ppm Chem-crete
SOX Can	120	Sun Oil Asphalt without Chem-crete
Scca Can	121	Sun Oil Asphalt with Chem-crete, 3-1-81, quality control sample
Sccb Can	122	Sun Oil Asphalt with Chem-crete used for US-81 in Enid. Sampled 3-2-82. Surface layer (June Core P).
BST	123	Big Springs, Texas pure asphalt
BSTa	124	Big Springs, Texas asphalt with Chem-crete added. Sampled 3-2-82. Used for US-91 in Enid. Base layer (June Core Q).
Paper Cup Sample	125	Unknown asphalt taken from road paving project
Rubber Asphalt	126	Used in rubber paving project
Chem-crete	127	Typical Chem-crete mixture with asphalt

Sample	No.	Description
Chem-crete a	128	3-23-82, pure batch of asphalt AC-3 with Chem-crete added.
Beaver County #1	401	Cold recycled asphalt project in Beaver County Control-1
Beaver County #2	402	Cold recycled asphalt project in Beaver County Control-2
Beaver County #3	403	Cold recycled asphalt project in Beaver County Recycled-2A
Beaver County #4	404	Cold recycled asphalt project in Beaver County Recycled-3
CMS-1 Highway	406	Medium setting emulsified asphalt taken from a road project while asphalt was being placed
25-1 Highway	407	Road core taken near the intersection of NW 69th and NW Highway near Bethany and Warr Acres. Laid with Chem-crete. The core was 2 years old.
June P	408	June Core taken from US-81; 3 1/2 miles South of Enid, Oklahoma; Cored 6-12-82, 1 month after laid; Sample P (0-5 cm in depth), top horizon, Sun Oil asphalt with Chem-crete; Sample Q (5-8 cm in depth), bottom horizon, Big Springs, Texas asphalt.
June Q	409	
Styrelf Core A1	411	Styrelf Core taken from US-177 between SH-59 and SH-9 (0-39.5 cm in depth)
Styrelf Core A2	412	
Styrelf Core B1	413	Horizon A: 0-12 cm in depth; laid July, 1971; Sample A1 (0-5 cm in depth) Sample A2 (5-12 in depth Horizon B: 12-39.5 cm in depth; laid January, 1932; Sample B1 (12-18 cm in depth; Sample B2 (21.5-39.5 cm in depth
Styrelf Core B2	414	
Abson #1	415	Core taken on day asphalt placed, 11-10-80
Abson #2	416	Core taken 11-25-80
Abson #3	417	Core taken 12-17-80
Abson #4	418	Core taken 12-25-80

APPENDIX B

Rostler-Sternberg Separation Procedure

The Rostler-Sternberg method of chemical precipitation separates asphalts into five fractions. This method was designed as a simple analytical technique for identifying the asphalt fractions. It is also used quantitatively to define asphalts by precentage composition.

The five main groups of components are determined on a single specimen by successively precipitating the fractions from pentane solution, evaporating the solvent from the nonprecipitated portion of the sample and weighing the residue after each precipitation.

Equipment:

Erlenmeyer flasks 250 or 300 ml
Erlenmeyer weighing flasks 125 ml
Cylinder with stopper
Distilling apparatus

Solvents:

n-Pentane Commercial Grade
98% Sulfuric Acid
85% Sulfuric Acid
30% free SO_3 fuming sulfuric acid
Source of HCl gas

A 1 gram sample of asphalt is placed in a weighed filter or soxhlet cup suspended in the upper portion of a long glass tube. (Coated glass beads can be used here.) The sample is refluxed with 100 mls of normal pentane. This separates the asphaltenes (insoluble in boiling n-pentane) from the other components - maltenes. Eighty-five percent sulfuric acid is then used to precipitate a fraction containing the most reactive portions of asphalt.

This portion contains all the nitrogen bases of the asphalt (N). Sulfuric acid of 98% strength is then used to precipitate the next most reactive fraction called first acidaffins (A_1). By using fuming sulfuric acid containing 30% SO_3 the fraction of next reactivity is precipitated. This fraction is named second acidaffins (A_2). The fraction that remains soluble in n-pentane is the paraffins (P).

The N fraction can be subdivided into two fractions, N_1 and N_2 by precipitation of nitrogen bases group 1 with gaseous HCl (Figure 1, page 5).

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[1] For a detailed description of the procedure see: Rostler, F.S. and Sternberg, H.W., "Compounding Rubber with Petroleum Products," Ind. and Eng., **41**, 598 (1949).

APPENDIX C

Coated Glass Beads

In the modified soxhlet extraction procedure used for separation, the fritted filter tends to clog up causing overflow and mixing of insoluble material.

It was found that coating glass beads with the sample to be extracted lessened the frequency of this problem.

Procedure:

1) Dissolve material (asphalt-treated coal) with CS_2 and filter on Buchner Funnel to remove insolubles

2) Filter again by gravity (fluted filter)

3) RotoVac to dryness with 4 mm glass beads

4) Glass beads coated with the weighed amount of material can now be used for Soxhelt extraction

APPENDIX D

n-Pentane Separation Procedure

Asphaltenes and maltenes are separated by precipitating the asphaltenes in 100 ml n-pentane per gram asphalt.

Equipment:

Büchner and gravity funnels

Filter paper

Erlenmeyer flasks

RotoVac

Weighed flasks

Solvents:

n-pentane

CCl_4

Activated alumina, or Fuller's earth

A 100-gram sample of asphalt is dissolved in 100 ml n-pentane/gm of asphalt to be separated. Precipitation is allowed to continue for approximately three hours. The solution is then filtered by gravity filtration. The fraction that precipitated in the n-pentane is a powder substance called asphaltenes. The n-pentane soluble portion is called maltenes. The maltenes fraction can then be further separated into resins and oils by treating the solution with activated alumna, Fuller's earth or another absorbant. The clay containing the absorbed material is washed with n-pentane. The filtrate contains the unabsorbed or oily constituents. The resins on the absorbed clay or alumina are not extracted or eluted with a polar solvent such as 1,1,1 trichloroethane or chloroform (without drying the absorbant) to obtain soluble extract materials, i.e. resins.

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