NASA Contractor Report 174761

Carbon-13 and Proton Nuclear Magnetic Resonance Analysis of Shale-derived Refinery Products and Jet Fuels and of Experimental Referee Broadened-specification Jet Fuels

Don K. Dalling, Brent K. Bailey, and Ronald J. Pugmire

University of Utah Research Institute
Salt Lake City, Utah

September 1984

Prepared for

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION
Lewis Research Center
Under Contract NAG 3-27

TABLE OF CONTENTS

SUMMARY

Economic conditions in world petroleum markets have created pressures for refining of jet fuels from alternate sources of hydrocarbons, such as shale, tar sands, and coal-derived liquids. However, production of aviation kerosenes from such sources may result in broadening of fuel specifications, both known and unknown. Nuclear magnetic resonance (NMR) spectroscopy has been recognized as a powerful tool with which to study the properties of hydrocarbon liquids, and it has been used here to study refinery products derived from shale oil, broadened-specification jet fuel, and related model compounds.

The study of saturated, acyclic isoprenoid compounds like those found in many crude and refined oil products is of interest to several disciplines. The distribution of stereoisomers in the isoprenoids found in naturally occuring hydrocarbons has been related to maturation and diagenesis. In the past, elucidation of the diastereomeric distribution was accomplished by means of chemical cleavage, derivatization, and vapor phase chromatographic identification. We have shown that it is possible to detect the diastereomers in farnesane, pristane, phytane, and squalane by use of high field carbon-13 NMR, including differentiation of natural and synthetic products.

Fractionation of hydrocarbon mixtures at 100 milligram levels for purposes of producing samples for use in NMR analysis has been of high interest for some time. Use of open column or high performance liquid chromatography (HPLC) does not provide adequate results because of the difficulties encountered in liberating the fractions from the elution solvent. Application of supercritical fluid chromatography (SCFC) using carbon dioxide resolves many of the difficulties associated with other techniques. Modifications to an existing HPLC apparatus and other procedures necessary to achieve preparative scale, quantitative SCFC have been developed and are presented.

Twenty-four samples have been extracted from the refinery stream in the process of producing three military grades of jet fuel from raw shale oil by Ashland Petroleum Co. The samples were examined by use of proton and carbon-13 NMR. Thirteen of the lighter samples were separated into saturates and aromatics fractions by means of SCFC. Virtually all of the straight chain material was detected in the saturates fractions. The fractions were analyzed for carbon and hydrogen and were subjected to simulated distillation for the purpose of determining their average molecular weights. An average parameter analysis scheme utilizing a minimum number of assumptions and some novel corrections was developed for the aromatic components. NMR spectra were acquired for all of the fractionated samples, and the average parameter analysis was applied. Formulation of model mixtures representing the mixtures

was demonstrated. The variation of quantity of aromatic material in the refinery products may be a more significant parameter than the intrinsic nature of the aromatic species present. Although product parameters varied in the manner to be expected as a result of specific refinery processes, they did not vary greatly in their inherent characteristics.

Three experimental referee broadened-specification (ERBS) fuels and a blending stock were studied initially by use of HPLC. The aromatic material was separated into one-, two-, and three-ring components. The two- and three-ring fractions were observed to contain very little saturated carbon other than methyl and ethyl groups. In the two-ring sample resonance lines attributable to all of the possible dimethylnaphthalenes were detected. The samples were fractionated using SCFC and examined by NMR spectroscopy. Average parameter analysis was again performed and model mixtures were developed. The ERBS products were found to resemble more the shale products before aromatic saturation, rather than the finished fuels.

Some theoretical considerations relative to the necessity of making an aromatics-saturates separation before performing average parameter analysis are presented. Some novel pulsing schemes, INEPT and DEPT, are explored relative to their application to complex hydrocarbon mixures. The specialized multiplicity and component information derivable from such data was discussed with examples from the shale oil products.

I. INTRODUCTION

A. Background

Events of the past few years indicate that the era of plentiful supplies of cheap petroleum for the production of aviation kerosene may have come to an end.[1, 2] Projected real shortages, market manipulation and competition for mid-distillate cuts have created pressure to utilize wider fraction cuts and lower quality crudes for the production of jet fuel. A recent study of the Department of Energy Fuels Data Bank revealed that jet fuels are already showing an increased aromatic content as a result of these pressures.[3] Present conditions in the petroleum market also make the production of jet fuels from alternative sources not only possible but perhaps attractive. The refining of alternative hydrocarbon sources, such as shale, tar sands, and coal derived liquids, may produce not only an increase in aromaticity, but may also affect other significant properties, such as heteroatom content. However, relaxation of property specifications has both supply and economic benefits. Those parameters which may be changed include the allowance of more aromaticity, higher freezing points, lower volatility, increased viscosity, and decreased thermal stability.

B. Objectives and Approaches

Nuclear magnetic resonance has long been recognized as a powerful tool for the elucidation of the components and properties of complex hydrocarbon mixtures. The principal objectives of this work were to use proton and carbon-13 NMR to characterize the hydrocarbon products produced by refining of shale oil, as well as some experimental referee broadened-specification (ERBS) turbine fuels. Another objective was the investigation of fuel-related model compounds. An additional objective was the exploration of some of the more modern procedures which have been developed in NMR technology as to their applicability to complex hydrocarbon products.

The model compound portion of this study focused on some simple isoprenoids having from 15 to 30 carbons, which are similar to those found in many types of geologically derived hydrocarbons. The relative distribution of stereoisomers in such molecules has been related to the maturation of hydrocarbon deposits, so such data is of great interest to petroleum engineers and geochemists. It was found that it is possible to distinguish the diastereomeric populations in these compounds by use of high field NMR. Long range conformational chemical shift effects resulting from steric centers up to seven bonds distant have been documented.

Twenty-four samples were recovered from various steps in the refining of shale oil by Ashland Petroleum Co. NMR analysis was undertaken. In the process of analysis of the whole samples, it was determined that it was essential to make a separation of the saturate and aromatic fractions if meaningful average parameters were to be obtained. That separation, however, proved to be nontrivial, as traditional, existing open column and high performance liquid chromatographic (HPLC) separations were found to be inadequate for production of samples for NMR analysis due to problems in isolating the separated fractions. To resolve the difficulty, we turned to a relatively new technique, supercritical fluid chromatography (SCFC) using carbon dioxide as the eluent on a modified HPLC. Preparative scale separation and recovery required development of some new technology, which is described. Thirteen of the lighter samples were separated by use of SCFC. Elemental analysis, molecular weight and NMR data were acquired for saturates and aromatic fractions. Most of the long aliphatic chains were found to reside in the saturates portion. Parameteric analysis was accomplished for the aromatic fraction, and model mixtures were formulated.

Three ERBS aviation turbine fuels with hydrogen contents of 12.8%, 12.3%, and 11.8% and a blending stock were fractionated using HPLC. The aromatic portions were further separated into one-, two-, and three-ring fractions. In the heavier fractions most of the aliphatic carbon was present as methyl and ethyl groups. SCFC separation and analysis were carried out on the fuel and blending stock in the same manner as for the shale samples.

The NMR techniques INEPT and DEPT were applied to some of the samples of this study and to some model compounds. The information which can be gleaned from such experiments was investigated.

II. MODEL COMPOUND STUDIES

A. Introduction

Carbon-13 nuclear magnetic resonance (NMR) has been used to characterize the aromaticity and average properties of naturally occuring hydrocarbons, including petroleum,[4] shale oil,[5] coal derived liquids,[6] and tar sand bitumens.[7] With few exceptions,[5, 8, 9] these studies have not focused on the determination of the actual constituency of the samples.

The origin and and diagenesis of natural hydrocarbon deposits has been of interest to organic chemists, biochemists and geochemists.[10] Acyclic alkanes of 20 and more carbons are found in a wide variety of organic sediments and petroleum.[5, 8, 9] The stereochemistry of these molecules is of significance, because it provides information about the source and chemical history of the compounds. For example, loss of stereospecificity in petroleum derived acyclic alkanes has been correlated with geological maturation.[11, 12] However, the identification of stereoisomers in geosamples has been limited to a few cases, utilizing vapor phase chromatography coupled with synthetic degradation procedures.[11, 12]

Stereoisomers are found in hydrocarbon deposits because they are derived from naturally occuring biochemicals which contain chiral centers, i.e. tetrahedral carbons substituted by four different groups. Such centers are designated R or S according to the relative configuration of their substituents by use of standard sequencing rules.[13] Molecular stereoisomers having n chiral centers can exist in 2^n forms. Enantiomers are nonsuperimposable mirror image isomers which have identical NMR spectra, as well as all other physical properties except for the direction in which they rotate the plane of polarized light. They also have identical chemical properties, except when interacting with reagents which are also chiral.

Diastereomers result from molecules which contain more than one chiral center. In meso compounds the stereoisomers are superimposable mirror images of one another and are not resolvable into enantiomers. However, diastereomers may exist in forms which are not superimposable nor interconvertible, neither are they enantiomers. The isomers in these cases generally have very similar chemical properties, but their physical properties may differ markedly. In particular, the NMR spectra of diastereomers will differ from one another (barring accidental degeneracy) whenever nuclei at corresponding positions of the isomers are close to two or more chiral centers and thus experience different environments. These effects are not averaged even when rotation about the various bonds is unrestricted in both kinetic and thermodynamic senses.[14] For ^{13}C NMR spectra, our experience has indicated that in open chain compounds otherwise equivalent carbons up to seven bonds distant from a chiral center may have distinguishable chemical shifts. Carbons influenced by two chiral centers may produce two resonance lines, while those close to three chiral carbons may produce as many as four lines. The intensity of the individual resonances in a related set will depend on the relative abundance of the various diastereomers in the mixture.

Our study of the composition of geologically derived hydrocarbon mixtures has indicated that, beyond simple straight chain alkanes, a significant portion of the saturated fraction in such samples appears to originate with saturated oligomers derived from isoprene (2-methyl-1,3-butadiene) and from lightly branched alkanes which could easily be viewed as fragments arising from partially demethylated or chain scissioned isoprenoids. For example, consider the ^{13}C spectrum of the saturates found in a Colorado shale oil shown in Figure II-1. The most easily recognized feature is, of course, the presence of long, straight-chain alkyls. By using previously published chemical shift substituent parameters,[15, 16, 17] we have been able to identify readily the second most intense set of resonances. They are attributable to isoprenoid fragments, which are known constituents.[18] In Figure II-2 the saturates portion of the ^{13}C spectrum of an aviation kerosene derived from a Mexican Isthmus light crude is displayed. The vertical scale has been increased so that the smaller lines are easily distinguishable, although this results in clipping of the straight-chain alkyl resonances. Use of the previously cited parameters again enables us to identify isoprenoid-like structures in the mixture, as well as isopropyl-terminated straight chains. In Figure II-3 the same spectrum is presented again but with the remaining second level resonances having been assigned. It is noteworthy that most of the prominant resonances have been assigned at this point, and that they are associable with lightly methylated chains.

These results stimulated us to study pure isoprenoid compounds like those found in naturally occuring hydrocarbons. The molecules of interest are 2,6,10-trimethyldodecane, 2,6,10,14-tetramethylpentadecane, 2,6,10,14-tetramethylhexadecane, and 2,6,10,15,19,23-hexamethyltetracosane. Hereafter they will be designated by their trivial names, farnesane, pristane, phytane, and squalane, respectively. The structures of these molecules are given in Figure II-4. The possible stereoisomers are given in Table II-1. Our studies have revealed that it is possible to distinguish diastereomeric populations in isoprenoid stereomixtures by use of ^{13}C NMR.

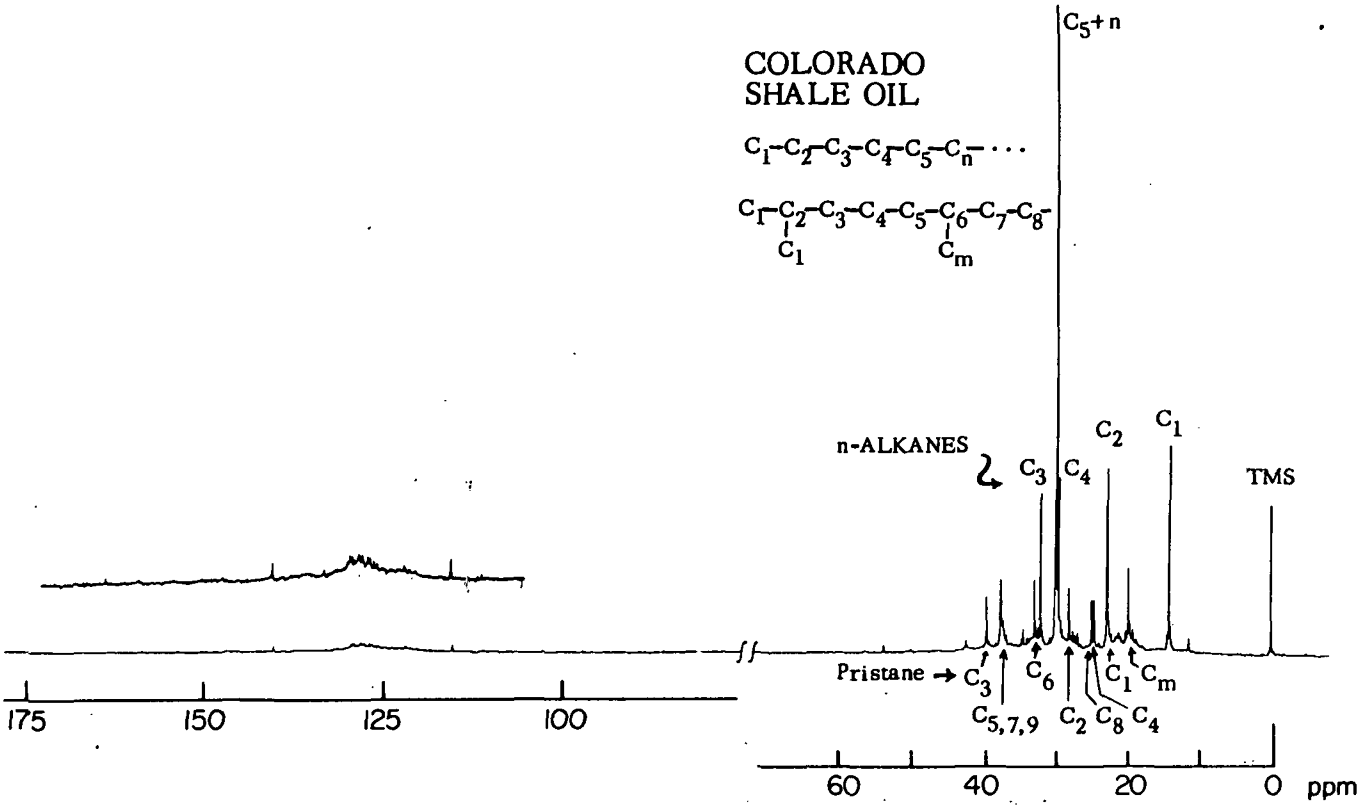


Figure II-1: The ^{13}C NMR spectrum of a Colorado oil shale. Resonance lines attributable to molecular fragments like pristane are readily identifiable.

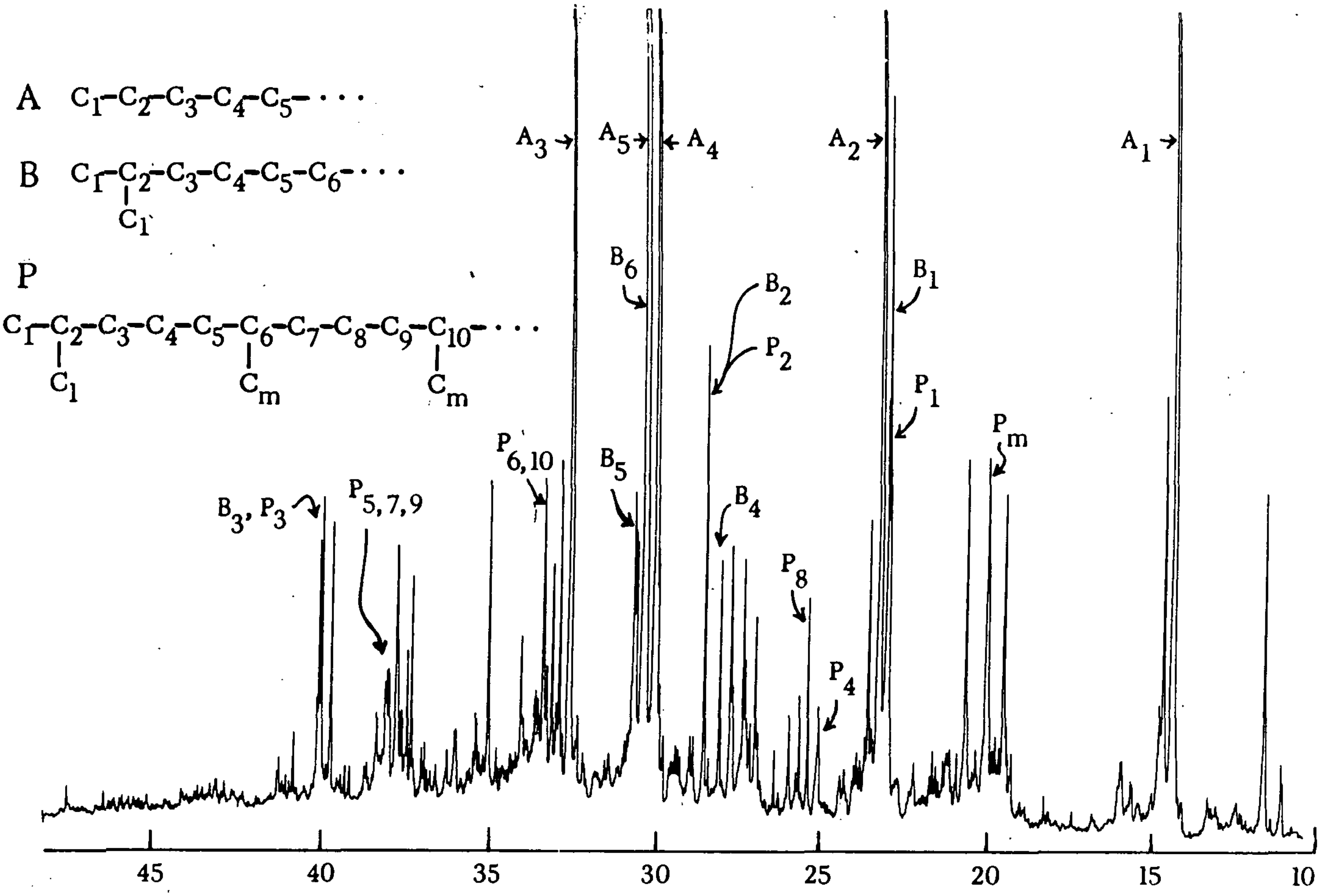


Figure II-2: The aliphatic portion of the ^{13}C NMR spectrum of an aviation kerosene derived from a Mexican Isthmus light crude oil. The vertical scale has been increased in order to display the less intense resonances. The spectral lines identified with straight chain, isopropyl terminated and pristane-like fragments are indicated.

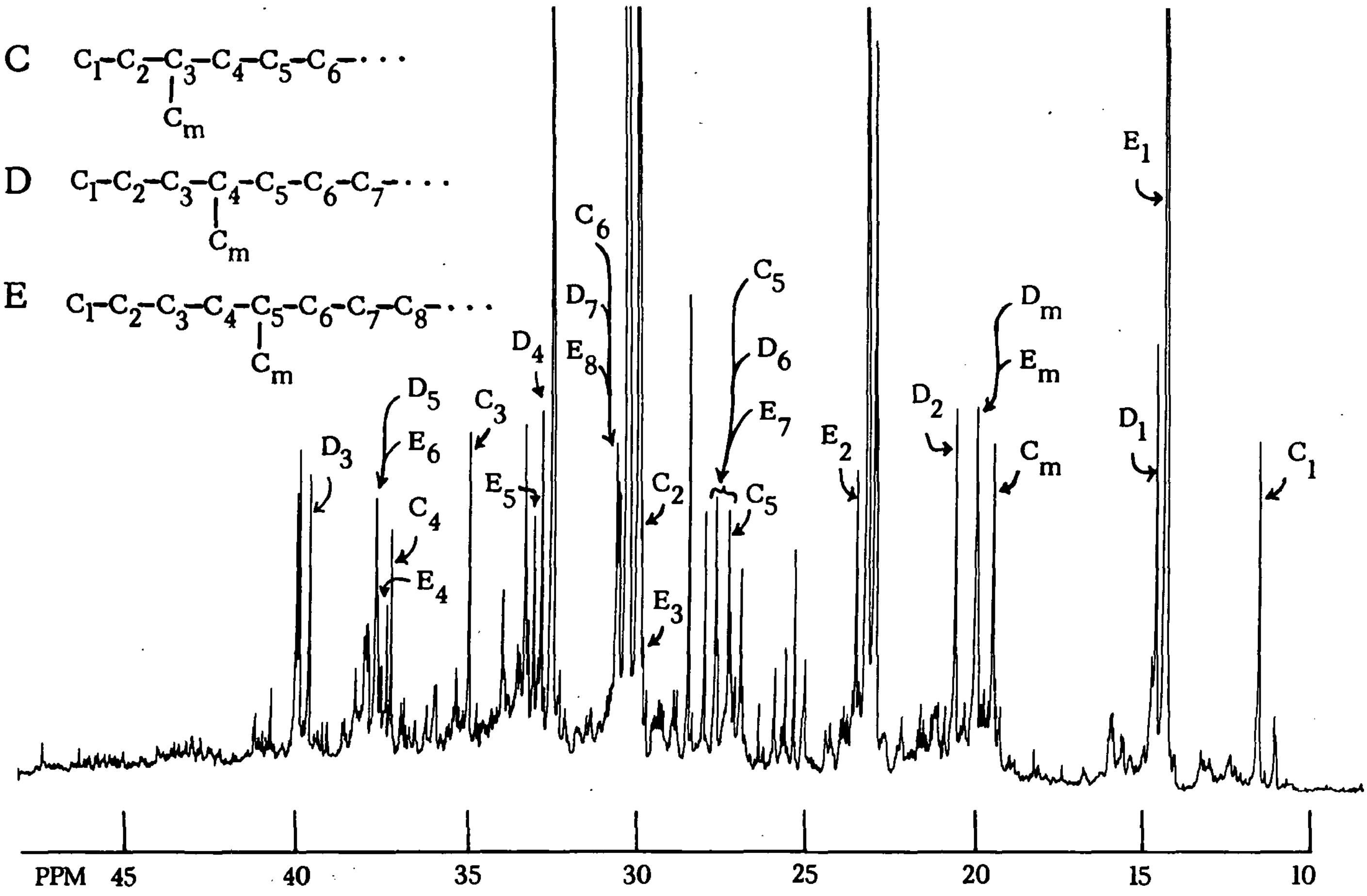


Figure II-3: The same spectrum as in Figure II-2, except that resonances which result from lightly methylated chains are indicated.

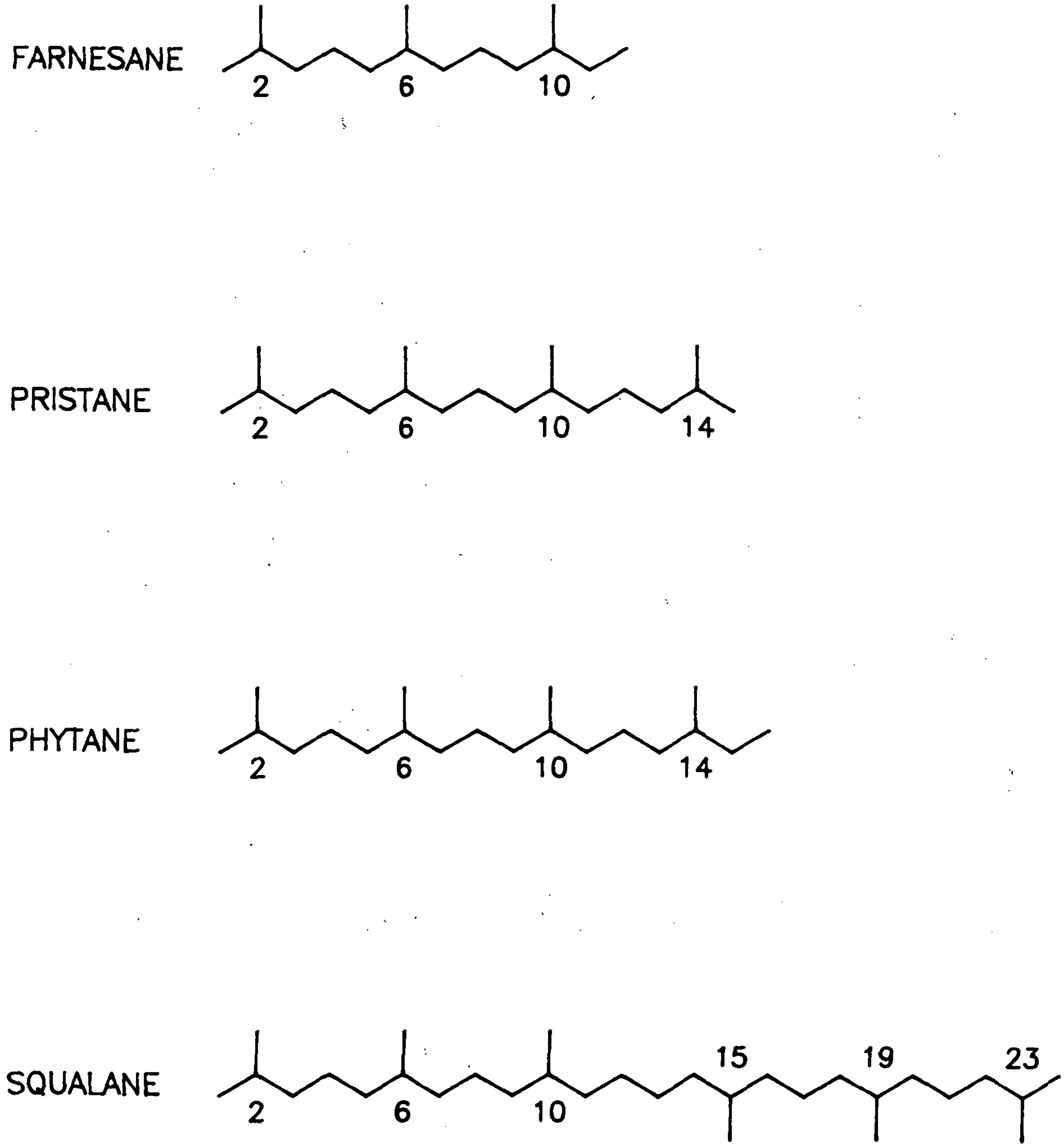


Figure II-4: The molecular structure of farnesane, pristane, phytane, and squalane.

Table II-1: Stereoisomers Which May Exist in the Isoprenoid Compounds of Figure II-4.

N[a]	Diastereomers/Enantiomers[b]				Environments[c]	Compound
1	R		S		1	
2	RR		SS			
	RS		SR		2	farnesane[d]
3	RRR		SSS			
	RRS		SSR			
	RSR		SRS			
	SRR		RSS		4	phytane
4	RRRR		SSSS			
	RRRS	SSSR	RSSS	SRRR		
	RRSR	SSRS	RSRR	SRSS		
	RRSS		SSRR			
	RSSR		SRRS			
	RSRS		SRSR		6	squalane[e]

a. The number of chiral centers in the molecule.

b. Enantiomers are given across the rows, diastereomers down the columns.

c. The number of possible resonance environments.

d. Pristane would also have this number of environments because of its center of symmetry.

e. The number of environments is reduced because of the center of symmetry in the molecule, which produces some meso isomers.

B. Experimental

The isoprenoid compounds studied here were obtained from standard commercial sources. They were used without further purification.

NMR spectra were obtained either at 75.5 MHz on the Varian SC-300 spectrometer in our laboratory or at 125 MHz on a Bruker WM-500 instrument at Karlsruhe, West Germany. Approximately 30% $CDCl_3$ was added to the samples as a lock and tuning solvent, together with a small amount of tetramethylsilane (TMS) used as an internal chemical shift reference. The instruments were operated in the pulsed, Fourier transform mode with broadband proton decoupling.

C. Results and Discussion

Carbon-13 NMR data for the four compounds of interest is presented in Table II-2. The chemical shifts for two of the molecules have been adjusted by a small amount in an effort to minimize concentration effects and to get all of the data on a common scale. Careful evaluation of Table II-2 reveals that the chemical shift environments of the carbons in these molecules may be segregated for general assignment purposes solely on the basis of the number of carbons which are located one bond (alpha), two bonds (beta), and three bonds (gamma) from the position of interest, i.e. the primary identifications may be make solely by counting the near neighbors of a given carbon. For example, a terminal methyl, having one alpha, two beta, and one gamma neighbors, will produce a resonance line near 25.0 ppm. These observations are summarized in Table II-3. Although there is some spread in the chemical shifts of the various environments due to the stereochemical effects, no overlap is found among the ranges, so that general assignments for related compounds can made without ambiguity by comparing chemical shifts with those given in Table II-3. Further identification of the individual resonances occuring within the ranges is also possible, as described below.

The ^{13}C spectrum of farnesane is given in Figure II-5. Inspection of that data reveals that most of the carbons beyond C-5 are represented by doublets of equal intensity. That result is indicative that our sample is the 6(R,S),10(R,S) compound, having uniform distribution of the possible stereoisomers. This spectrum is consistent with that expected for a synthetic substance, probably prepared by stereorandom hydrogenation of the relevant olefin.

The spectrum of pristane is presented in Figure II-6. In this case it is evident that each carbon position has produced only a single resonance line, leading to the conclusion that the spectrum was indeed produced by a pure diastereomer. Pristane from biological sources is normally the 6(R),10(S) compound,[11] and thus our sample is probably a natural product of that stereochemistry.

Phytane produced initially unexpected results. There are three chiral centers in that molecule, so that it is possible to have a mixture of four diastereomers, each consisting of an enantiomeric pair. However, as inspection of Figure II-7 reveals, none of the carbon positions produced the four resonance lines that would be expected for a mixture of random chirality. In fact, positions C-5, C-6, and C-6a produced only singlets rather than the doublets which would be expected from a compound with 6(R,S),10(R,S) chirality. Doublets are observed for C-7 and C-9 through C-16. These findings indicate that our phytane sample exhibits mixed stereochemistry, having only

Table II-2: ^{13}C Chemical Shifts of Selected, Saturated Acyclic Isoprenoids

Position	Farnesane[a,b]	Pristane	Phytane[c]	Squalane[d]
1,1'	22.67	22.69	22.69	22.72
	22.76	22.78	22.78	22.82
2	28.12	28.08	28.09	28.05
3	39.62	39.51	39.53	39.53
4	25.02	24.92	24.94	24.94
				24.95
5	37.55	37.43	37.44	37.46
	37.64			37.55
6	32.97	32.92	32.92	32.86
	32.99			32.89
6a	19.71	19.81	19.82	19.77
	19.77			19.83
7	37.66	37.60	37.56	37.57
	37.71		37.61	37.62
8	24.70	24.59	24.63	24.61
9	37.20		37.51	37.55
	37.25		37.56	37.57
				37.59
				37.62
10	34.62		32.91	32.86
			32.94	32.88
				32.89
				32.91
10a	19.22		19.80	19.78
	19.28		19.86	19.80
				19.85
				19.86
11	29.65		37.61	37.27
	29.75		37.65	37.28
				37.37
				37.38
12	11.38		24.60	27.58
	11.40		24.61	27.60
				27.60
				27.61
13			37.10	
			37.15	
14			34.55	
			34.56	
14a			19.26	
			19.32	
15			29.59	
			29.69	
16			11.45	
			11.47	

a. All chemical shifts are in ppm from TMS.

b. In an effort to minimize concentration and/or solvent effects, 0.1 ppm was subtracted from measured values.

c. Carbons 7, 9, and 11 are not assigned incontrovertibly and may be interchanged.

d. Same as b, except the data was shifted by 0.3 ppm.

Table II-3: The Carbon-13 Chemical Shift Ranges Encountered for Various Environments in Selected, Saturated Acyclic Isoprenoids

Environment[a] αβγ	Farnesane[b]	Pristane	Phytane	Squalane	Δδ
231	39.7	39.5	39.5	39.8	0.3
232	37.3-37.8	37.4-37.6	37.1-37.6	37.6-37.9	0.8
321	34.7		34.6		0.1
322	33.1	32.9	32.9	33.2	0.3
221	29.8		29.6		0.2
311	28.2	28.1	28.1	28.4	0.3
223				27.9	0.0
224	24.8-25.1	24.6-24.9	24.6-24.9	24.9-25.2	0.6
121	22.8	22.7-22.8	22.7-22.8	23.0-23.1	0.4
122	19.3-19.9	19.8	19.3-19.8	20.1-20.2	0.9
112	11.5		11.5		0.0

a. The numbers of carbons located one, two, and three bonds, respectively, from the carbon of interest.

b. All chemical shifts measured from TMS without correction for concentration effects.

one configuration present at C-6 and C-10, but both R and S geometries at C-14. Naturally occurring phytol is a 7(R),11(S) compound with a double bond at C-2 and an OH function at C-1. Random saturation of the double bond and removal of the OH would result in a mixture with a 6(R),10(S),14(R,S) stereochemistry, in agreement with the observed results. Thus we conclude that this sample of phytane was produced from the natural product. Note that C-7 appears as a doublet, although it is seven bonds distant from the nearest carbon positon of random chirality at C-14. In the past it has not been possible to identify conformational effects originating at such remote positions, because the small chemical shifts involved are normally impossible to distinguish from solvent, concentration, etc. effects of similar magnitude. The presence of internal fiducial marks, i.e. resonances of corresponding carbons in other isomers, allows the long-range effects to be certified.

Squalane is not known to occur in nature, but the corresponding unsaturated compound, squalene, i.e. the 2,6,10,14,18,22-hexaolefin, is a natural product. Thus it is probable that commercial squalane is derived from squalene by saturation of the double bonds. Non-selective hydrogenation would produce a mixture of random (R,S) configuration. The spectrum of squalane is, in fact,

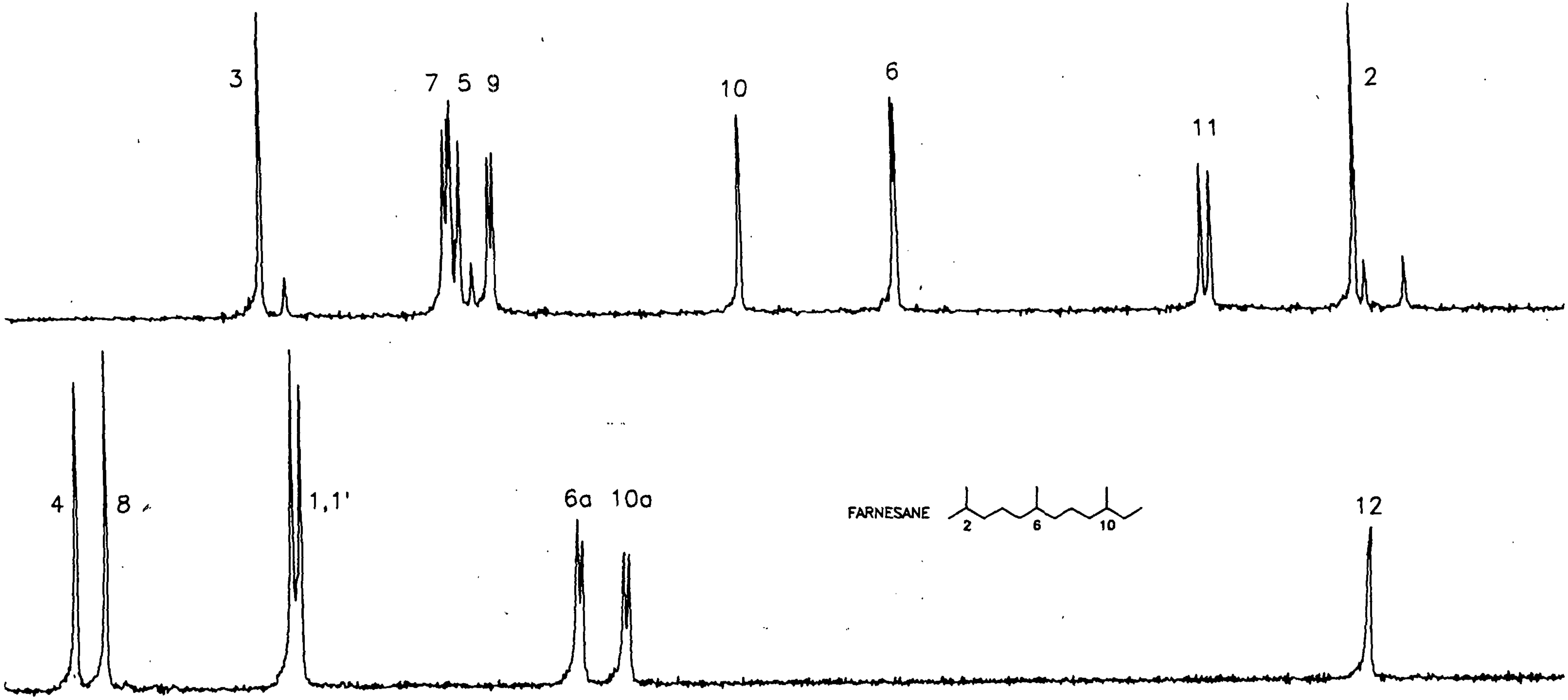


Figure II-5: The 75 MHz ^{13}C spectrum of farnesane. Random stereochemistry is evidenced by the presence of two resonance lines at many positions.

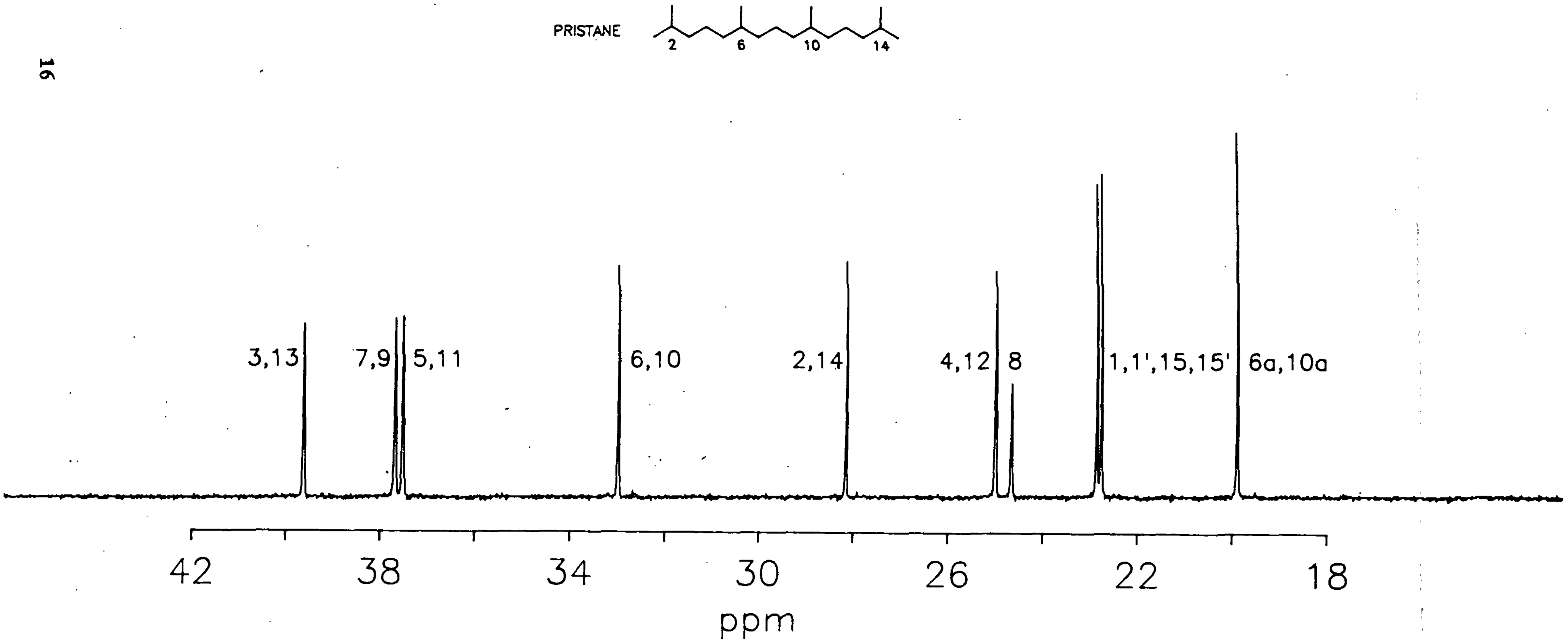


Figure II-6: The 75 MHz ^{13}C spectrum of pristane. Only a single diastereomer is detected.

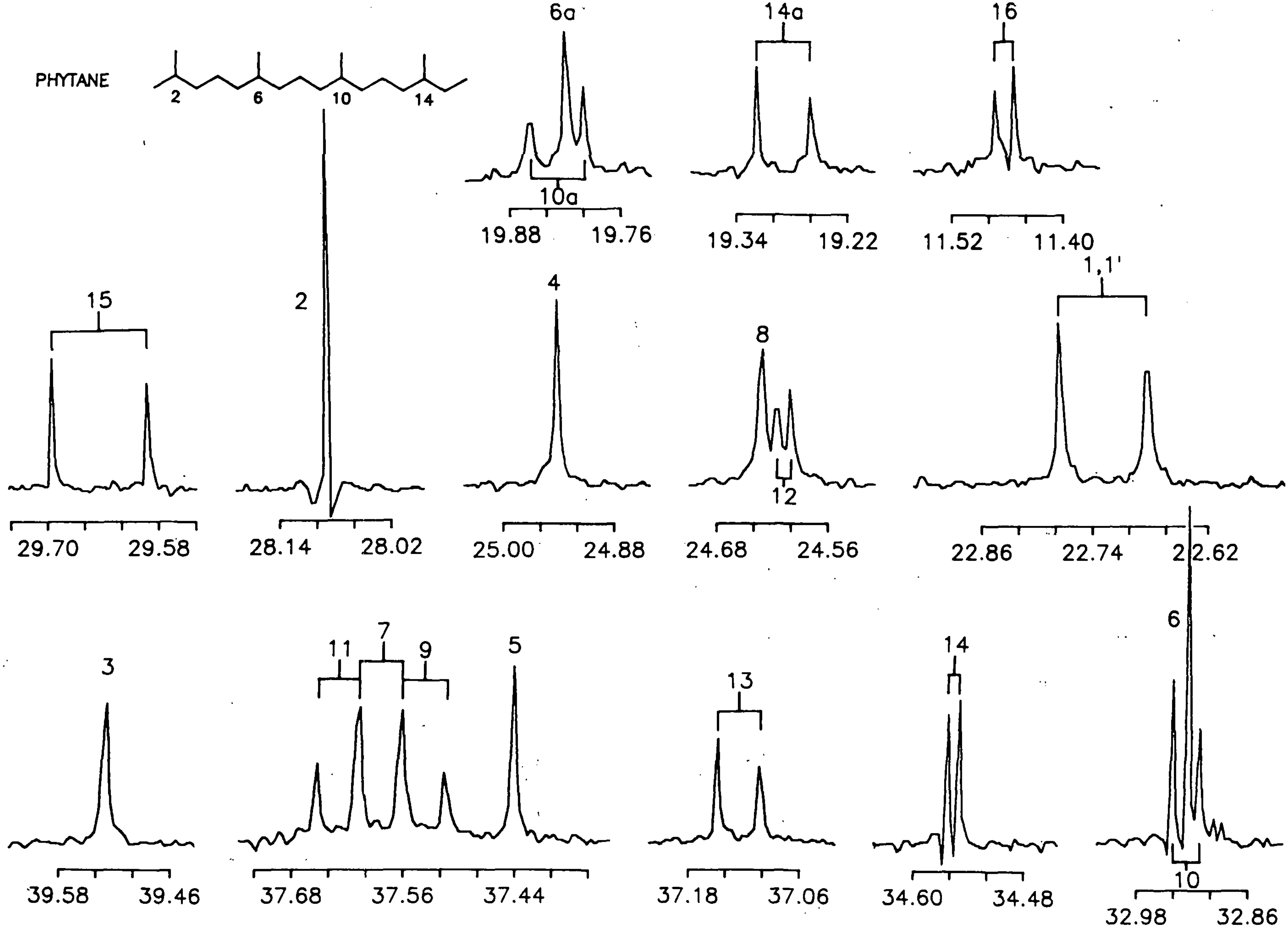


Figure II-7: The 75 MHz ^{13}C spectrum of phytane, resolution enhanced and plotted on an expanded scale (.04 ppm/division). Mixed stereochemistry is indicated, because no quartets are detected while doublets are.

the most complex of the compounds studied here, since the environment of some of the carbons is influenced by three of the six (R,S) chiral centers, resulting in four resonance lines for those positions. The detailed spectrum has been resolution enhanced and plotted on an expanded scale in Figure II-8. Assignments of the closely spaced lines to specific carbon positions is facilitated by the quartet structure observed for one of each of the pairs 6,10 and 6a,10a. For the four carbons appearing near 37.6 ppm the same criterion may be used to segregate C-5, C-7 from C-9, C-11. Further assignments within closely spaced groups of peaks may be made here by observing the regularity of the chemical shift differences which occur for carbons in similar environments. For example, methylenes adjacent to a chiral carbon, but not between chiral centers (e.g. C-15 of phytane), exhibit a diastereomeric shift difference of 0.09-0.10 ppm, while alpha methylenes between chiral centers, such as C-7 of squalane, are separated only by 0.04-0.05 ppm. Similar generalizations may be made for other environments in the molecules. Since these splitting patterns are common to all three of the compounds which exhibit stereoisomerism, a self-consistent set of assignments can be generated. These results are summarized in Table II-4.

It would be desirable to assign the resonances of Table II-2 to specific diastereomeric configurations, but this is extremely difficult to do reliably because of the small chemical shift differences involved. The most certain method would be to obtain pure diastereomers of known stereochemistry, mix them in proportions other than 1:1, and obtain the NMR spectra. Unfortunately, such isomers of known, pure stereochemistry are not readily available. A calculational method has been implemented by Beierbeck and Saunders[19] for determination of chemical shifts as a weighted average of possible rotamers. In principle, this method could be used to distinguish diastereomers, providing that the calculation can be extended from its present three bonds to six or seven bonds. This approach has not been tried by us because of the enormous complexity of the extended analysis and the very small chemical shift separations involved.

The work of Elgert and Ritter[20] on an analogous polymer molecule, poly[1-methyltetramethylene], may be used to make tentative assignments for some of the isomeric shifts of Table II-2. Working at 22.6 MHz, they observed fine structure in the ^{13}C spectrum of the polymer for only the alpha methylene and methyl resonances, corresponding for example, to C-9 and C-10a of phytane. The above polylmer resonances were found to be sensitive to triad structure, which produces four chemical shift environments as a result of proximity to three chiral centers. For the alpha methylene, the syndiotactic configuration (racemic, racemic, or rr), generated the most downfield resonance, while the isotactic configuration (meso, meso or mm), produced the most upfield line.

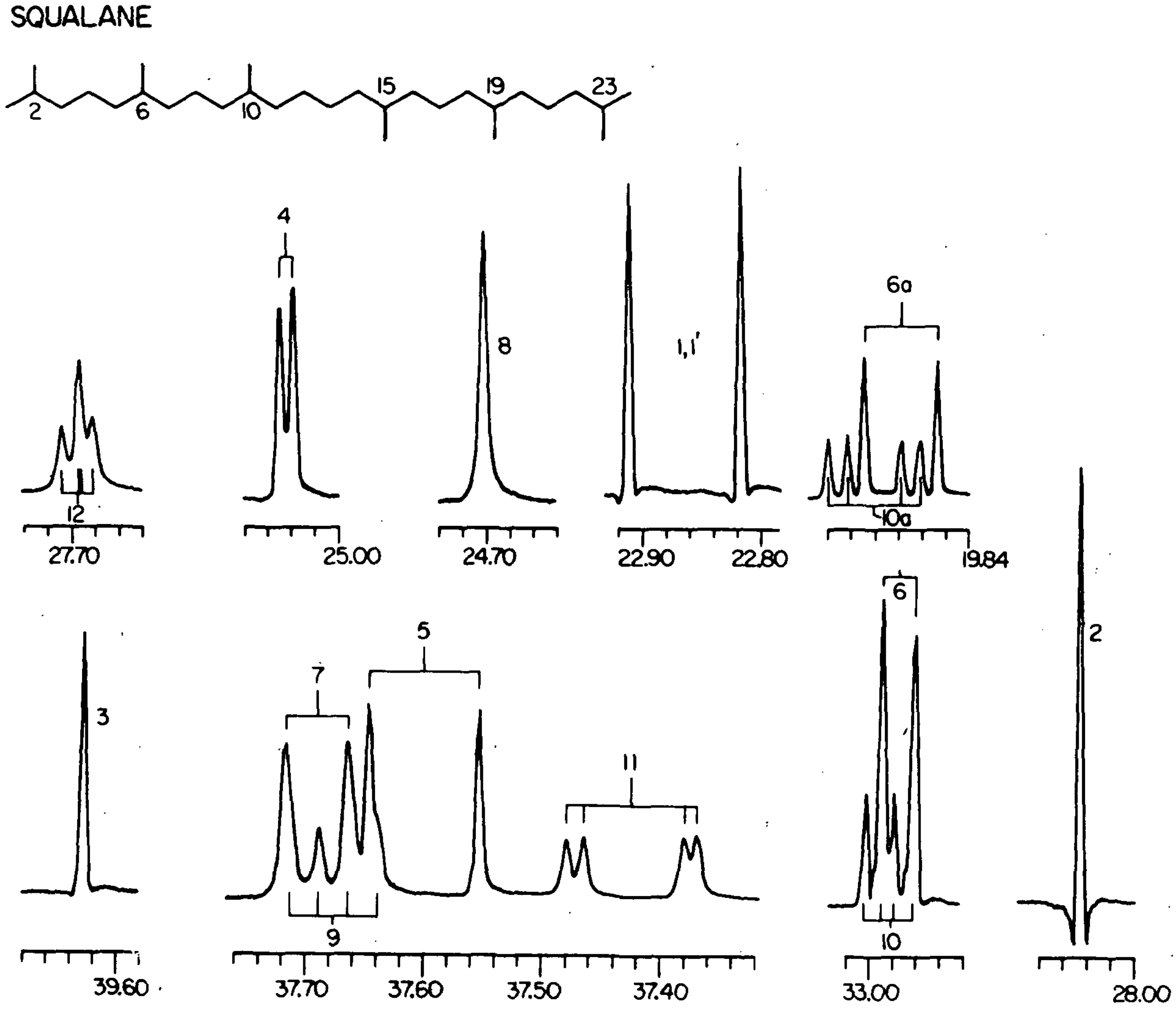


Figure II-8: The 125 MHz ^{13}C spectrum of squalane, resolution enhanced and plotted on an expanded scale (.02 ppm/division). Four lines are observed for carbons which are influenced by three chiral centers.

Table II-4: Carbon-13 Chemical Shift Ranges Produced by Diastereomeric Effects in Selected, Saturated Acyclic Isoprenoids

Environment[a]	Observed $\Delta\delta$[b]	Representative Examples[c]
CH_2 α to CC, not between four-bond CC's	0.09-0.10	F-5, P-15, S-5
CH_3 α to CC	0.06-0.07	F-6a, P-14a, S-10a
CH_2 α to CC, between four-bond CC's	0.04-0.05	F-7, P-11, S-9
CH at CC	0.00-0.03	F-10, P-10, S-10
CH_2 β to two CC's[d]	0.00-0.01	F-8, P-12, S-8
Long range, due to third CC	0.00-0.03	S-8, S-9, S-10
Terminal *gem* methyls[e]	0.09-0.10	F-1, P-1, S-1

a. CC = chiral center, α = one bond removed, β = two bonds removed.

b. In parts per million.

c. F = farnesane, P = phytane, S = squalane.

d. Also β to one CC and one prochiral center; examples: F-4, P-4, S-4.

e. Shift difference results from presence of only one CC, which makes terminal methyls diastereotopic.

The resulting order, low to highfield, for the resonances was rr, *r*m, *m*r, mm, the primary position of the carbon of interest being indicated for the heterotactic sites. If the acyclic isoprenoids of this study are assumed to be analogous, then the downfield resonances of pairs belonging to C-7 and C-9 of farnesane (37.71 and 37.25 ppm, respectively) can be assigned to the 6(R),10(R) and 6(S),10(S) enantiomeric pair, while the upfield lines (37.66 and 37.20 ppm, respectively) would then be attributed to the RS isomers, and similarly for relevant positons in the other molecules. In the case of the methyls, the ordering is opposite, as the isotactic methyls produce the farthest downfield resonance, and the syndiotactic isomers generate the most upfield line of the set. The corresponding assignment for C-10a of phytane would be 19.86 ppm to the 6(R),10(S),14(S) compound and 19.80 ppm to the 6(R),10(S),14(R) isomer. Again, similar tentative assignments may be made in the other molecules having methyls in analogous environments.

The above results demonstrate that high field ^{13}C NMR can be of great utility in the study of diastereomeric compounds. We have been able to segregate natural products from synthetic ones in a rather simple manner. It has also been shown that it is possible to distinguish the relative populations of diastereomers in a mixture of unknown proportions. Ready access to such information may provide geochemists with a powerful new tool which may be used to characterize the diagenesis and maturation of geoderived hydrocarbons. Other branches of chemistry involved in the synthesis of sterespecific molecules may also be able to utilize the above described techniques. Biocompounds of unknown stereochemistry may be amenable to characterizaton by this type of analysis as well. We envision that there will be increasing usage of high-field ^{13}C NMR analysis in many areas of chemistry involving diastereomeric compounds.

Page intentionally left blank

Page intentionally left blank

III. PREPARATIVE SCALE SUPERCRITICAL FLUID CHROMATOGRAPHY

A. Background

The accurate determination of the average parameters of fuels by use of NMR requires that the fuels be separated into saturates and aromatics fractions. In the past this separation has been effected by use of gas chromatography, high performance liquid chromatography, and various types of open column liquid chromatography. Each of these techniques suffers from some deficiencies as far as NMR spectroscopists are concerned. In gas chromatography it is often difficult and tedious to acquire sufficient fraction size and to separate mixtures containing high molecular weight components. In liquid chromatography it is necessary that the fuel fractions be recovered intact from any solvent which has been used in the separation process. This often proves to be quite difficult to do and, especially if low molecular weight compounds are present, likely results in partial sample loss or residual solvent contamination. The solution to the above problems may be application of a novel technique termed supercritical fluid chromatography or SCFC.

When a substance is heated above its critical temperature, it can no longer be induced to make a phase transition from gas to liquid by an arbitrary increase in pressure. However, densities can be achieved which are similar or even greater than those found in the liquid state. Gaseous substances of high density above their critical temperature are called supercritical fluids. They have viscosities comparable to those of normal gases, which is approximately two orders of magnitude less than the corresponding liquids. Their diffusivity, however, usually falls midway between that of a normal gas and liquid. The solubilizing power of supercritical fluids is similar to that of normal liquids. A successful application of the SCFC technique was first demonstrated in 1961.[21] SCFC has attracted the recent attention of analytical chemists, because of the possibility of using it in separation procedures involving high molecular weight compounds, extended molecular weight ranges, and thermally labile compounds. Recent articles have detailed the current practice of the technique as it is currently being developed.[22, 23, 24]

Although quite a number of compounds have been employed as solvents in SCFC, perhaps the ideal effluent for most NMR applicatons is carbon dioxide. It is nontoxic and nonflammable. Its critical temperature (31.3 °C) is near normal laboratory temperatures, and it is readily purchasable as a liquid in standard siphon steel cylinders. CO_2 has no protons to interfere in ^1H NMR, and its single carbon resonance is in the carboxyl area of the ^{13}C spectrum, which will not normally create interference in fuels samples. In fact, our experience has indicated that CO_2 is sufficiently insoluble in liquid hydrocarbons at ambient temperatures and pressures that we have never detected a residual solvent peak in our fractionated samples.

B. Instrumentation and Procedure

SCFC separations were performed on a modified Perkin-Elmer Series 3B Liquid Chromatograph. The instrument has dual reciprocating piston pumps, each with two heads, and a pumping capacity of 30 ml/min. Detection is accomplished with a Perkin-Elmer LC75 Spectrophotometric Detector connected to a Tracor stripchart recorder.

The Magnum 20 columns utilized were purchased from Whatman Inc. They are 50 cm in length with a 22 mm ID and contain 10 micron silica gel particles. The active phases were either cyano-amino (Partisil-10 PAC) or octadecylsilane (Partisil-10 ODS). The separation column was mounted vertically in a plexiglas bath in which water was circulated from a reservoir, regulated by a Haake D-1 temperature controller. Outlet pressure to the UV detector was controlled by a Tescom Corp. regulator.

Waste and sample routing was accomplished by use of an eight position valve supplied by Valco Instruments Co., Inc. Waste was collected in a standard CO_2 pressure cylinder, while sample flow was directed into high pressure (1800 psi) collectors. The collection vessels consisted of a 500 ml upper chamber and a 70 ml lower chamber. The two vessels were connected to each other and to the switching valve with high pressure Whitey valves.

In order to function adequately for supercritical operation, several modifications were made to the chromatograph. Liquid CO_2 was fed directly to the pump from a siphon tank without regulation. However the liquid was cooled enroute to the pump by passing through a loop immersed in an ice water bath in order to prevent premature vaporization. Because of the large amount of heat generated by the high compression ratio piston pumps, dry ice heat exchangers were mounted on the outside of the pump heads, and these were kept filled during operation.

CO_2 was pumped as a liquid to a desired pressure, as indicated by the transducer readout on the instrument itself and by an exterior manual pressure gauge teed at the pump outlet (or equivalently, at the column inlet). A graph of column inlet pressure versus pump speed is presented in Figure III-1. The instrument has been fitted with a backflush valve which allows flow in either direction across the column. A high pressure loop injector system has also been added, which has an injection capacity of 2 ml. Before reaching the column, the effluent passes through a coil which is immersed in the temperature reservoir. This heating brings the CO_2 to supercritical conditions.

A second mechanical pressure gauge has been added to the outlet of the UV detector, tapped into the system by way of a three-way on/off valve, so that it may be isolated during actual separations. This guage has been added to the system to protect the seals of the UV cell, which can only withstand a pressure of 2000 psi. For extended operation a maximum outlet pressure of 1200 psi is recommended.

The elution of a complete sample through the column requires quite a long time, usually 45 minutes to one and one-half hours. In order to make the separation of saturates and aromatics more efficient, the following mode of operation was adopted: After injection, the effluent was dumped into the waste receptacle until collection of the saturates fraction was begun. The saturates fraction was collected until the recorder deflection indicated that the first aromatic peak was coming through. At that point the flow was reversed, taking the aromatics back onto the column. Collection was then continued for a few more minutes to assure that all of the saturates fraction had cleared the backpressure valve, which has a significant holdup. The effluent was then directed into the waste collector again, until the aromatics again began to come off the column, at which time they were gathered in a second collection apparatus. Since the column has been reversed, all of the aromatics come off the column in a single peak. This not only significantly shortens the time required to perform the separation, but also obviates the necessity of using more than one collector for the aromatics fraction, which otherwise would be of a volume too great to be held in a single collector.

Quantitative fraction collection is accomplished in the following manner: The product collection vessels are cleaned and oven dried previous to use. The 70 ml bottle must be tared with an internal CO_2 atmosphere if accurate fraction weights are to be determined. This is accomplished by introducing CO_2 from the siphon tank via a drain hose connected to the chromatograph pumping system. Exposing the liquid to the atmosphere produces a mixture of gas and CO_2 snow, which is injected into the small cylinder for about 15 sec. A high pressure valve is then screwed into place, and the vessel is allowed to come to ambient pressure and temperature before weighing. The small bottle is then connected to the bottom of the 500 ml vessel, which also has a high pressure valve attached at the top. After the relevant fraction has been collected, the bottles are removed from the chromatograph with the topmost valve closed, and they are immersed in a dewar of liquid nitrogen until completely frozen or until only a very slight positive pressure is detected when the top valve is cracked. The cylinders are then positioned vertically in a thawing rack and

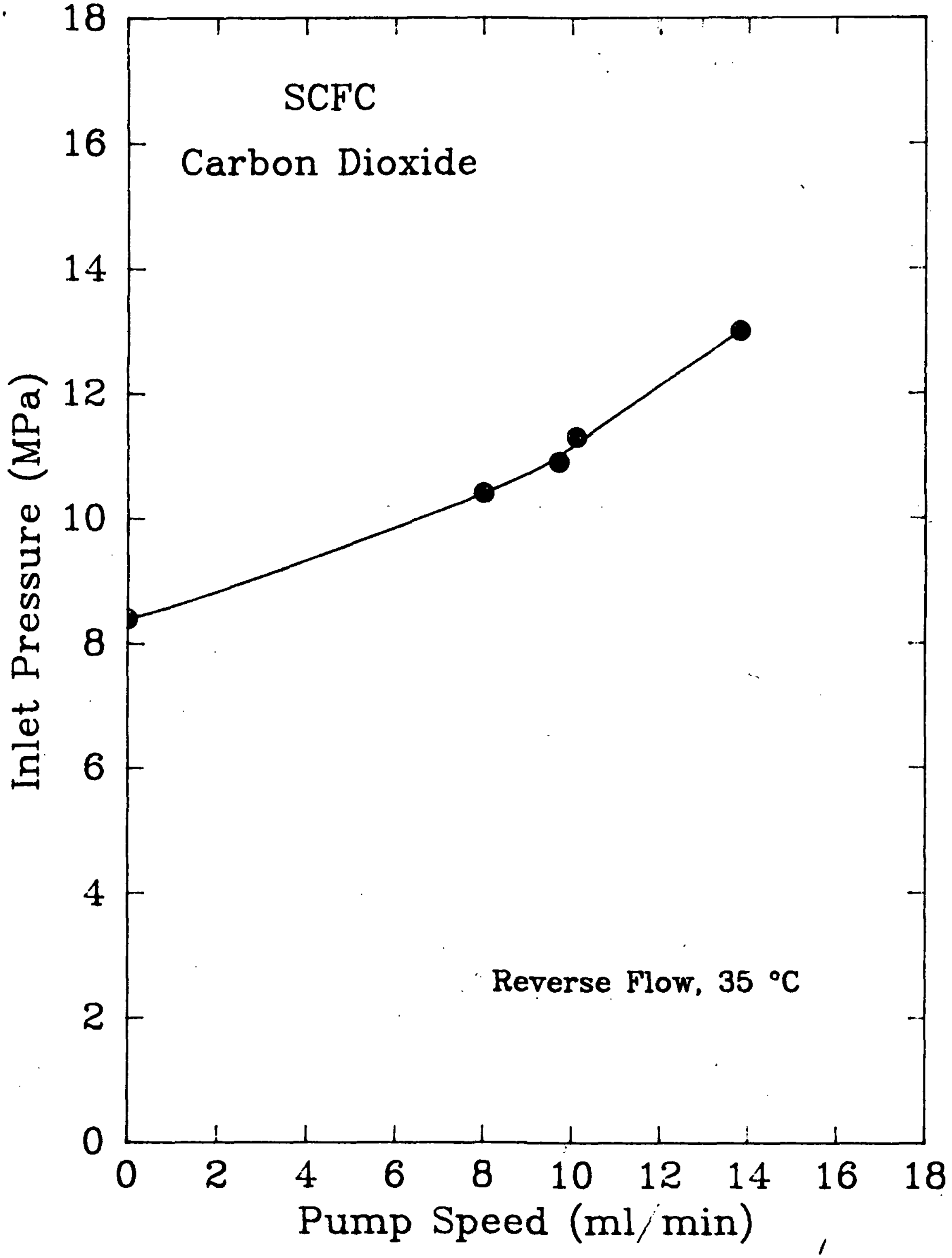


Figure III-1: The variation of column inlet pressure with pump speed when pumping liquid CO_2 in SCFC.

the CO_2 is allowed to sublime away. This usually requires about three hours; progress may be monitored by noting the thawing of ice which accumulates on the outside of the vessels. Completion of the process may be ascertained by closing the top valve for a few minutes and then reopening it to see if any pressure has accumulated. After all of the CO_2 has dissipated, the valve between the cylinders is closed, and the top vessel is removed. The 70 ml bottle may then be wiped clean and reweighed to determine the weight of fraction collected. At that point the sample may be transfered to a more customary storage container by means of a disposable pipette or other suitable transfer device.

C. Discussion

The use of SCFC on complex fuel samples provides a similar separation to that obtainable with HPLC. This is illustrated by comparison of Figures III-2 and III-3. The latter were acquired on microliter injections as full prep scale injection normally produces off-scale peaks. Of course, there is no way to detect the saturates fraction in SCFC, but the general separation by number of aromatic rings appears to be very similar for the two cases.

Since it is not possible to detect the saturates in normal operation, and the saturates and single-ring aromatics peaks appear to elute in very close proximity, it is necessary to perform some very careful calibrations before attempting a saturates-aromatics separation. We performed the calibration using dodecane and toluene. Three quantities must be determined: The length of time which an unretained solute requires to pass through the column to the detector, the time between the saturates and the first aromatic material (as measured at the baseline), and the variation of peak width under various conditions. The length of time required for 1 ml of dodecane to pass through our system is illustrated in Figure III-4. The period between the dodecane and toluene peaks varies on our apparatus with pump speed as shown in Figure III-5. The peak width as a function of both pump speed and injection volume is illustrated in Figure III-6 It is necessary to choose a pump speed and injection volume such that the width of the saturates peak is less than the separation between it and the one-ring aromatics.

The success of the separation is attested by the results shown in Table V-2 of Chapter V. The hydrogen content given for the ERBS samples there was calculated from the fractions, and is seen to agree with the values determined by a very accurate proton NMR method to within one percent.

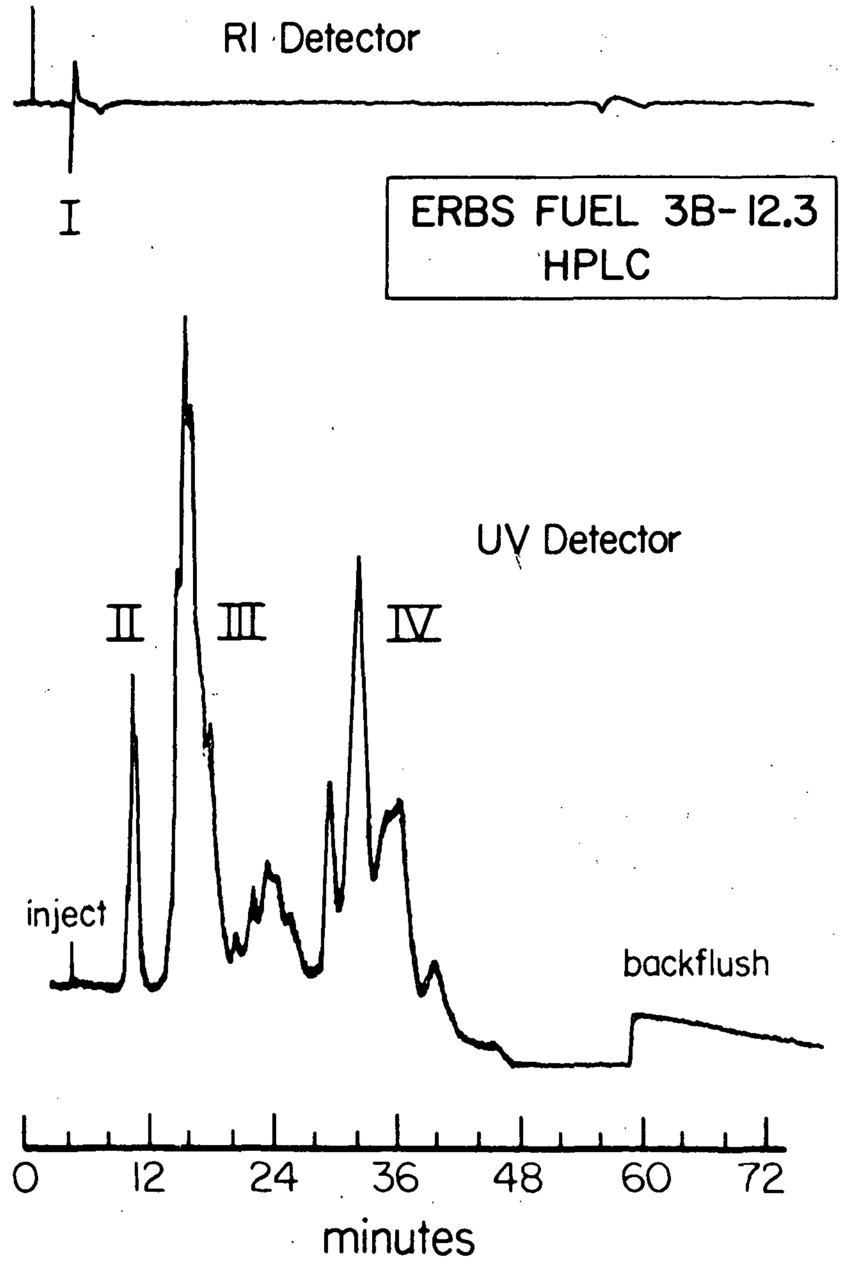


Figure III-2: The HPLC separation of one of the ERBS samples discussed in Chapter V. I, saturates; II, one-ring aromatics; III, two-ring aromatics; IV, three- and four-ring aromatics.

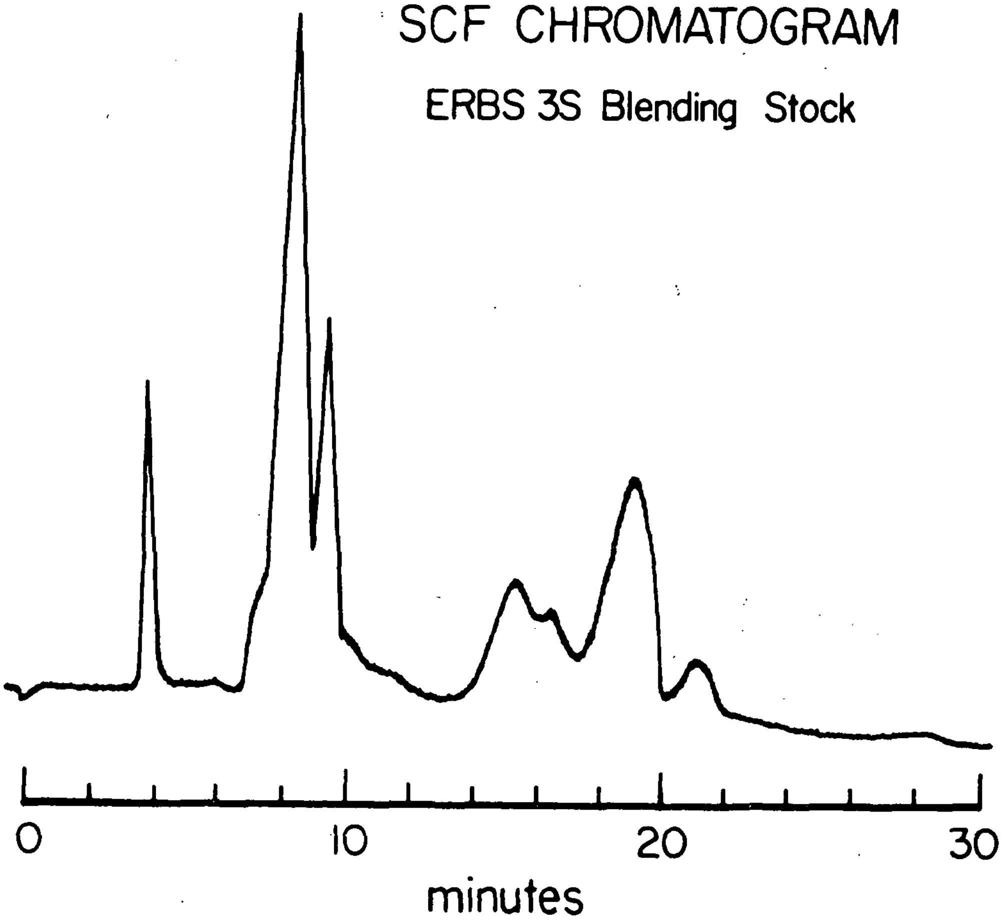


Figure III-3: The SCFC separation of the ERBS-3S sample discussed in Chapter V. Although saturates cannot be detected, the separation of the ring compounds is very similar to that noted for HPLC in Figure III-2.

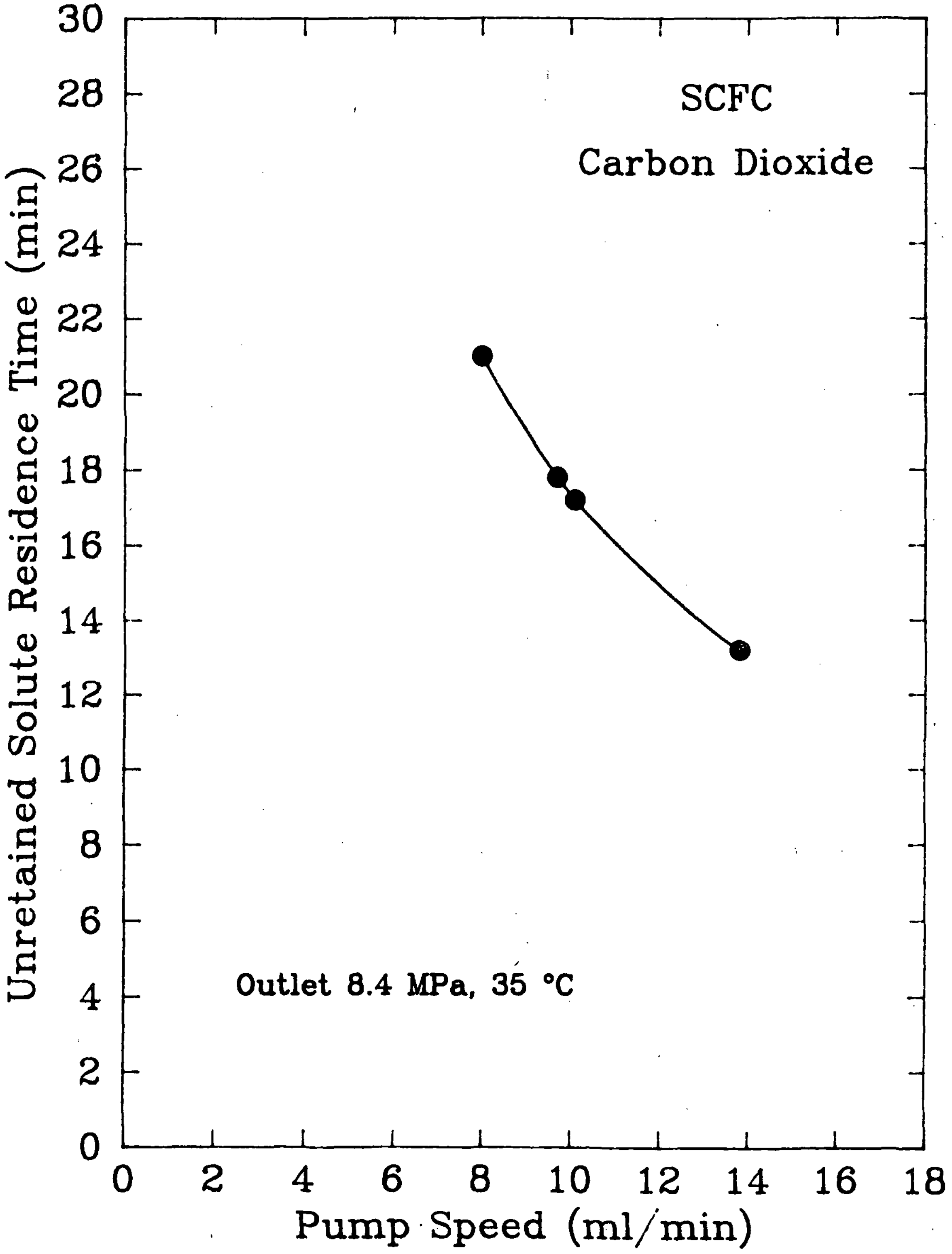


Figure III-4: The time which an unretained solute requires to pass through the cyano-amino Magnum-20 column versus pump speed for SCFC utilizing supercritical CO_2. A one ml injection was employed.

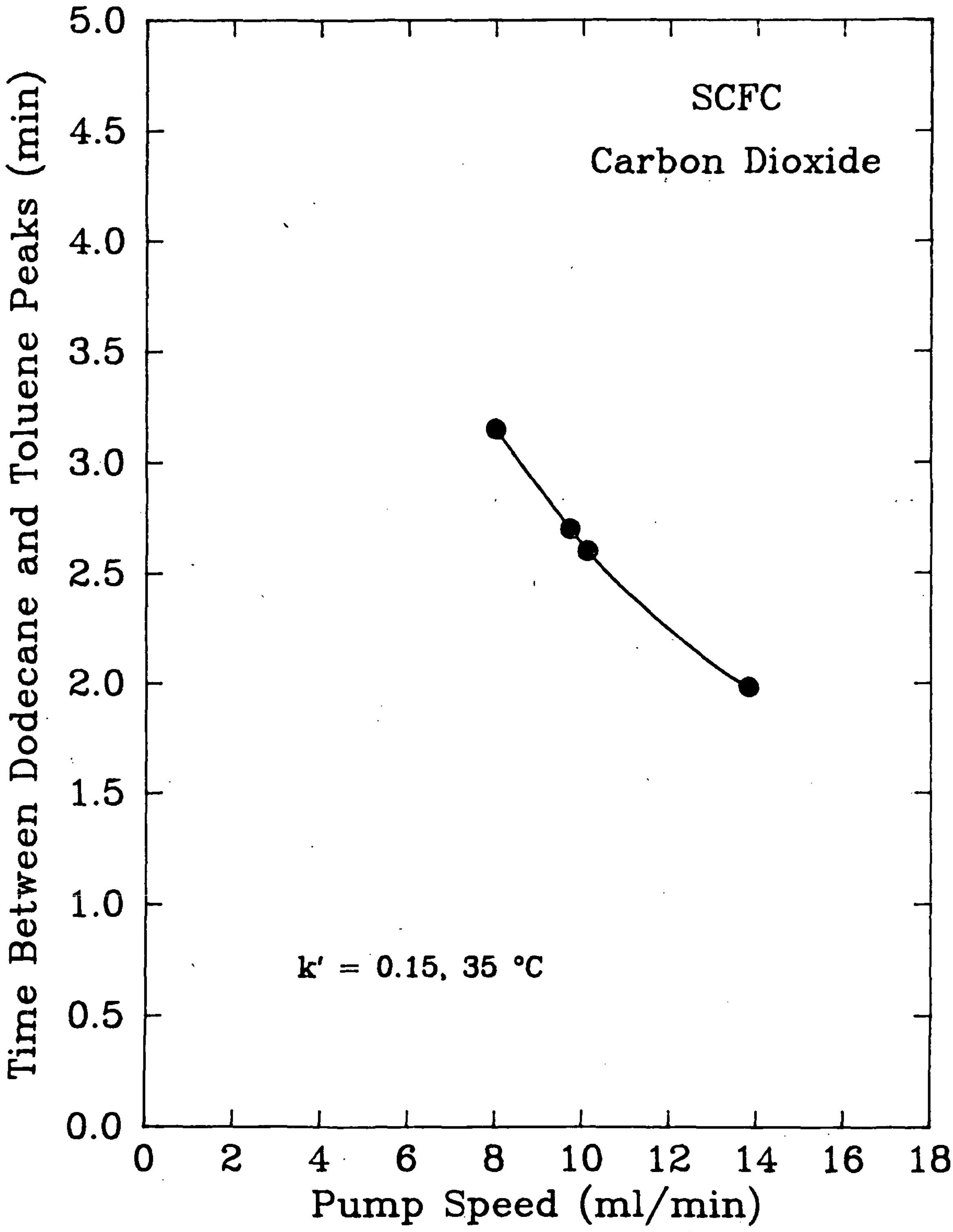


Figure III-5: The resolution time between toluene and dodecane peaks, as measured at the baseline, versus pump speed, for SCFC utilizing supercritical CO_2. A one ml injection was employed.

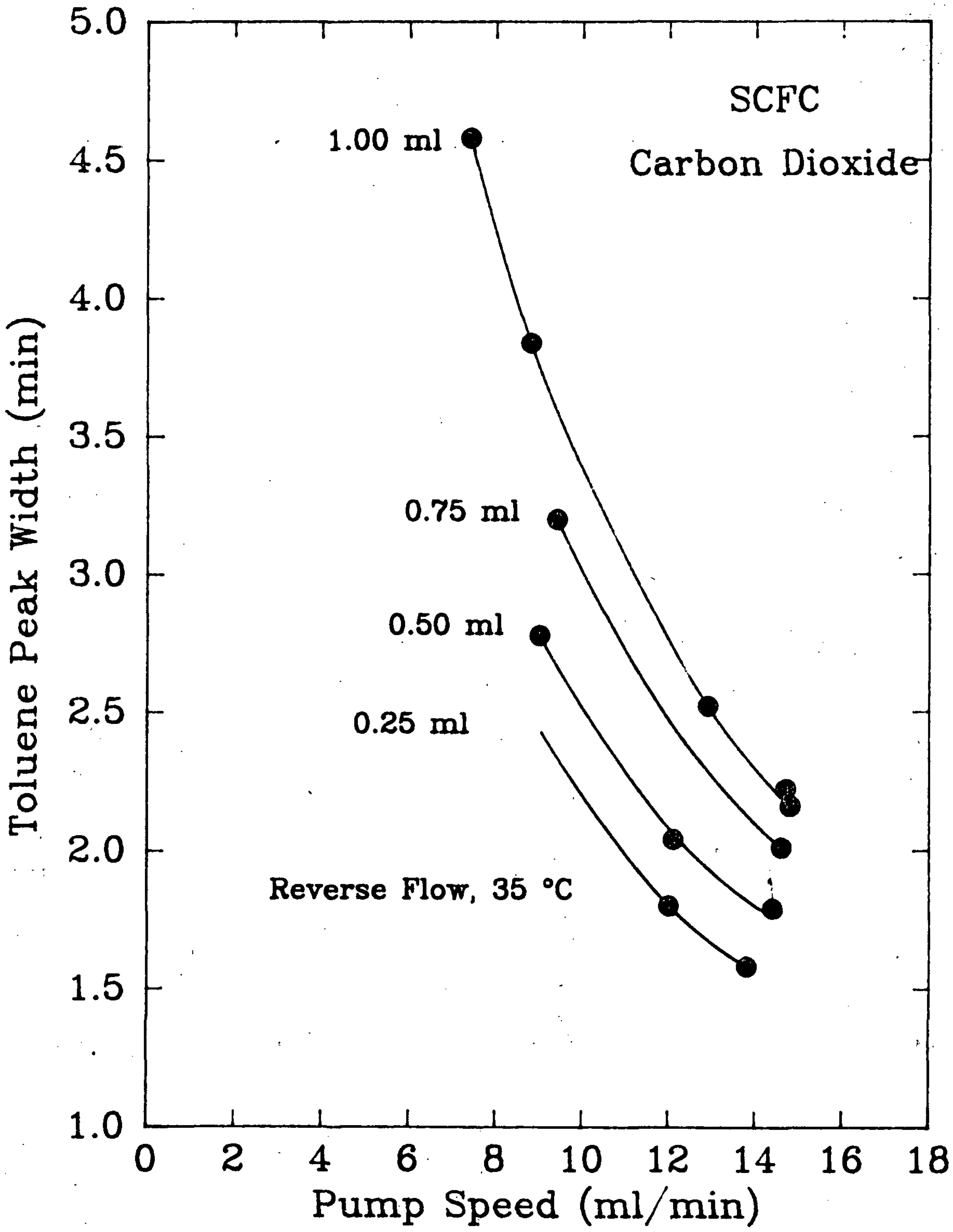


Figure III-6: The variation of elution peak width, measured at the baseline, with pump speed and with the volume of sample injected for SCFC. The standard sample is toluene.

IV. ANALYSIS OF SHALE OIL REFINERY PRODUCTS

A. Introduction

As a result of uncertainties in crude petroleum source and supply which developed in the 1970's, the National Aeronautics and Space Administration (NASA) and the United States Air Force (USAF) undertook the evaluation of alternate, nontraditional crude feedstocks as sources for the refining of aviation kerosene. Oil bearing shale is considered to be one of the prime candidates as an alternative source of fuel hydocarbons, and both internal[25, 26] and contract[27, 28, 29] research programs were developed to determine the feasibility of using shale derived crude oil as a source for military jet fuels.

Although refining of jet fuels from shale may not result in changes in the traditional macrospecifications, such as freeze point, viscosity, etc. which are applied to them, there may be significant changes in properties which are not normally monitored, but which may be important to proper operating characteristics. For this reason it was decided to examine shale oil refinery products by use of NMR. The samples chosen for study were generated by the Extractacracking Process developed by Ashland Petroleum Co. under contract to the USAF.[29]

B. Analysis of the Refinery Products

Twenty-four samples were extracted from the refinery stream for purposes of this study. They are listed in Table IV-1; the location of these samples in the refining scheme is given in Figure IV-1, insofar as we were able to decipher the proprietary process with the information supplied. Apparently, some of the finished fuel was derived from processing of distillation overhead which was not subjected to fluid catalytic cracking, while other fuel was produced from a blend of 65% hydrotreatment distillation (600- °F) overhead, 35% fluid catalytic cracked overhead. It was not always abundantly clear from which of these sources later samples were derived, or whether the two streams were recombined at some point.

Proton and carbon-13 NMR spectra have been acquired for all of the samples. In order to obtain quantitative estimates of the various kinds of carbon in the products, it is necessary to obtain ^{13}C spectra for which the nuclear Overhauser enhancement (NOE) is suppressed by gated decoupling techniques. A relatively long acquisition cycle time must also be used to minimize saturation effects in the unprotonated carbons, which occur principally in the aromatic spectral region at the substituted and bridgehead positions. Cycling

Table IV-1: Samples Obtained from the Ashland Extractacracking Process

A. Occidental crude shale oil

B. Hydrotreated shale oil, 0.5 LHSV, 3000 SCFH H_2

C. Hydrotreated shale oil, distilled overhead, 600- °F

D. Hydrotreated shale oil, distilled bottoms, 600+ °F

E. Liquid product from fluid catalytic cracker (100% fresh feed)

F_1. FCC hydrotreated cycle oil (one pass, 100% recycled)

F_2. FCC distillation overhead 600- °F cut (no recycle hydrotreatment)

G. Charge to acid extractor

H. Raffinate from acid extractor, 600- °F (no recycle hydrotreatment)

I. Nitrogen compounds (acids removed: 65% overhead from distillation, 35% from FCC)

J. Guardcase hydrotreated full range product, 700 °F (65%, 35% feed)

K. FCC bottoms residual fuel (recycled through FCC but not through hydrotreater)

L. Effluent from reformer, JP-8 pool

M. Input to reformer, JP-4 pool

N. Output from reformer, JP-4 pool

O. JP-8, saturation product

P. JP-8, broadrange, saturation product

Q. JP-4, saturation product

R. JP-8, final product

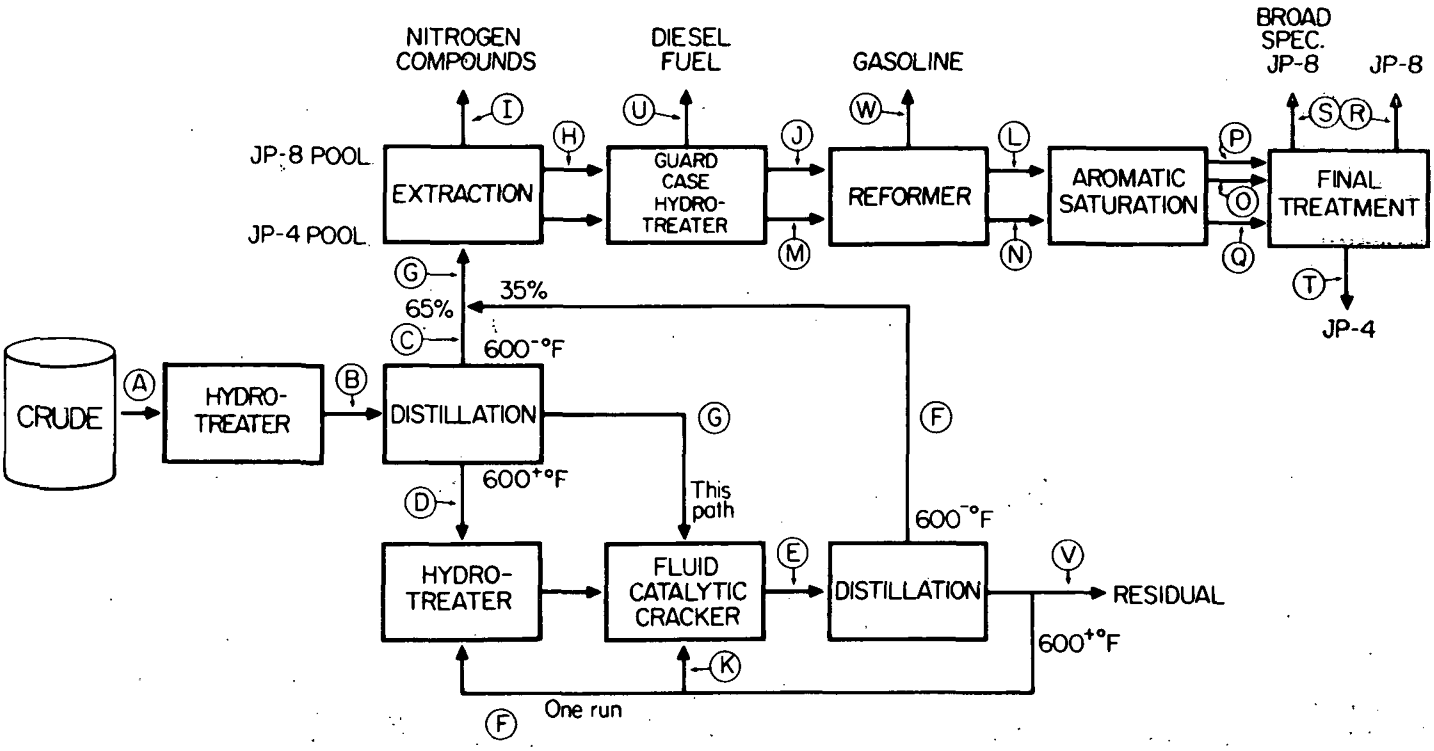
S. JP-8, broadrange, final product

T. JP-4, final product

U. Diesel fuel, final product

V. Burner fuel, final product

W. Gasoline component, final product



ASHLAND EXTRACTACRACKING PROCESS

Figure IV-1: A flow chart of the Ashland Extractacracking Process for refining shale oil. Circled letters indicate the points at which samples were removed for analysis. They are identified in Table IV-1.

at the optimal rate necessitates excessively long data acquisition periods, so a compromise must be made. We have found that a pulse angle of 45° and a pulse delay of ten seconds appears to provide adequately quantitative data for an overnight (12 to 15 hours) spectrometer run.

Aromaticities, f_a, of the various samples, as determined by ^{13}C and ^{1}H NMR, are given in Table IV-2. Reference to Figure IV-1 clarifies some of the trends indicated by the data of Table IV-2. Some of the more salient points are discussed here:

(1)The carbon spectrum of the Occidental whole crude shale (sample A), presented in Figure II-1 of Chapter II, reveals that it contains some terminal olefins, as indicated by the sharp isolated resonance lines at the extremes of the aromatic spectral region. Our understanding is that these olefins do not occur in the native shale but are generated by the retorting process. The straight chain and isoprenoid-like fragments noted in this spectrum have already been discussed (Chapter II).

(2)Initial hydrotreatment does not greatly affect f_a^H but decreases f_a^C by one-third and apparently reduces the olefins (sample B). The alkyl region of the carbon spectrum shows very little change.

(3)The 600- °F overhead from the hydrotreatment, sample C, produces a ^{13}C spectrum which indicates that the average alkyl chain length present is considerably shortened over that of Sample B and more pristane-like material is in evidence (<u>cf</u>. Figure IV-2). The aromatic spectral region has more structure, indicating the presence of some prominent species. The distillation bottoms fraction (sample D, shown in Figure IV-3), on the other hand, reveals the presence of little aromatic fine structure and markedly longer alkyl chains.

(4)Unfortunately, no sample seems to have been taken after the second hydrotreatment. Passage of sample D through the hydrotreater and fluid catalytic cracker produces a material, sample E, which has a higher aromaticity than the original shale oil, and judging from the proton spectrum, contains some olefins.

(5)There is some ambiguity in the flow chart at this point, as there have been four different sources for the samples which have been input to the fluid catalytic cracker. The sample which appears most to be a product derived from sample E is sample F_1, labelled "FCC hydrotreated cycle oil," but it contains no olefins. Sample F_2 is labelled "FCC distillation overhead," but it is more aromatic than sample E and contains more olefinic material, making it appear to have been recycled through the FCC several times. The f_a^C's of the olefin

Table IV-2: Aromaticities (f_a) of Petroleum Fractions Derived from Shale Oil as Determined by NMR Measurements

Sample[a]	f_a^C	f_a^H
A[b]	0.28	0.05
B	0.19	0.04
C	0.21	0.07
D	0.23	0.03
E[b]	0.31	0.08 (0.05)
F_1	0.24	0.05
F_2[b]	0.41	0.11 (0.07)
G[b]	0.26	0.12 (0.09)
H[b]	0.26	0.11 (0.08)
I[c]	0.44	0.06
J	0.20	0.05
K	0.48	0.17
L	0.33	0.09
M	0.22	0.05
N	0.37	0.11
O	0.08	0.02
P	0.19	0.05
Q	0.06	0.02
R	0.12	0.02
S	0.17	0.05
T	0.11	0.04
U	0.11	0.03
V	0.52	0.16
W	0.38	0.14

a. Aromaticities are integral of aromatic portion/total integral. Estimated precision: ± 0.03 for ^{13}C, ± 0.01 for ^1H. See Table IV-1 for sample identification.

b. Includes olefin content; parenthetical number, when present, discounts olefin contribution.

c. Contains NH signals.

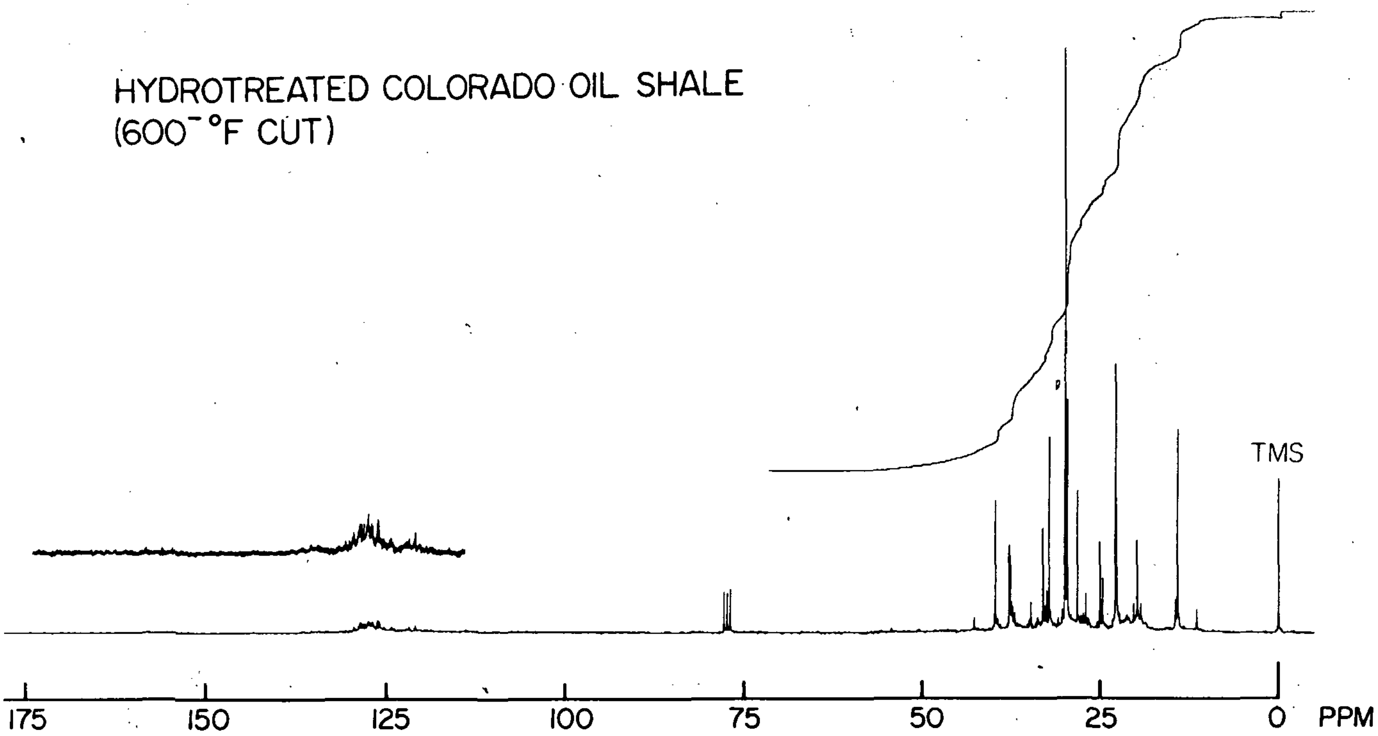


Figure IV-2: The ^{13}C NMR spectrum of overhead from the distillation of hydrotreated shale oil (sample C).

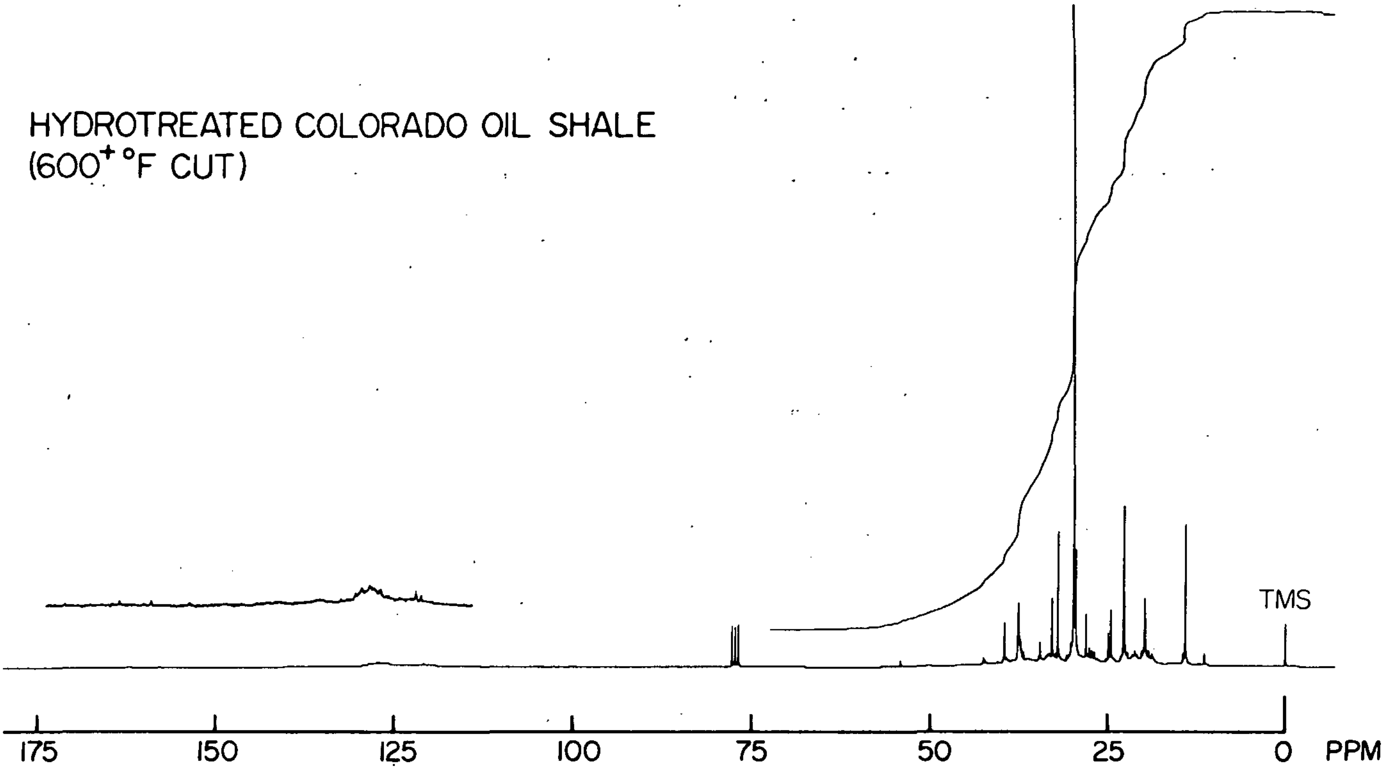


Figure IV-3: The ^{13}C NMR spectrum of distillation bottoms from the hydrotreatment of shale oil. In comparison to the overhead, the alkyl chains are much longer, and the aromatic spectral region is more complex.

containing samples are, of course, too high, because it is not possible, in general, to distinguish olefinic carbons from aromatic ones, except for those molecules having terminal double bonds.

(6)Sample K is the recycle bottoms fraction from one of multiple recycle passes to the FCC. It is highly aromatic and the alkyl chains present are rather long. There seem to be no olefins present in K.

(7)The most highly aromatic sample is V, the residual burner fuel product. The aromatic spectral region of this sample is banded, indicating great complexity. The average length of the residual alkyl chains is, however, not too great.

(8)Sample G, labelled "charge to acid extractor," is a mixture of 65% of sample C and 35% of a distillation overhead from a sample which has passed through the FCC but not the second hydrotreatment. Olefins are very evident in this sample and naphthenic content is fairly high.

(9)The raffinate from the acid extraction, sample H, produces spectra which are very similar to those of G. All of the olefins appear to have remained in this fraction.

(10)The spectra of sample I, the extracted nitrogen compounds, are very unusual, like those of no other sample in this set. The carbon spectrum of this sample is presented in Figure IV-4, upon which are indicated some of the possible types of compounds whose presence may be inferred from the resonance lines observed. Interestingly, there seems to be no observable concentration of side chains of greater than two or three carbons present in the mixture, nor are there many carbons which could be attributed to aliphatic amines.

(11)Three products were sampled from effluent of the guardcase hydrotreater unit; full range product for the 65%, 35% feed (sample J), input to the reformer for the JP-4 pool (sample M), and the final diesel fuel product (sample U). This treatment reduces the aromaticity and eliminates the olefins. For these three samples, the longest alkyl chains are found in sample U and the shortest in sample M, which average very short indeed.

(12)Passage through the reformer produces samples L, N, and W. Sample W, the final gasoline component, is quite highly aromatic, mostly from single-ring species; alkyl chains are again very short, and naphthenicity is high. The spectra of samples L (JP-8 pool) and N (JP-4 pool) are rather similar and have f_a^C's similar to that of sample W. The variation in the f_a^H's of these three samples appears significant and may be reflective of the differences in the three products.

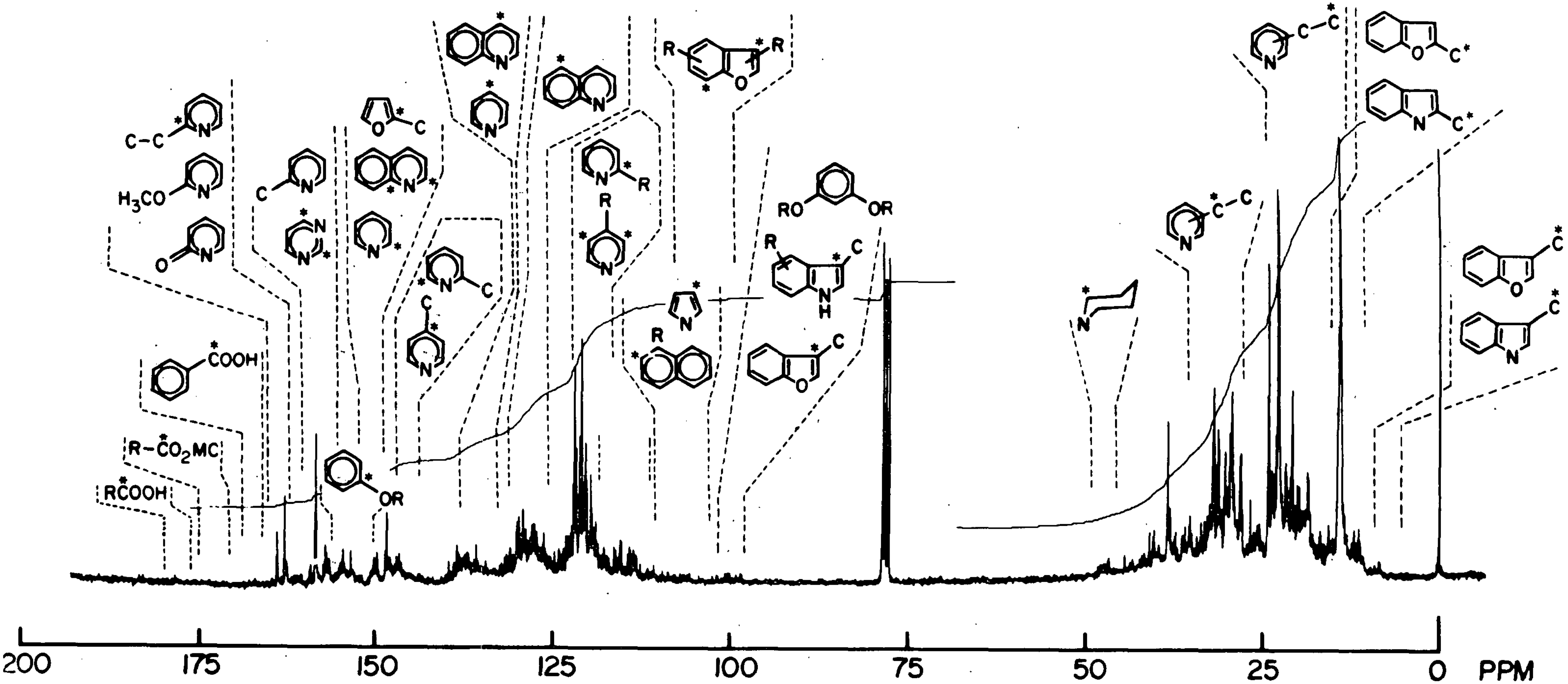


Figure IV-4: The ^{13}C NMR spectrum of nitrogen compounds removed from the hydrotreated shale oil by acid extraction. The figures indicate the types of compounds which may be consistently associated with the observed resonance lines.

(13)Aromatic saturation results in samples O, P, and Q. Aromaticities have, as expected, dropped dramatically at this step, although less so in the broad-range JP-8 product. The spectra of the final products, R, S, and T, do not differ markedly from those of their predecessors, although it does appear that a relatively simple aromatic compound has been added to sample T, probably to bring its properties in line with specifications. As an example, the proton and carbon-13 spectra of the broad-range JP-8 final fuel product are given in Figure IV-5.

C. Average Parameter Analysis by Use of Proton and Carbon-13 NMR

The amount of structural information which is derivable from proton and carbon NMR data of complex hydrocarbon mixtures is dependent on the extent to which resonance signals deriving from different molecular fragment types may be quantitatively distinguished. Various divisions of the carbon and proton chemical shift ranges have been suggested,[4, 30, 31, 32, 33, 34] some of which are rather complex.[30, 32, 33] Although some of the more detailed partitions of the chemical shifts are useful for qualitative purposes, we have found that the overlap between some of the proposed characteristic regions is rather severe for quantitative determinations. The partition of the various chemical shift regions which we have chosen to utilize is summarized in Table IV-3. In the carbon spectra we have chosen to use only the general aromatic and aliphatic integrals. In the proton spectra, integrals are determined for five regions. The aromatic region is taken from 6.0-9.0 ppm, although for qualitative analysis this region may be subdivided into one-, two- and three-ring portions (c.f. Table IV-3). Protons other than methyl on carbons adjacent (alpha) to aromatic rings were measured in the range from 2.3-4.0 ppm, while alpha methyl protons were determined from 1.9-2.3 ppm. Methylenes and methynes further removed than two bonds from aromatic centers are generally found from 1.0 to 1.9 ppm. Methyl protons more than two carbons distant from an aromatic center are assumed to resonate from 0.5-1.0 ppm. We have generally chosen to ignore the CH_3 of ethylaromatics, which resonates near 1.2 ppm. However, if large amounts of ethylaromatic are known or suspected to occur in a sample, appropriate compensation should be made in the integral distribution. Although some overlap may occur for these aliphatic regions, we have found that at 300 MHz the resulting errors are minimal.

By combining the proton and carbon NMR results with those derived from elemental analysis and determination of average molecular weight, the yield of parametric information may be maximized. The determinable structural parameters may be divided into two classes: 1) those which depend only on the quality of the raw data for their accuracy, and 2) those which are dependant upon the accuracy of previously determined parameters or upon assumptions

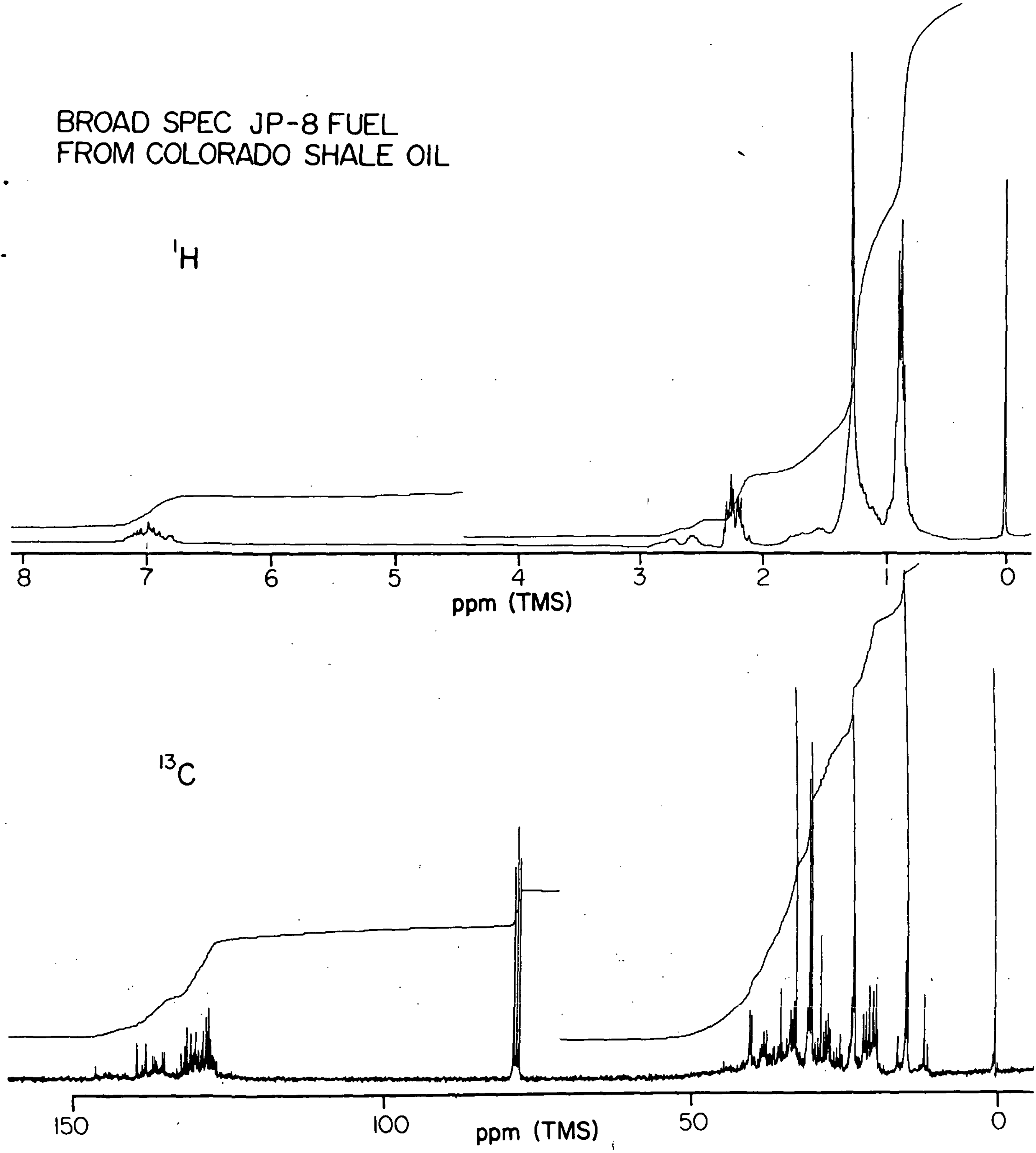


Figure IV-5: The ^{13}C and ^{1}H NMR spectra of one of the finished fuels derived from shale oil , broad-range JP-8.

Table IV-3: Chemical Shift Regions Assigned to ^1H and ^{13}C NMR Spectra

	Chemical Shift Region[a]
HYDROGEN	
aliphatic	0.5-4.0
alpha	1.9-4.0
CH_2	2.3-4.0
CH_3	1.9-2.3
beta and gamma	0.5-1.9
CH_2 (and beta CH_3)	1.0-1.9
CH_3	0.5-1.0
olefinic	4.0-6.0
aromatic[b]	6.0-9.0
1-ring	6.0-7.3
2-ring	7.3-7.8
3-ring	7.8-9.0
CARBON	
aliphatic	5.0-50.0
straight chain[c]	
branched and other	
aromatic[d]	100.0-150.0

a. In ppm from TMS. This scheme follows basically that proposed by Netzel and Hunter.[35]

b. This entry specifies the region which determines fraction of aromatic hydrogen, f_a^H.

c. The carbons associated with straight chains resonate at or very near 14.0, 23.0, 32.0, 29.0, and 29.5 ppm.

d. This entry specifies the region which determines fraction of aromatic carbon, f_a^C.

about the nature of the sample. The parameters of the first type are relatively self explanatory; they are presented in a general form in Table IV-4.

The parameters which depend on factors other than the quality of the experimental data are given in Table IV-5. An attempt has been made to exclude from that set any parameters which depend on more than one assumption. The reliability of the majority of these factors hinges, in fact, upon the correct determination of a single number, which is the average length of alkyl side chains attached to aromatic moieties. The latter parameter may be calculated by more than one method. A calculation for that number which is similar to the approach used in many of the treatments found in the literature is the first one given in Table IV-5. It is based on the presumption that the carbon/hydrogen distribution at the alpha position of alkyl substituents is identical to that of the remainder of the alkyl chains. However, our experience indicates that there are many cases for which that assumption does not appear to be valid. In fact, our examination of a variety of samples has indicated that the C/H ratio at the alpha position often differs from that found in the total alkyl fractions. One immediate consequence of that circumstance is that the estimate of the average length of alkyls is then in error, which also decreases the validity of all other calculations which depend upon its value, which includes all of the other parameters given in Table IV-5.

In assessing the possibility of improving the determination of the average length of alkyls, we have observed that when alkyl chain length in model compounds is overestimated that the calculated number of aromatic rings possible for a given number of aromatic carbons is then also overestimated. By determining the maximum number of aromatic rings possible for a given number of aromatic carbons, we can establish an alternative method for estimating of the average length of alkyls. That equation is also given in Table IV-5. The number of rings possible in a compound is a strict function of the number of aromatic carbons present, depending only the distribution of cata and peri condensation, as depicted in Figure IV-6. The number of aromatic rings which may result from a given number of aromatic carbons is given in Table IV-6. (We have considered only benzenoid ring systems, as they are normally predominant.) When the number of aromatic rings calculated by use of the value obtained from the traditional equation for the average length of alkyls exceeds the values given in Table IV-6, then the average alkyl length parameter may be recalculated using the alternative equation. All other factors depending on that value are also redetermined.

The equations of Tables IV-4 and IV-5 have been programmed in FORTRAN. The efficacy of the analysis has been tested on several model compounds. The

Table IV-4: A Group of Average Structure Parameters Derivable from NMR, Elemental Analysis and Average Molecular Weight Data Which Depend Only on the Quality of the Experimental Data for their Accuracy

fraction[a] (type of)[b] carbon = (type of) carbon integral/total carbon integral
fraction (type of)[c] hydrogen = (type of) hydrogen integral/ total hydrogen integral

percent (type of)[b] carbon = percent carbon X fraction (type of) carbon
percent (type of)[c] hydrogen = percent hydrogen X fraction (type of) hydrogen

C/H weight ratio of alkyl groups = percent aliphatic carbon/percent aliphatic hydrogen
H/C atomic ratio of alkyl groups = atomic wt. C/(C/H wt. ratio X atomic wt. H)

number of (type)[b] carbons = average molecular wt. X percent (type of) carbon/ (100 X atomic wt. C)
number of (type)[c] hydrogens= average molecular wt. X percent (type of) hydrogen/(100 X atomic wt. H)

equivalent percent of carbon occupied by heteroatoms = sum[d] (percent heteroatom X atomic wt. C/ atomic wt. heteroatom)

percent unsubstituted aromatic carbon = percent aromatic hydrogen X atomic wt. C/ atomic wt. H

total rings[e] = total carbons X (1-fraction aromatic carbon/2) - total hydrogens/2 + 1

number of methyl carbons = number of methyl hydrogens/3

---

[a] The equations are given here in a generalized form.
[b] Where _type_ (_of_) = aromatic or aliphatic.
[c] Where _type_ (_of_) = aromatic, or alpha, or beta and gamma, or gamma methyl.
[d] The sum is over whichever heteroatoms are present (_e.g._ N, O, S).
[e] This equation becomes less rigorous when significant amounts of aliphatic nitrogen are present in the sample.

Table IV-5: A Group of Average Structure Parameters Derivable from NMR, Elemental Analysis and Average Molecular Weight Data Which Depend on Correct Determination of Other Parameters

---

average[a] length of alkyls(1)[b] = (fraction nonmethyl alpha hydrogen + fraction beta and gamma hydrogen + (fraction alpha methyl + fraction gamma methyl) X 2/3 + ring correction[c])/(fraction nonmethyl alpha hydrogen + fraction alpha methyl X 2/3)

average length of alkyls(2)[b] = number of aliphatic carbons/(number of aromatic carbons - number of aromatic hydrogens - 2 X (maximum aromatic rings-1))

percent substituted aromatic carbon = percent aliphatic carbon/average length of alkyls

percent nonbridge aromatic carbon = percent substituted aromatic carbon + percent unsubstituted aromatic carbon

number of nonbridge aromatic carbons = average molecular wt. X percent nonbridge aromatic carbon/100 X atomic wt. C

percent substitution of aromatic rings = 100 X percent substituted aromatic carbon/percent nonbridge aromatic carbon

number of alkyl substituents = number of nonbridge aromatic carbons - number of aromatic hydrogens

number of aromatic rings = 1/2(number of aromatic carbons - number of aromatic hydrogens - number of alkyl substituents) + 1

number of naphthenic rings = total rings - number of aromatic rings

---

a. The equations which depend solely on accurate experimental data are given in Table IV-4. The equations given here are in a generalized form.

b. The first equation for average length of alkyls is used only if it does not produce a value of number of aromatic rings in excess of maximum aromatic rings. See Table IV-6 and text for discussion of the latter parameter.

c. The ring correction amounts to one hydrogen for each napthenic ring and is calculated iteratively.

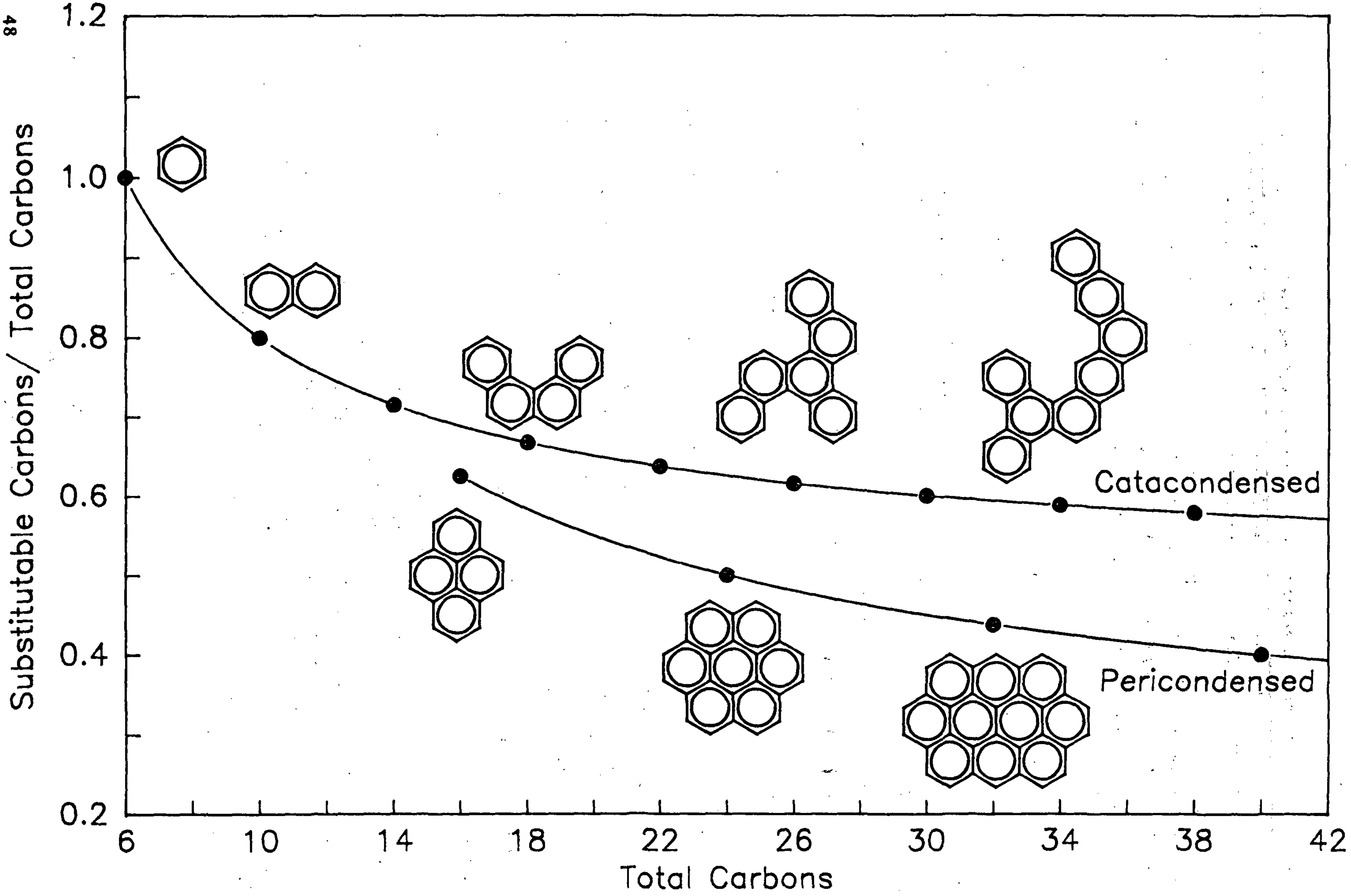


Figure IV-6: The number of condensed aromatic rings which may result from a given number of aromatic carbons. Average parameters must fall in the region between the curves.

Table IV-6: Ranges for Determining the Maximum Number of Aromatic Rings Possible, Given the Number of Aromatic Carbons Present

Number of Aromatic Carbons[a]	Maximum Number of Aromatic Rings
$> 0, \leq 6$	1
$> 6, \leq 10$	2
$>10, \leq 14$	3
$>14, \leq 18$	4
$>10, <22$	5
$\geq 22, \leq 26$	7
$>26, \leq 30$	9
$>30, \leq 34$	10

a. If heteroatoms occupy a significant fraction of aromatic sites, it may be necessary to include them here.

compounds and the results are given in Table IV-7. Although the model substances vary from a simple substituted benzene to a relatively complex tetrahydroanthracene, the program is able to calculate accurately all of the various factors.

Additionly, the computer analysis has been tested by purposefully introducing some reasonable errors into the data, as shown in Table IV-8. A 10% error in the determination of the molecular weight is seen to produce a similar error in the calculations of the numbers of the several types of carbons and hydrogens but does not affect other parameters. A low value for the integral of the aromatic region of the carbon spectrum might result from an experimental recycle time which was too short. Such an error causes inaccurate values to be calculated for the average length of alkyls and the number of aromatic carbons per molecule, as well as the other parameters which depend upon those numbers. An error in the determination of the aromatic proton integral produces again a nonphysical situation in the ratio of total aromatic carbon to nonbridge aromatic carbon and distorts the determination of the ring parameters. The final error situation involved addition of a 10% hexane impurity into the sample. A proportional discrepancy then occurs in the average chain length, and many other parameter values are also distorted.

D. Analysis of the SCFC Fractionated Samples

A supercritical fluid chromatographic separation was performed on 13 selected samples of those listed in Table IV-1. Those samples are listed in

Table IV-7: Comparison of Theoretical and Calculated Average Structure Parameters for Some Model Compounds

sample[a]	1		2		3	
parameter[b]	theor	calc	theor	calc	theor	calc
fraction of aromatic carbon	0.6	0.6	0.4	0.4	0.6	0.6
fraction of aliphatic carbon	0.4	0.4	0.6	0.6	0.4	0.4
fraction of aromatic hydrogen	0.3	0.3	0.2	0.2	0.3	0.3
fraction of aliphatic hydrogen	0.7	0.7	0.8	0.8	0.7	0.7
fraction α to aromatic rings	0.4	0.4	0.3	0.3	0.4	0.4
fraction α methyl	0.2	0.2	0.2	0.2	0.2	0.2
fraction β and γ	0.1	0.1	0.3	0.3	0.2	0.2
fraction γ methyl	0.2	0.2	0.3	0.3	0.2	0.2
carbons per alkyl side chain	2.0	2.0	2.7	2.7	2.0	2.0
C/H weight ratio of alkyl groups	4.8	4.8	5.6	5.6	5.5	5.5
H/C atomic ratio of alkyl groups	2.5	2.5	2.1	2.1	2.2	2.2
percent aromatic carbon	53.7	53.7	38.3	38.3	57.1	57.1
% nonbridge aromatic carbon	53.7	53.7	38.3	38.3	45.7	45.7
% substituted aromatic carbon	17.9	17.9	19.1	19.1	17.1	17.1
% unsubstituted aromatic carbon	35.8	35.8	19.1	19.1	28.6	28.6
% alkyl subs. of aromatic carbons	33.3	33.3	50.0	50.0	37.5	37.5
aromatic carbons pam[c]	6.0	6.0	6.0	6.0	10.0	10.0
aromatic nonbridge carbons pam	6.0	6.0	6.0	6.0	8.0	8.0
aromatic hydrogens pam	4.0	4.0	3.0	3.0	5.0	5.0
total rings pam	1.0	1.0	2.0	2.0	3.0	3.0
aromatic rings pam	1.0	1.0	1.0	1.0	2.0	2.0
naphthenic rings pam	0.0	0.0	1.0	1.0	1.0	1.0
alkyl substituents pam	2.0	2.0	3.0	3.0	3.0	3.0
aliphatic carbons pam	4.0	4.0	8.0	8.0	6.0	6.0
aliphatic hydrogens pam	10.0	10.0	17.0	17.0	13.0	13.0
α hydrogens pam	5.0	5.0	6.0	6.0	7.0	7.0
α methyls pam	1.0	1.0	1.0	1.0	1.0	1.0
γ methyls pam	1.0	1.0	2.0	2.0	1.0	1.0

a. The compounds are 1: methylpropylbenzene, 2: 3-ethyl-1,6-dimethyltetralin, and 3: 2,6-dimethyl-1,2,3,4-tetrahydroanthracene.

b. The parameters are defined in Tables IV-4 and IV-5.

c. Pam = per average molecule.

Table IV-8: The Effect Produced by Various Simulated Data Errors on the Calculated Average Structure Parameters for Methylpropylbenzene

		error[a]			
parameter[b]	theor	1	2	3	4
fraction of aromatic carbon	0.6	0.6	0.6	0.6	0.6
fraction of aliphatic carbon	0.4	0.4	0.4	0.4	0.4
fraction of aromatic hydrogen	0.3	0.3	0.3	0.3	0.3
fraction of aliphatic hydrogen	0.7	0.7	0.7	0.7	0.7
fraction α to aromatic rings	0.4	0.4	0.4	0.4	0.3
fraction α methyl	0.2	0.2	0.2	0.2	0.2
fraction β and γ	0.1	0.1	0.1	0.1	0.2
fraction γ methyl	0.2	0.2	0.2	0.2	0.2
carbons per alkyl side chain	2.0	2.0	2.1	2.0	2.3
C/H weight ratio of alkyl groups	4.8	4.8	5.1	4.9	4.8
H/C atomic ratio of alkyl groups	2.5	2.5	2.4	2.4	2.5
percent aromatic carbon	53.7	53.7	51.4	53.7	50.1
% nonbridge aromatic carbon	53.7	53.7	54.1	55.9	50.1
% substituted aromatic carbon	17.9	17.9	18.3	17.6	16.7
% unsubstituted aromatic carbon	35.8	35.8	35.8	38.3	33.4
% alkyl subs. of aromatic carbons	33.3	33.3	33.8	31.5	33.3
aromatic carbons pam[c]	6.0	5.4	5.7	6.0	5.4
aromatic nonbridge carbons pam	6.0	5.4	6.0	6.2	5.4
aromatic hydrogens pam	4.0	3.6	4.0	4.3	3.6
total rings pam	1.0	1.0	1.1	1.0	0.9
aromatic rings pam	1.0	1.0	0.8	0.9	1.0
naphthenic rings pam	0.0	0.0	0.3	0.1	0.0
alkyl substituents pam	2.0	1.8	2.1	2.0	1.8
aliphatic carbons pam	4.0	3.6	4.3	4.0	4.2
aliphatic hydrogens pam	10.0	9.0	10.0	9.7	10.4
α hydrogens pam	5.0	4.5	5.0	4.9	4.5
α methyls pam	1.0	0.9	1.0	1.0	0.9
γ methyls pam	1.0	0.9	1.0	1.0	1.1

a. The errors are 1: 10% low molecular wt., 2: 10% low aromatic carbon integral, 3: 10% low aromatic proton integral, and 4: 10% hexane impurity.

b. The parameters are defined in Tables IV-4 and IV-5.

c. Pam = per average molecule.

Table IV-9. With a few exceptions, lighter materials were chosen for separation. Attempts to fractionate some of the heavier mixtures were frustrated by low recoveries, the missing portions remaining on the column. Since cleaning and restoring of the column is a lengthy and tedious process involving dismantling of the supercritical setup and flushing with a series of HPLC solvents, only the unretained samples were analyzed. This difficulty could undoubtedly be overcome by use of an appropriate column packing material.

The percentage of material in aromatic fractions of the product refinery streams is portrayed graphically in Figure IV-7. It was not always clear from sample labeling as to the actual sequence of products, so less certain relationships have been indicated by use of dashed lines. There is a significant increase in aromaticity during the reforming process (cf. Table IV-2), and two-ring aromatics are detected which were not present in samples M or J. However, the weight % of the aromatic fraction has decreased significantly in samples L and N. These results are consistent with the formation of two-ring aromatics, accompanied by dealkylation reactions. The average molecular weights of these samples in Table IV-9 also support that conclusion. Hence, both reforming and aromatic saturation have produced a significant reduction in aromatic content for all three product streams, JP-4, JP-8, and JP-8 broad range fuels. However, final treatment has resulted in an increase in aromatic fraction for JP-8 BR, a decrease for JP-8, and almost no change for JP-4. As expected, diesel fuel has a low aromatic component and gasoline a rather high one. The properties of the fuels may, in fact, be influenced more by the relative amounts of contained aromatic material, as shown in Figure IV-7, than by the absolute nature of the aromatic species present, at least insofar as all products are derived from the same source, so that the nature of the aromatic component does not vary widely. The relative invariance of the aromatic structural types in the later stages of refining is evident from the NMR spectra and from the average parameter analysis.

The saturate and aromatic fractions, as well as some of the unfractionated samples, were subjected to elemental analysis and to simulated distillation by vapor phase chromatography. The elemental analysis was reported to four figures, but the second figure beyond the decimal is probably not significant. Universal Oil Products Method 375-59[36] was used to calculate molecular weights for the mixtures. The results are contained in Table IV-9. The unfractionated samples were not submitted for analysis in all cases, because it was found that the carbon/hydogen and molecular weight values for them could be obtained from the results for the fractions to within one percent.

Carbon-13 and proton NMR spectra were acquired for all of the fractions listed in Table IV-9. Analysis of the saturate fractions produced the results

Table IV-9: Analytical Data for Selected, Shale-derived Refinery Products

Sample[a]	Wt. %[b]	%C[c]	%H[c]	Ave. Molecular Wt.[d]
C[e]	85.9	86.03	12.69	175
sat	48.9	85.48	14.67	151
aro	51.1	86.56	10.79	198
J[e]	100.3	87.27	12.67	190
sat	32.7	85.41	14.69	170
aro	67.3	88.17	11.69	199
L[e]	89.6	87.35	12.55	163
sat	53.1	84.86	15.03	150
aro	46.9	90.16	9.75	178
M[e]	100.0	88.07	11.71	158
sat	30.4	85.36	14.77	140
aro	69.6	89.25	10.38	166
N[e]	95.5	86.89	13.15	147
sat	62.6	85.06	15.15	140
aro	37.4	89.94	9.79	160
O	100.0	86.11	13.74	153
sat	72.2	85.41	14.62	150
aro	27.8	88.85	11.08	174
P	98.1	86.74	13.25	157
sat	59.2	85.27	14.77	153
aro	40.8	89.40	10.79	172
Q	98.7	86.14	13.92	145
sat	78.9	85.39	14.50	141
aro	21.1	88.64	11.26	164
R	99.6	86.26	13.72	160
sat	75.3	85.47	14.51	159
aro	24.7	88.95	10.96	174
S	97.5	86.82	13.19	160
sat	55.3	85.25	14.85	155
aro	44.7	89.20	10.94	173
T	94.1	86.29	13.99	136
sat	80.1	85.09	14.88	131
aro	19.9	88.78	11.22	160
U[e]	88.8	86.45	13.58	195
sat	68.8	85.41	14.70	193
aro	31.2	88.73	11.11	201
W	95.6	88.07	12.06	141
sat	37.7	84.76	15.44	132
aro	62.3	90.14	9.86	141

a. The samples are identified in Table IV-1.

b. As determined by SCFC. The number given for the whole sample is recovery.

c. C/H analyses performed by Huffman Laboratories, Inc. except as indicated.

d. Determined from API gravity and average B.P. (from simulated distillation) by use of UOP Method 375-59, except as indicated.

e. The unfractionated sample was not analyzed; values are calculated by use of the data obtained from the fractions.

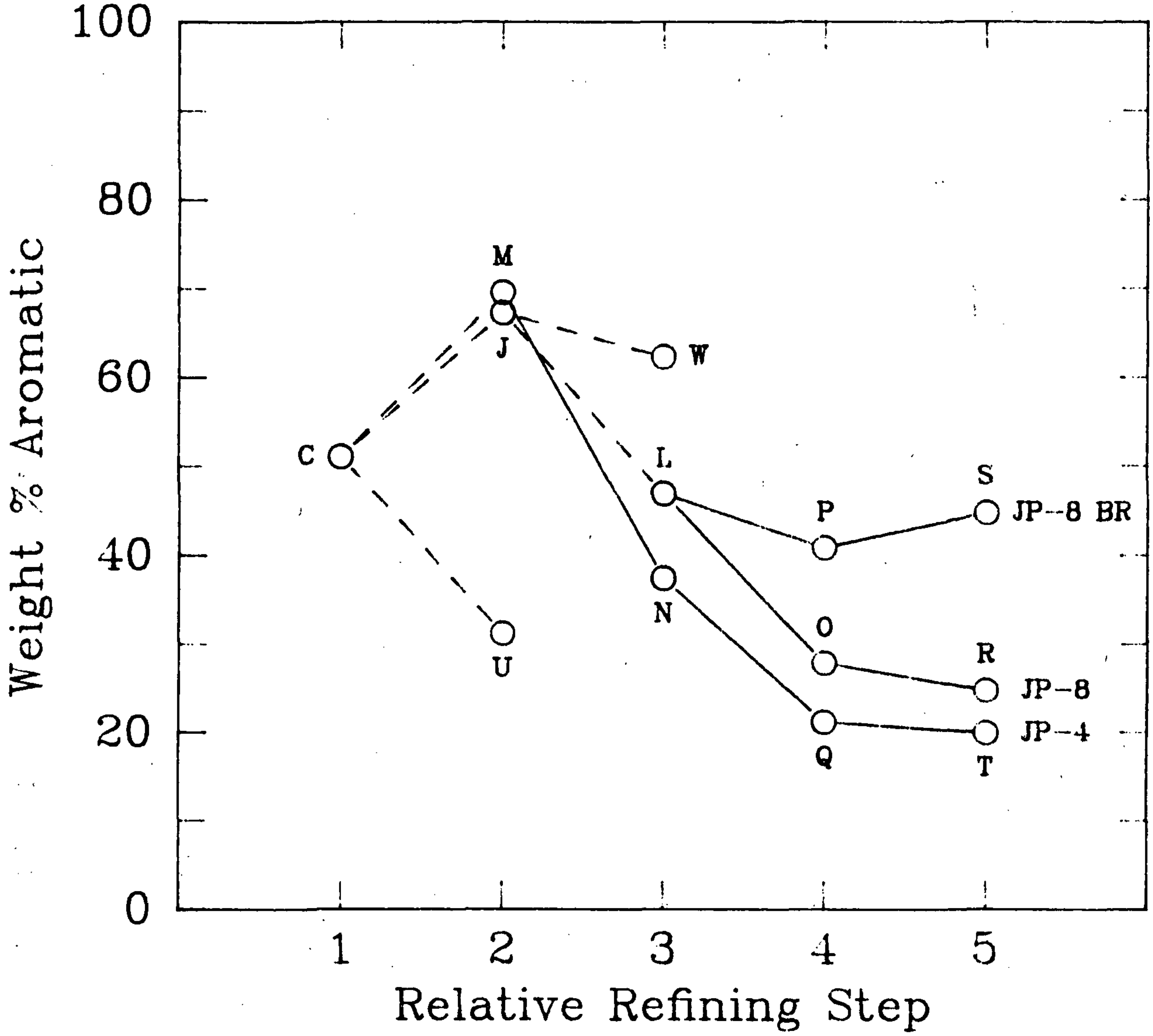


Figure IV-7: The weight % of the aromatic fraction for the samples of Table IV-1 which were separated by use of SCFC. These values include both saturated and aromatic carbon and hydrogen which are contained in the aromatic fraction. Less well defined relationships are indicated by dashed lines.

given in Table IV-10 for branchiness index, percent naphthenic carbon, fraction straight chain carbon, and average length of chains. The branchiness index is defined in the literature[37] as the ratio of the methyl hydrogen integral to the acyclic methylene integral. We have used it as the ratio of the methyl integral to all other hydrogen, since it is somewhat difficult to separate acyclic methylene from acyclic methyne and from cyclic methylene and methyne. The latter three types are generally not prominent. The branchiness index has been related to several other properties, such as viscosity and percent naphthenic carbon. We have used the equation of Williams[37] (given in Table IV-10) to calculate the percent of carbon in naphthenic environments. It is felt that the absolute value of the numbers should be regarded with some caution, since the calculation has never been tested rigorously under our spectrometer and sample conditions. However, the relative value of the naphthenicity is probably accurate and of some utility. The concentration of normal chains is seen to decrease during early refining steps, for example sample G to sample L, although sample M seems anomalously low. Straight chain concentration varies slowly in later samples. The average length of normal chains also decreases from initial values, but tends to change slowly toward the end of the refining process. The broad range JP-8 seems to have had some long chain material added to it in the finishing step, whereas the n_{ave} of the JP-4 has decreased considerably, and that of JP-8 changed very little.

In examining the proton spectra of the aromatic fractions, we find that very few of them exhibit detectable concentrations of two ring aromatics. The samples which do are C, L, and N, with traces in U and W. Since samples M and J do not indicate the presence of naphthalenes, it is likely that the reforming procedure is dehydrogenating some tetralins or otherwise generating two-ring aromatics. The aromatic saturation, however, seems to be very successful in reducing such compounds, as they do not appear in samples P, O, or Q.

The aromatic fractions were subjected to average structure parameter analysis as described in the previous section. Tables IV-11 and IV-12 contain the results of that analysis. Examination of the tables reveals that there is not a wide variation in most properties among the various fractions. This may again be indicative, as stated above, that fuel properties are determined more by the relative amount of aromatic material present, rather than the changing properties of the aromatic contribution. Inspection of the numbers indicates that the aromatic carbon number is less than six on some occasions, which would seem to represent a nonphysical situation for any fraction not containing pure saturates. However, as demonstrated in Table IV-8, relatively minor errors in the raw data tend to result in numbers such as those found in Tables IV-11 and IV-12. Unfortunately, the errors of around 10% in NMR

Table IV-10: Branchiness Index, Percent Naphthenic Carbon, Fraction Normal Chains, and Average Chain Length of SCFC Saturates Fractions of Selected Shale Refinery Products

Sample[a]	HBI[b]	$\%C_N^c$	f_n^d	n_{ave}^e
C	0.57	36.4	0.36	13.1
J	0.56	35.8	0.33	11.5
L	0.67	41.8	0.28	10.0
M	0.80	48.9	0.21	8.4
N	0.72	44.5	0.34	9.5
O	0.59	37.5	0.20	9.6
P	0.59	37.5	0.25	9.7
Q	0.74	45.6	0.19	9.3
R	0.69	42.9	0.19	9.7
S	0.63	39.6	0.25	10.0
T	0.76	46.7	0.19	8.5
U	0.58	36.9	0.33	12.2
W	0.92	55.4	0.30	8.8

a. The samples are identified in Table IV-1.

b. Hydrogen branchiness index = methyl H integral/ other H integral.

c. Percent naphthenic carbon as calculated by the equation of Williams,[37] which is $\%C_N = 54.3(\text{HBI} + 0.10)$.

d. Fraction normal chains = carbon straight chain integral/ total C integral.

e. Average length of straight chains.

integrals or molecular weights represent the probable precision of the determinations involved. It is anticipated that the relative changes beyond experimental error will be valuable as a means of estimating the changing properties of the products from the refinery stream. For example, note how few changes are observed in going from the products of aromatic saturation to the finished fuels, i.e. from samples P, O, Q to samples S, R, T in Table IV-1.

One approach is to develop model compounds from the derived parameters, following the changes which must be made in the models in order to follow the refinery process. We have illustrated this procedure in Table IV-13 for samples L and P. It turns out to be rather difficult to simulate the parametric analysis data using only a single compound, so we have chosen to utilize a simple model mixture. Of course dozens, or perhaps hundreds, of appropriate molecules might be used in the formulation. As may be noted in

Table IV-11: Average Structure Parameters for the Aromatic Fractions of Selected Shale-derived Refinery Products

parameter[a]	sample[b]	C	J	L	M	N	O	P
fraction of aromatic carbon		0.4[c]	0.3	0.6	0.6	0.6	0.4	0.5
fraction of aliphatic carbon		0.6	0.7	0.4	0.4	0.4	0.6	0.5
fraction of aromatic hydrogen		0.1	0.1	0.2	0.2	0.3	0.1	0.1
fraction of aliphatic hydrogen		0.9	0.9	0.8	0.8	0.7	0.9	0.9
fraction α to aromatic rings		0.4	0.3	0.5	0.5	0.5	0.4	0.4
fraction α methyl	0.2	0.2	0.2	0.3	0.3	0.3	0.3	
fraction β and γ	0.4	0.4	0.2	0.2	0.2	0.4	0.3	
fraction γ methyl	0.2	0.2	0.1	0.1	0.1	0.2	0.1	
carbons per alkyl side chain		2.7	3.4	1.7	1.8	1.6	2.1	2.2
C/H weight ratio of alkyl groups		5.4	5.5	4.3	4.5	4.9	5.2	4.8
H/C atomic ratio of alkyl groups		2.2	2.2	2.8	2.6	2.5	2.3	2.5
percent aromatic carbon	36.7	30.0	58.1	51.5	54.8	38.0	44.3	
% nonbridge aromatic carbon		32.8	30.0	45.8	45.4	52.1	38.0	37.6
% substituted aromatic carbon		18.8	17.0	19.0	21.1	21.6	23.7	20.6
% unsubstituted aromatic carbon		14.0	12.9	26.8	24.3	30.5	14.3	17.0
% alkyl subs. of aromatic carbons		57.3	56.8	41.5	46.5	41.5	62.5	54.7
equivalent % C occupied by hetero		2.5	0.0	0.0	0.0	0.0	0.0	0.0
aromatic carbons pam[d]	6.1	5.0	8.6	7.1	7.3	5.5	6.3	
aromatic nonbridge carbons pam		5.4	5.0	6.8	6.3	6.9	5.5	5.4
aromatic hydrogens pam	2.3	2.1	4.0	3.4	4.1	2.1	2.4	
total rings pam	1.9	1.6	1.5	1.2	1.6	1.6	1.4	
aromatic rings pam	1.3	1.0	1.9	1.4	1.2	1.0	1.5	
naphthenic rings pam	0.6	0.6	0.0	0.0	0.4	0.6	0.0	
alkyl substituents pam	3.1	2.8	2.8	2.9	2.9	3.4	2.9	
aliphatic carbons pam	8.2	9.6	4.8	5.2	4.7	7.4	6.5	
aliphatic hydrogens pam	18.3	20.9	13.2	13.7	11.5	17.1	16.0	
α hydrogens pam	7.2	6.1	8.1	8.2	7.5	7.0	7.9	
α methyls pam	1.2	1.4	1.3	1.9	1.7	1.8	1.8	
γ methyls pam	0.6	1.8	0.5	0.5	0.4	1.1	0.8	

a. The parameters are defined in Tables IV-4 and IV-5.

b. The samples are identified in Table IV-1.

c. Olefin content is included in the aromatic fractions.

d. Pam = per average molecule.

Table IV-12: Average Structure Parameters for the Aromatic Fractions of Selected Shale-derived Refinery Products, Continued

parameter[a]	sample[b]	Q	R	S	T	U	W
fraction of aromatic carbon		0.4	0.4	0.5	0.5	0.5	0.7
fraction of aliphatic carbon		0.6	0.6	0.5	0.5	0.5	0.3
fraction of aromatic hydrogen		0.1	0.1	0.1	0.1	0.1	0.3
fraction of aliphatic hydrogen		0.9	0.9	0.9	0.9	0.9	0.7
fraction α to aromatic rings		0.4	0.4	0.4	0.3	0.3	0.5
fraction α methyl	0.3	0.3	0.2	0.3	0.2	0.4	
fraction β and γ	0.4	0.4	0.3	0.4	0.4	0.2	
fraction γ methyl	0.2	0.1	0.1	0.2	0.2	0.1	
carbons per alkyl side chain		2.1	2.2	2.2	2.0	2.8	1.5
C/H weight ratio of alkyl groups		5.0	5.2	4.9	4.9	4.7	4.1
H/C atomic ratio of alkyl groups		2.4	2.3	2.4	2.5	2.5	2.9
percent aromatic carbon	38.7	38.5	42.5	42.3	41.5	60.7	
% nonbridge aromatic carbon		38.7	38.5	37.6	42.3	29.6	50.9
% substituted aromatic carbon		23.4	23.2	21.0	22.8	17.2	19.6
% unsubstituted aromatic carbon		15.3	15.3	16.6	19.5	12.4	31.3
% alkyl subs. of aromatic carbons		60.6	60.2	55.9	53.9	58.1	38.4
aromatic carbons pam[c]	5.3	5.6	6.1	5.6	7.0	7.1	
aromatic nonbridge carbons pam		5.3	5.6	5.4	5.6	5.0	6.0
aromatic hydrogens pam	2.1	2.2	2.4	2.6	2.1	3.7	
total rings pam	1.3	1.6	1.4	1.1	1.3	1.1	
aromatic rings pam	1.0	1.0	1.4	1.0	2.0	1.6	
naphthenic rings pam	0.3	0.6	0.0	0.1	0.0	0.0	
alkyl substituents pam	3.2	3.4	3.0	3.0	2.9	2.3	
aliphatic carbons pam	6.8	7.3	6.7	6.2	7.9	3.5	
aliphatic hydrogens pam	16.2	16.7	16.4	15.2	20.1	10.1	
α hydrogens pam	6.5	7.6	7.9	6.0	7.0	7.2	
α methyls pam	1.9	1.7	1.5	1.7	1.3	1.9	
γ methyls pam	1.1	0.8	0.8	1.0	1.5	0.3	

a. The parameters are defined in Tables IV-4 and IV-5.

b. The samples are identified in Table IV-1.

c. Pam = per average molecule.

Table IV-13, sample L was found to be adequately represented by a 1:1 mixture of 6-methyltetralin and 2-ethyl-6-methyl-3-propylnaphthalene. In order to simulate sample P with similar compounds, it was necessary to saturate one ring, remove one carbon, and move a carbon from a gamma to an alpha position in the second component. The resulting mixture was of 6-methyltetralin as before, plus an equal molar amount of 3-ethyl-1,6,7-trimethyltetralin. The results are seen to be consistent with refinery process occuring at this step in the process.

As another example of the utility of the parametric analysis, examination of the carbon spectra of the aromatic fractions reveals that the resonance lines attributable to straight chain alkyl fragments appear prominently only in samples C and J, with an easily detectable amount in sample U. In all of the other aromatic fractions methyl and ethyl are the only prominent saturate substituents detected. That observation is consistent with the parametric analysis results discussed above in that only samples C, J, and U exhibit an average alkyl chain length which approaches three carbons. On the other hand, the samples with the shortest average chain length were L, N, and W, which are the samples for which the presence of two-ring aromatics was noted, again leading one to the conclusion that the two-ring aromatic materials are being produced by the cyclization and dehydrogenation of substituted benzenes.

The fact that unbranched hydrocarbons of any length are not usually detectable in the aromatic fractions is initially somewhat surprising. This may be a result, at least in part, of the fact that aromatic centers substituted by long chains have boiling points above those which have been used for the distillation cuts in the mixtures being studied here.

Page intentionally left blank

Page intentionally left blank

V. ANALYSIS OF ERBS FUELS

A. Introduction

On the basis of the situation now existing in world petroleum markets and the need for alternative sources of aviation kerosenes, as discussed in the introductory chapter, the formulation of an experimental fuel having less restricted properties was proposed at a workshop held in Cleveland at NASA Lewis in 1977. This was called an experimental referee broadened-specification (ERBS) aviation turbine fuel.[38] In 1979 a panel instituted by the Coordinating Research Council recommended some modifications in the original property requirements.[39]

After investigation of a number of possible sources, it was found that a mixture of 65% traditional kerosene with 35% hydrotreated catalytic gas oil (HCGO) was able to meet the majority of the specifications.[40] This initial fuel contained 12.8% hydrogen and was call ERBS 3B-12.8. Later, fuels of lower hydrogen content (12.3% and 11.8%) were created by blending of the 3B-12.8 fuel with a mixture of HCGO and xylene bottoms. The blending stock was called ERBS 3S.

The above fuels have been characterized by traditional analytical methods. However, because of the possibility that some of the characteristics of the alternate fuels will be determined by properties not currently tested, it was decided to analyze these fuels also by use of NMR, which can give additional insight into the actual moleular content in order to complement traditional analytical methods currently in use.

B. Characterization of the Whole Fuels and HPLC Fractions

The proton NMR spectra of the three ERBS fuels and the blending stock are given in Figure V-1. Each spectrum has been divided into general regions according to the scheme given in Chapter IV. The distribution of integrated intensity is given in Table V-1. In the spectrum for the 12.8% fuel, one may note that although 5% of the hydrogen comes from aromatic sites, there are no easily discernible, well resolved resonances in the region from 6.6-8.3 ppm, indicating that there are no prominent single species. On the other hand the spectrum of the blending stock, which is,as mentioned above, a mixture of xylene bottoms and HCGO, exhibits many individual lines, representative of a relatively small number of compounds in high concentration. The proton spectra of the 12.3% and 11.8% hydrogen ERBS fuels in Figure V-1 reveal essentially the same pattern in the aromatic region as that of the blending stock. The spectral region from 1.9 to 4.0 ppm of those samples is also dominated by signals resulting from addition of the 3S stock. The triplet near 1.2 ppm of sample 3S undoubtedly results from the CH_3 of an ethyl group attached to an aromatic ring.

The carbon-13 NMR spectra of the three fuels and the blending stock are given in Figure V-2. The 100.0-150.0 ppm aromatic carbon region of the 3B-12.8 sample contains considerably more detail than is found in the corresponding proton spectrum. In the aliphatic region straight chain hydrocarbons are quite prominent, representing almost half of all saturated carbon. It is also possible to detect isoprenoid-like compounds in the spectra (cf. Chapter II). In the 3S sample characteristic lines are observed for xylenes and ethylbenzene, which are the most prominent species, although trimethylated benzenes are in evidence. Ethyl benzene is identifiable in the spectrum due to the presence of resonances at 15.7, 28.9, and 144.3 ppm. Ortho-xylene is distinguishable by the occurence of lines at 19.5 and 136.2 ppm. Meta-xylene and/or mesitylene (1,3,5-trimethylbenzene) are represented by the lines at 21.1 and 137.5 ppm, while para-xylene may be identified through lines at 20.8 and 134.4 ppm. The remaining prominent lines, which are at 20.8, 136.0, 134.4, and 133.2 ppm, indicate the presence of pseudocumene (1,2,4-trimethylbenzene) in the sample. Results from the HPLC studies, described below, indicate that the straight chain hydrocarbon resonance lines observed in the spectrum are derived almost entirely from the HCGO component.

The ERBS fuels and blending stock were separated into five fractions by use of HPLC, as illustrated previously in Figure III-2. Fraction I represents the saturates component, fraction II single-ring aromatics, fraction III two-ring aromatics, and fraction IV principally three- and four-ring aromatics. Fraction V, obtained by backflushing the column, contained polar compounds. The areas under the curve of the UV detector are not quantitative, as there is actually a rather small amount of material in fractions III-V. Although the trace shown is for an analytical column, similar resolution was attainable on the Magnum 20 column previously described with up to 1.5 grams sample loading. Although the HPLC separation were very effective, difficulties were encountered in isolating the fractions from the HPLC solvents, which were iso-octane and n-hexane. Because recovery problems prevented isolation of quantitative HPLC fractions, the following discussion will be limited to a qualitative basis only.

As a typical example of the proton results, spectra of the first three fractions of the 11.8% sample are given in Figure V-3. One may note that the purification of the saturates fraction is quite good, and there is no detectable integral for any aromatic hydrogen in the spectrum. The bulk of the resonance signals here is attributable to methyls and methylenes. The one-ring aromatic fraction is, as expected, dominated by presence of methy-

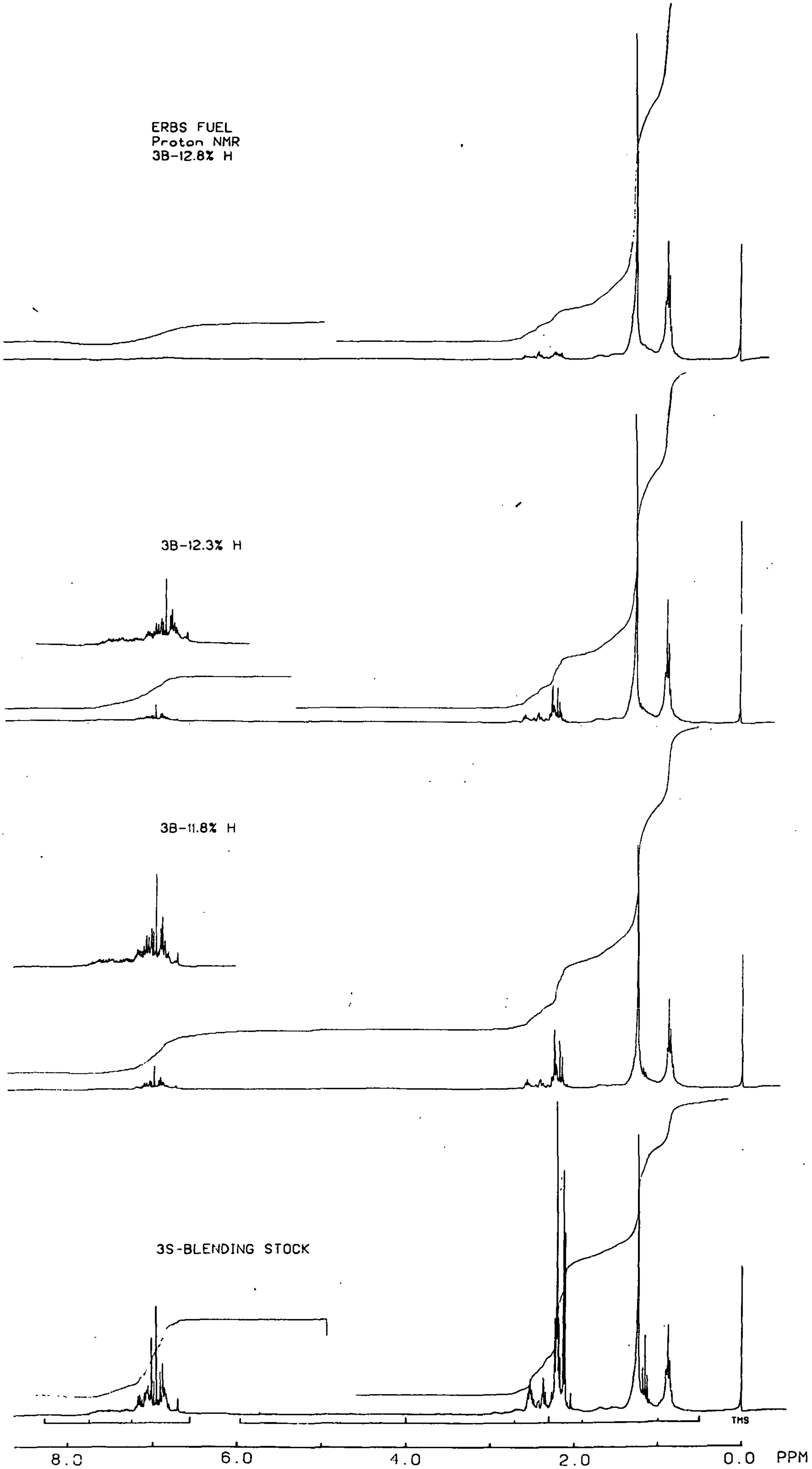


Figure V-1: Proton NMR spectra of three ERBS aviation fuels and of the blending stock which was added to fuel 3B-12.8 in order to produce fuels 3B-12.3 and 3B-11.8. The digital integral is given above each spectrum.

Table V-1: Normalized Distribution of Integrated Intensity in the Proton and Carbon-13 NMR Spectra of ERBS Turbine Fuels and Blending Stock

Chemical Shift Region[a]	3B-12.8	3B-12.3	3B-11.8	3S
HYDROGEN				
aliphatic	0.95	0.92	0.90	0.78
alpha	0.09	0.14	0.20	0.35
CH_2	0.05	0.06	0.07	0.10
CH_3	0.04	0.08	0.13	0.25
beta and gamma	0.86	0.78	0.70	0.43
CH_2 (and beta CH_3)	0.55	0.50	0.46	0.31
CH_3	0.31	0.28	0.24	0.12
olefinic	0.00	0.00	0.00	0.00
aromatic[b]	0.05	0.08	0.10	0.22
1-ring	0.04	0.06	0.09	0.18
2-ring	0.01	0.03	0.02	0.03
3-ring	0.00	0.00	0.00	trace
CARBON				
aliphatic	0.70	0.67	0.61	0.42
straight chain	0.30	0.19	0.18	0.09
branched and other	0.40	0.48	0.43	0.33
aromatic[c]	0.30	0.33	0.39	0.58

a. As specified in Table IV-3.

b. This entry specifies the fraction of aromatic hydrogen, f_a^H.

c. This entry specifies the fraction of aromatic carbon, f_a^C.

lated benzenes, although there is a small amount of aliphatic straight chain alkyl substitution evident. In the two-ring fraction there is almost no straight chain aliphatic material, and most of the aliphatic component derives from methyl, or a small amount of ethyl, substituents. Of course this is a minor portion of the original sample, barely observable in the spectrum of the whole fuel.

The proton spectrum of the polar compounds, obtained by backflushing the column after separation of the blending stock, is given in Figure V-4. This fraction is very small, and great difficulty was encountered in accumulating a sufficient quantity for analysis. The majority of compounds present appear to be aliphatic ethers. No carbon spectrum was acquired for this fraction.

The highly aromatic nature (f_a^C is 0.68) of the two-ring fractions is

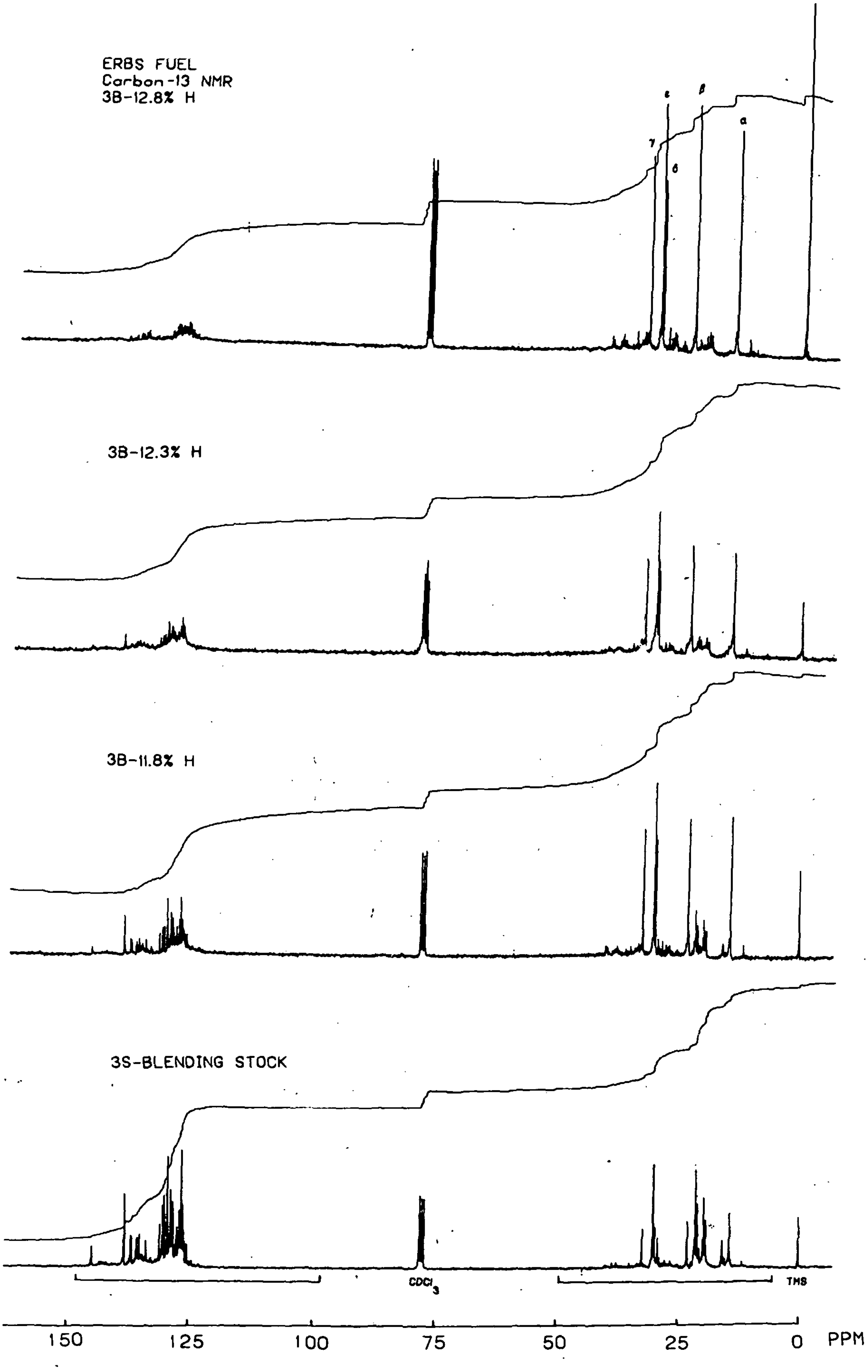


Figure V-2: Carbon-13 spectra for the same ERBS fuels and blending stock noted in Figure V-1. The 3S spectrum contains prominent resonances for the methyl carbons of xylenes and the ethyl of ethylbenzene.

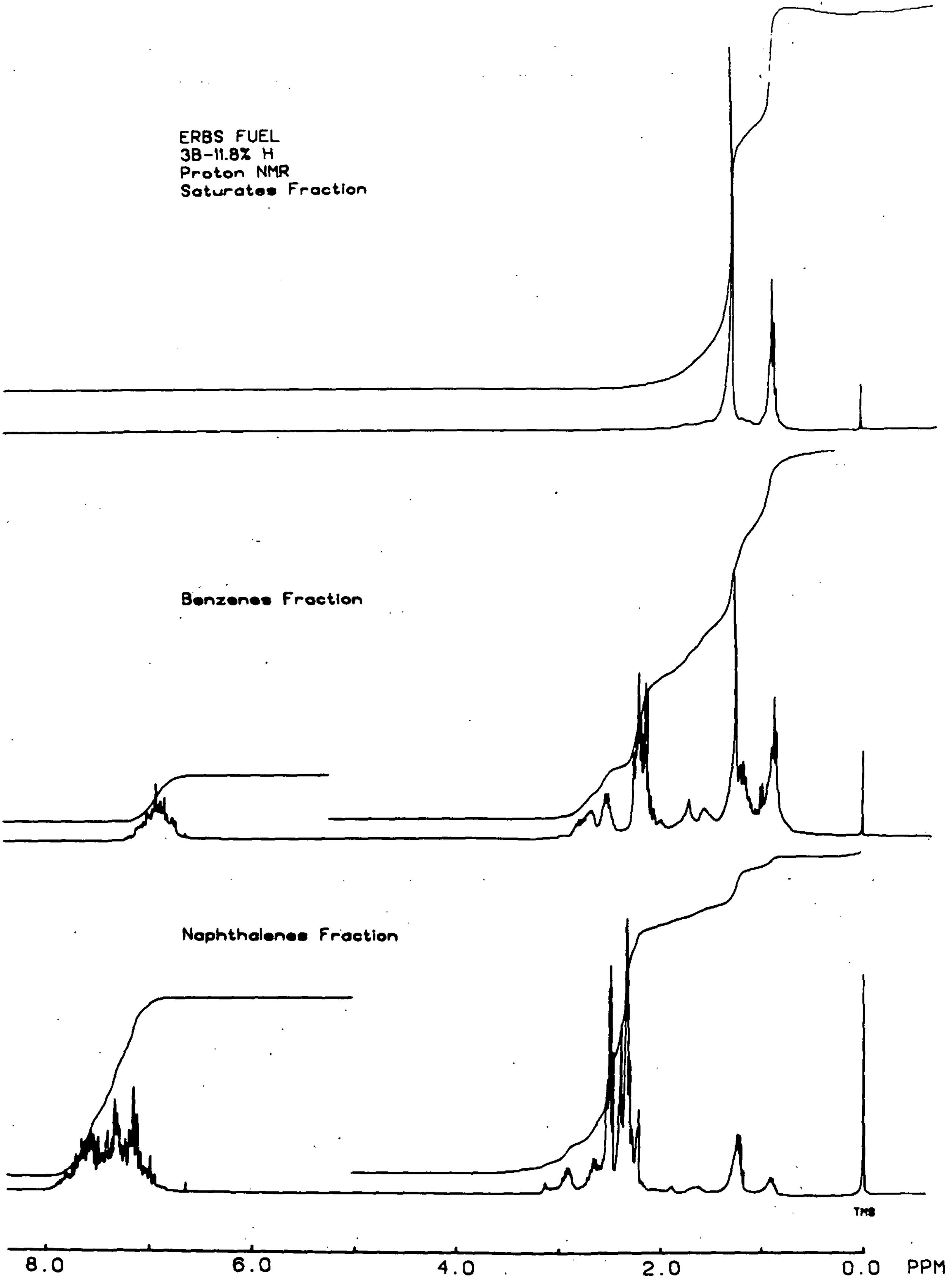


Figure V-3: Proton NMR spectra for three of the HPLC fractions of ERBS sample 3B-11.8. The saturates cut contains no evidence of any aromatic material. The aliphatic resonances in the two-ring fraction result predominantly from methyls attached to aromatic rings.

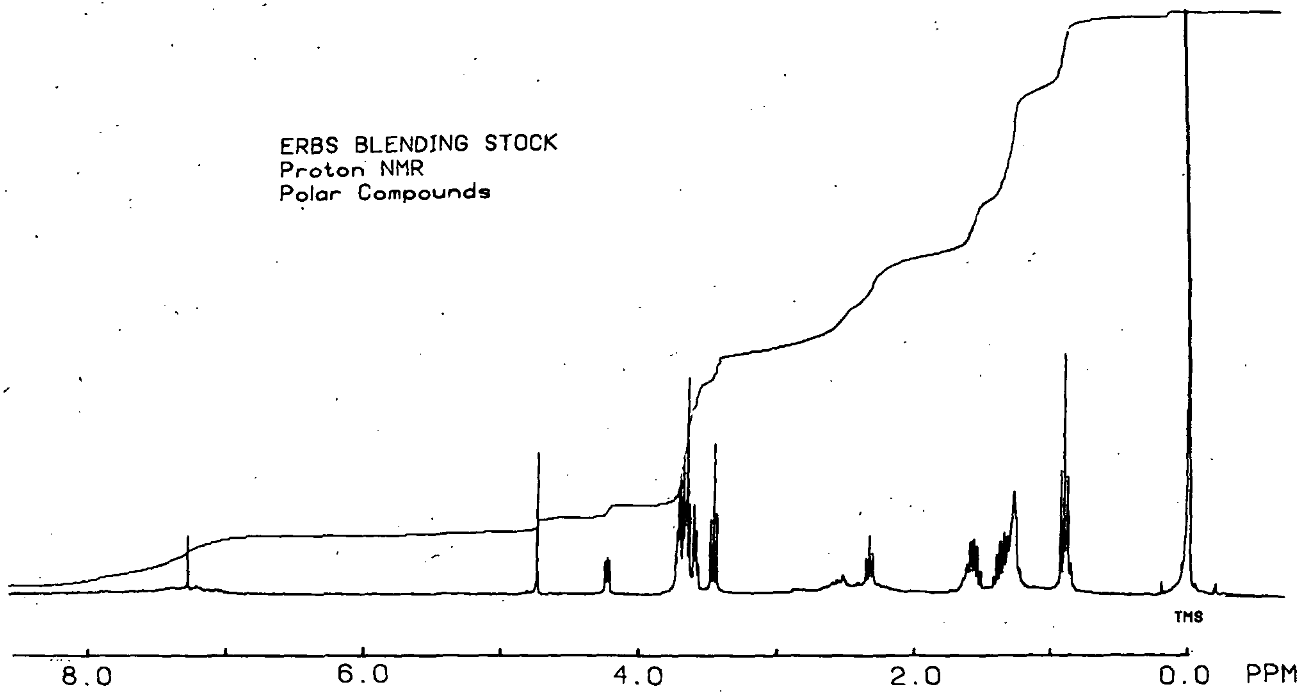


Figure V-4: A proton NMR spectrum of the polar compounds obtained from sample 3S by backflushing the HPLC column.

further demonstrated by the carbon spectrum presented in Figure V-5, where it can be seen that very little aliphatic carbon is present outside of methyl and ethyl groups. It is possible to identify readily the following compounds as being present:[41, 42] 1-methyl- and 1,x-dimethylnaphthalenes, chemical shifts near 19.2 ppm, where x = 3 to 7; 2-methyl- and 2,y-dimethylnaphthalenes, where y = 4 to 8, chemical shifts near 21.6 ppm; 1,2-dimethylnaphthalene, 14.4 and 20.6 ppm; 2,3-dimethylnaphthalene, 21.6 ppm; and 2-ethylnaphthalene 15.6 and 29.1 ppm. There is also a resonance (25.9 ppm) corresponding to the methyl of 1,8-dimethylnaphthalene, although the presence of that compound is somewhat surprising, since it is a higher energy isomer often considered to be absent from such mixtures.

Fraction IV was most abundant in the blending stock, although it is not observed at the detection level displayed in the proton spectra given in Figure V-1. In the ^{13}C spectrum shown in Figure V-6, it will be noted that this fraction consists primarily of aromatic carbon (f_a^C = 0.88), and that there is almost no aliphatic carbon other than methyl groups present in the sample. The chemical shifts noted are characteristic of substituted anthracenes and phenanthrenes,[42, 43] but very little ^{13}C NMR data has been published on polyaromatic compounds and thus a more detailed analysis is not possible at this time.

The fact that only the saturates and one-ring aromatics fractions of these materials contained substantial amounts of straight chain hydrocarbon fragments was somewhat unexpected. However, since addition of long substituents to the larger aromatic compounds would increase their molecular weights significantly, it is perhaps not surprising that they are not found in samples of modest boiling point.

C. Analysis of the SCFC Fractionated Samples

The three ERBS fuels and the blending stock were separated by use of SCFC. Later NMR work revealed that the separation of the last two samples, the 3B-12.3 and 3S mixtures, was not as clean as achieved previously, as aromatic protons could be detected in the proton spectra of the saturates fractions, which condition was not observed for any previous case. Upon repeating these separations, we found the results to be even worse, apparently due to degradation of quality of the column packing. The approach of the end of the contract period and prior commitment of the chromatograph to other tasks prevented achievement of a totally clean separation for those two samples. However, the resulting errors are apparently not too serious, as the values obtained in the various analyses do not reveal gross inconsistencies.

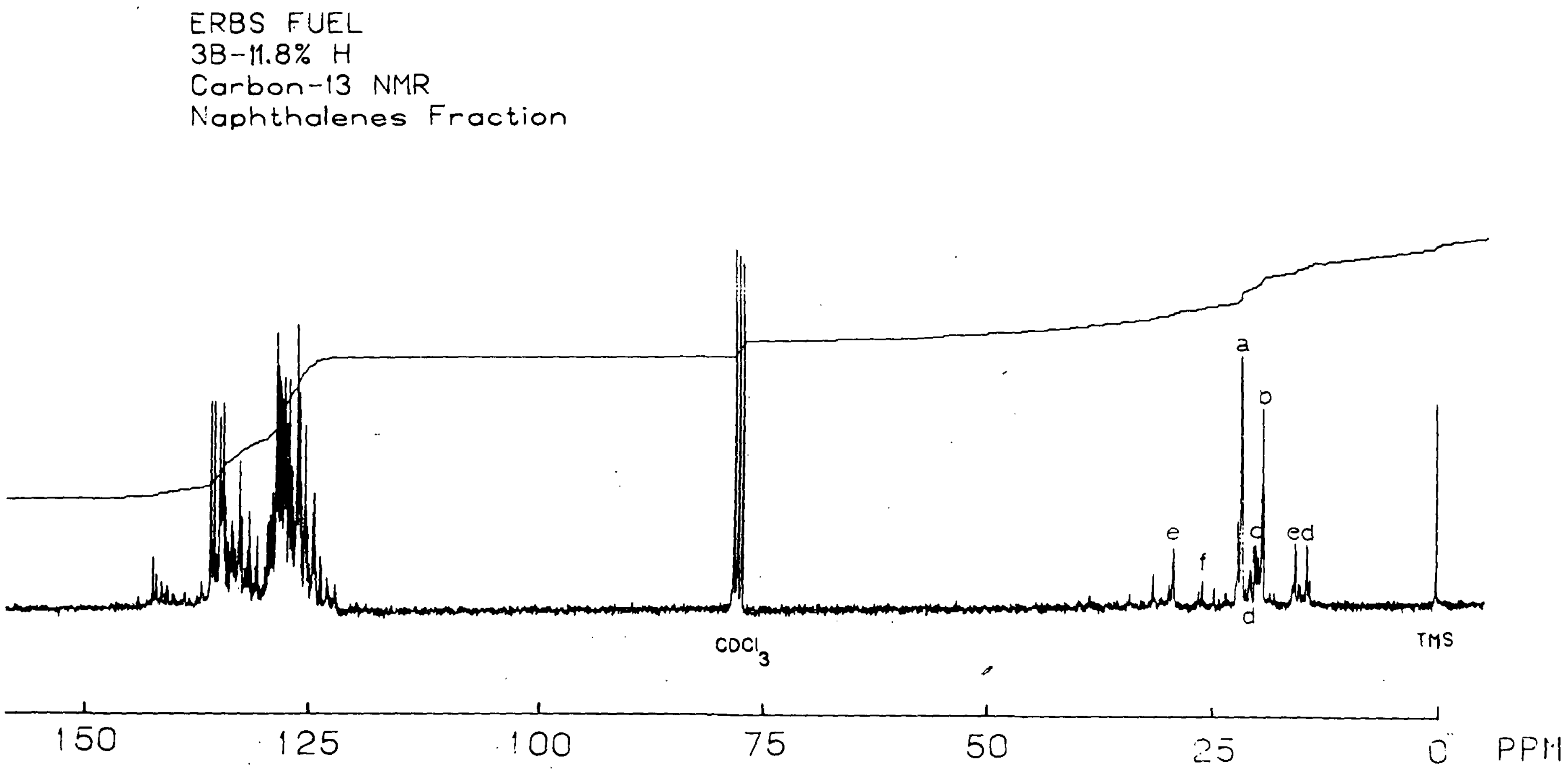


Figure V-5: The two-ring aromatics HPLC fraction of ERBS fuel 3B-11.8 is found by carbon-13 NMR to be dominated by substituted naphthalenes. The identified compounds are a: 2-methyl and 2,y-dimethyl, b: 1-methyl and 1,x-dimethyl, c: 2,3- dimethyl, d: 1,2-dimethyl, e: 2-ethyl, and f: 1,8-dimethyl.

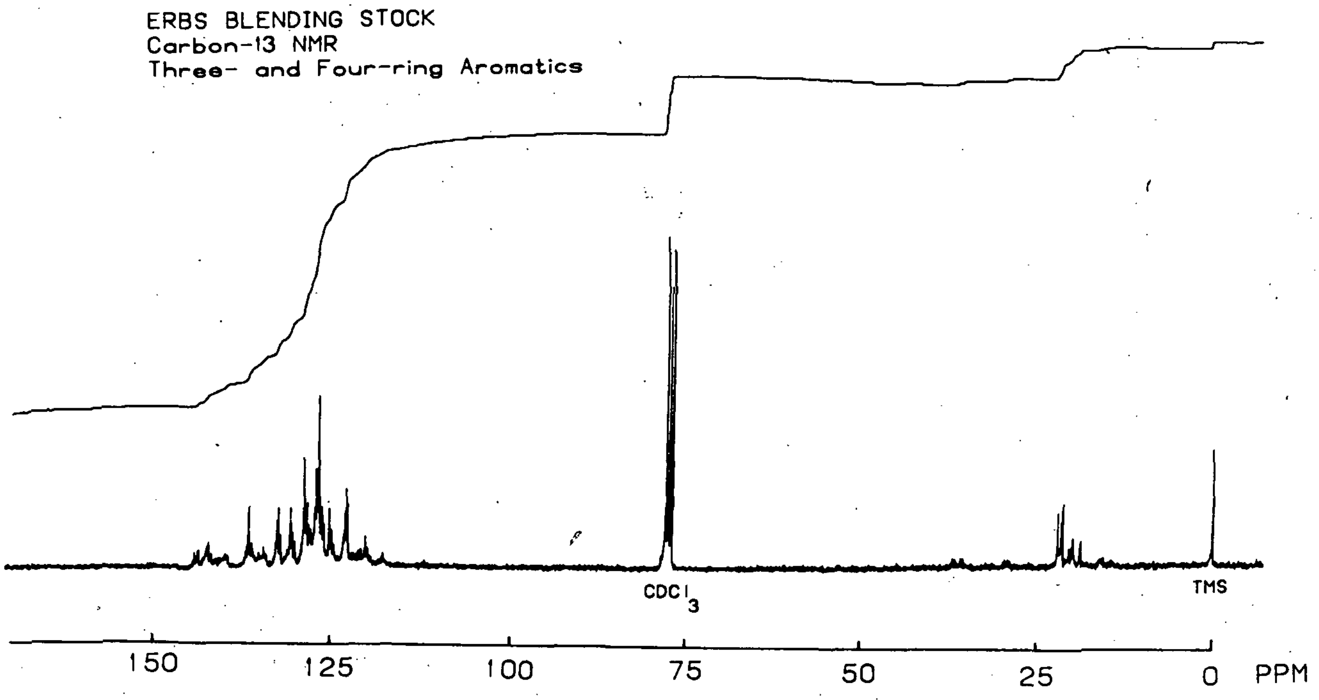


Figure V-6: A carbon-13 spectrum of the three- and four-ring aromatic compounds separated from the 3S blending stock by HPLC. The majority of the aliphatic carbon appears as methyl.

The ERBS fractions were subjected to carbon/hydrogen analysis and simulated distillation. Average molecular weights were calculated by means of Universal Oil Products method 375-59.[36] Those results, together with the SCFC yields and fraction distributions, are contained in Table V-2. Inspection of that table indicates again that the proportion of the fuel mixture which is contained in the aromatic fractions is an important parameter, as it ranges from 37 to 61% over the samples. Some confidence may be gained in the separation technique by noting the hydrogen content of the whole fuels, which were not subjected to direct elemental analysis. Rather, the C/H content for them has been calculated from the values obtained from the fractions. Note that they are within one percent of the values obtained by use of a very accurate NMR method in the original analysis performed upon them. The molecular weights of the ERBS fuels are higher and the hydrogen contents lower than those of the finished fuels from the shale processing (*cf*. samples R, S, and T of Table IV-9).

Table V-2: Analytical Data for ERBS Fuels

Sample[a]	Wt. %[b]	%C[c]	%H[c]	Ave. Molecular Wt.[d]
3B-12.8	97.6	86.96	12.81	181
sat	63.0	85.28	14.70	172
aro	37.0	89.82	9.59	196
3B-12.3	96.0	87.72	12.33	179
sat	52.0	85.66	14.55	169
aro	48.0	89.95	9.93	190
3B-11.8	98.4	88.29	11.71	167
sat	39.3	85.44	14.68	172
aro	60.7	90.14	9.78	164
3S	84.0[e]	88.99	10.72	160
sat	26.4	86.06	14.07	151
aro	73.6	90.16	9.53	163

a. The unfractionated samples were not analyzed; values are calculated by use of the data obtained from the fractions.

b. As determined by SCFC. The number given for the whole sample is recovery.

c. C/H analyses performed by Huffman Laboratories, Inc. except as indicated. The second figure beyond the decimal is undoubtedly not significant.

d. Determined from API gravity and average B.P. (from simulated distillation) by use of UOP Method 375-59, except as indicated.

e. This low recovery was due to column failure, and it was impractical to repeat the experiment.

Carbon-13 and proton NMR spectra were acquired for all of the fractions listed in Table V-2. The saturates fractions of the ERBS samples were analyzed for branchiness, percent naphthenic carbon, fraction straight chains, and average chain length according the procedures given in Chapter IV. The results are presented in Table V-3. The branchiness is seen to be greater and naphthenic content proportionately higher than those of sample S, the broad range JP-8 fuel evaluated on page 56 of Chapter IV. Straight chains constitute a much larger fraction of the saturate material in the ERBS, and the average chain length is also notably greater.

Table V-3: Branchiness Index, Percent Naphthenic Carbon, Fraction Normal Chains, and Average Chain Length of ERBS Saturates Fractions

Sample	HBI[a]	$\%C_N$[b]	f_n[c]	n_{ave}[d]
3B-12.8	0.53	34.2	0.40	11.1
3B-12.3	0.58	36.9	0.40	11.1
3B-11.8	0.60	38.0	0.42	11.2
3S	0.29	21.2	0.47	11.8

a. Hydrogen branchiness index = methyl H integral/ other H integral.

b. Percent naphthenic carbon as calculated by the equation of Williams,[37] which is $\%C_N = 54.3(HBI + 0.10)$.

c. Fraction normal chains = carbon straight chain integral/ total C integral.

d. Average length of straight chains.

Inspection of the proton spectra of the aromatic fractions of the ERBS fuels indicates the presence of substantial amounts of two-ring aromatics, the presence of which was noted in the discussion of the whole samples. Naphthalenes are present in the HCGO which was used to produce both the ERBS 3B-12.8 fuel and was also added to xylene bottoms to produce the 3S blending stock. Since there is considerably more single ring material in the 3S sample, it is expected that the aromatic rings per average molecule would be less in this sample, as is found. No naphthalene was detectable in the aromatic fractions of the finished fuels studied in the previous chapter. Naphthalenes are undesirable constituents in finished fuels, as they have been postulated as nucleation compounds for smoke formation.[1] Protons substituted on alpha carbons are very prominent in the spectra.

The aromatic fractions of the ERBS have somewhat higher average molecular weights than those of the shale products, indicating that they also have higher boiling points. Whereas normal alkyls were hardly detectable in the shale derived fuels, they are readily observed in the carbon spectra of the ERBS. Methyl and ethyl substituents are, however, more prominent.

Average parameter analysis was performed on the aromatic fractions as described in the previous chapter. Table V-4 contains the results. As expected the properties of the various samples do not vary widely. They have a higher proportion of aromatic carbon and fewer substituents than do the R, S, and T fuels. In fact, a comparison of the numbers indicates that the ERBS samples are much more like samples M, L, and N than the finished fuels. If broad specification fuels are found to perform adequately, they could perhaps be produced more effectively by traditional refinery methods carried through reforming, rather than blending of finished fuels.

The parameters of Table V-4 were used to formulate some model compounds corresponding to samples 3B-12.8 and 3S. It is often difficult to mimic a complex mixture by a single molecule, which was true for the 3B-12.8 fuel. As mentioned previously, dozens of substances could be imagined which could succeed in modeling a given sample, although they would all have to have many common features. In this case, a 1:1 mixture of 2-methyl-3-propyltetralin and 6,7-dimethyl-1,2,3,4-tetrahydroanthracene were found to represent the fuel in an adequate fashion, as illustrated in Table V-5. For the 3S sample a single compound, 6-methyltetralin, was found to provide an adequate representation, although the model may be improved somewhat by the addition of 20% dimethylnaphthalene, which is consistent with the known composition. Although these molecules may not actually occur in the mixtures of interest, they are seen to be generally representative of them.

Table V-4: Average Structure Parameters for the Aromatic Fractions of the ERBS Fuels and Blending Stock

parameter[a]	ERBS 3B-12.8	3B-12.3	3B-11.8	3S
fraction of aromatic carbon	0.6	0.6	0.6	0.6
fraction of aliphatic carbon	0.4	0.4	0.4	0.4
fraction of aromatic hydrogen	0.2	0.2	0.2	0.3
fraction of aliphatic hydrogen	0.8	0.8	0.8	0.7
fraction α to aromatic rings	0.4	0.4	0.4	0.5
fraction α methyl	0.2	0.2	0.2	0.3
fraction β and γ	0.3	0.3	0.3	0.2
fraction γ methyl	0.1	0.1	0.1	0.1
carbons per alkyl side chain	2.0	2.2	2.0	1.6
C/H weight ratio of alkyl groups	5.2	4.6	4.9	5.2
H/C atomic ratio of alkyl groups	2.3	2.6	2.4	2.3
percent aromatic carbon	50.4	54.6	53.4	54.6
% nonbridge aromatic carbon	43.9	43.1	45.5	54.8
% substituted aromatic carbon	19.3	16.5	18.2	22.9
% unsubstituted aromatic carbon	24.6	26.6	27.4	31.9
% alkyl subs. of aromatic carbons	44.0	38.2	39.9	41.8
aromatic carbons pam[b]	8.2	8.6	7.3	7.4
aromatic nonbridge carbons pam	7.2	6.8	6.2	7.4
aromatic hydrogens pam	4.0	4.2	3.7	4.3
total rings pam	2.2	1.6	1.7	1.8
aromatic rings pam	1.5	1.9	1.5	1.0
naphthenic rings pam	0.7	0.0	0.2	0.8
alkyl substituents pam	3.2	2.6	2.5	3.1
aliphatic carbons pam	6.4	5.6	5.0	4.8
aliphatic hydrogens pam	14.6	14.5	12.2	11.1
α hydrogens pam	7.4	7.1	6.4	7.6
α methyls pam	1.0	1.2	1.3	1.4
γ methyls pam	0.7	0.7	0.5	0.2

a. The parameters are defined in Tables IV-4 and IV-5.

b. Pam = per average molecule.

Table V-5: A Comparison of Sample and Model Average Structure Parameters for the Aromatic Fractions of the ERBS 3B-12.8 and 3S Samples

	3B-12.8		3S		
parameter[a]	sample	model[b]	sample	model 1[b]	model 2[b]
fraction of aromatic carbon	0.6	0.5	0.6	0.5	0.6
fraction of aliphatic carbon	0.4	0.5	0.4	0.5	0.4
fraction of aromatic hydrogen	0.2	0.2	0.3	0.2	0.3
fraction of aliphatic hydrogen	0.8	0.8	0.7	0.8	0.7
fraction α to aromatic rings	0.4	0.4	0.5	0.5	0.5
fraction α methyl	0.2	0.2	0.3	0.2	0.3
fraction β and γ	0.3	0.3	0.2	0.3	0.2
fraction γ methyl	0.1	0.2	0.1	0.0	0.0
carbons per alkyl side chain	2.0	2.3	1.6	1.7	1.7
C/H weight ratio of alkyl groups	5.2	5.6	5.2	5.4	5.2
H/C atomic ratio of alkyl groups	2.3	2.1	2.3	2.2	2.3
percent aromatic carbon	50.4	48.2	54.6	49.3	55.1
% nonbridge aromatic carbon	43.9	42.8	54.8	49.3	50.3
% substituted aromatic carbon	19.3	18.7	22.9	24.6	21.0
% unsubstituted aromatic carbon	24.6	24.1	31.9	24.6	29.2
% alkyl subs. of aromatic carbons	44.0	43.7	41.8	50.0	41.9
aromatic carbons pam[c]	8.2	8.0	7.4	6.0	6.8
aromatic nonbridge carbons pam	7.2	7.1	7.4	6.0	6.2
aromatic hydrogens pam	4.0	4.0	4.3	3.0	3.6
total rings pam	2.2	2.5	1.8	2.0	2.0
aromatic rings pam	1.5	1.5	1.0	1.0	1.3
naphthenic rings pam	0.7	1.0	0.8	1.0	0.7
alkyl substituents pam	3.2	3.1	3.1	3.0	2.6
aliphatic carbons pam	6.4	7.0	4.8	5.0	4.4
aliphatic hydrogens pam	14.6	15.0	11.1	11.0	10.0
α hydrogens pam	7.4	7.0	7.6	7.0	6.8
α methyls pam	1.0	1.0	1.4	1.0	1.2
γ methyls pam	0.7	1.0	0.2	0.0	0.0

a. The parameters are defined in Tables IV-4 and IV-5.

b. The model compounds are for 3B-12.8: a 1:1 mixture of 2-methyl-3-propyl-tetralin and 6,7-dimethyl-1,2,3,4-tetrahydroanthracene; for 3S: model 1 is 6-methyl-tetralin; model 2 is the same plus 20% dimethylnaphthalene.

c. Pam = per average molecule.

Page intentionally left blank

Page intentionally left blank

VI. NEW SPECTROSCOPIC TECHNIQUES

A. Theoretical Considerations

It has been proposed by some workers that ^{13}C NMR data on whole fuels could be used for average parameter analysis. We demonstrate here why that assumption produces significant errors in all calculations involving average lengths of substituted chains.

Pure normal alkanes of length greater than eight carbons produce a five line carbon spectrum (cf. Figure II-2 of Chapter II), which we designate C_1, C_2, C_3, C_4 and C_n, corresponding to $\alpha, \beta, \gamma, \delta$ and ε. Now the ratio, R, of the integral of line C_n to that of any of the other four lines for a hydrocarbon of length n carbons will be $R=(n-8)/2$. If we wish to determine the average chain length in a mixture of hydrocarabons, it is necessary to measure R experimentally and calculate n. The result is then $n=2R+8$. Now a normal alkyl chain of length m, greater than eight carbons, with a substituent at one end will generally produce a nine line spectrum: C_1, C_2, C_3, C_4 and C_n being the same as above, plus C_m, C_{m-1}, C_{m-2}, and C_{m-3} at the other, substituted end of the chain, which will not be readily identifiable in a complex mixture, as they will vary by substituent. For a normal alkyl fragment the ratio, R', of the integral of C_n to that of one of C_1, C_2, C_3 or C_4 (C_1 may be best, as C_3 and C_4 do not always shift, and the intensity of C_2 is often coincident with methyls attached to aromatic rings), is now $R'=n-8$. If we again measure R' and calculate n, the result will be $n=R'+8$, which is obviously not in agreement with the result obtained above for unsubstituted alkanes. Thus it is not possible to calculate an accurate value of average chain length, or any parameter which depends on it, from carbon integrals obtained from a sample containing a mixture of simple and substituted normal alkanes.

B. New Pulsing Techniques

Some new pulsing techniques have been developed which may have broad implications for the interpretation of complex ^{13}C spectra in the near future. These techniques include J-resolved 2D spectroscopy,[44, 45] INEPT,[46] and DEPT.[47] The latter two will be illustrated briefly here.

The INEPT pulse sequence is given in Figure VI-1. It involves phased pulsing of the proton channel coherently with the carbon channel, and pulse delays based on the value of the C-H spin-spin (J) coupling. By properly varying Δ of Figure VI-1, the various multiplicities (CH_3, CH_2, or CH) present in a spectrum may be differentiated. This is illustrated for the aliphatic portion of the fairly simple spectrum of the oil shale of Figure II-1 in

Figures VI-2 and VI-3. In Figure VI-2 signals resulting from methyl and methyne carbons are positive, while those due to methylene carbons are inverted. In Figure VI-3, using a different delay, only signals from CH carbons, normally obscured, are retained, while those due to carbons with two or three attached hydrogens are (almost) nulled.

The next four figures demonstrate application of the technique to a much more complicated spectrum, that of the nitrogen compounds, sample I of Table IV-1. In Figure VI-4 the aromatic region of the spectrum is illustrated. The unprotonated carbons are very clearly identified, providing a great deal of potential information about the species which may be present. For example, the occurence of protonated carbons near 149 ppm indicates the presence of pyridine derivatives, as there are very few protonated carbons which may be found at that field. Figure VI-5 shows the aliphatic portion of the same spectrum, and in Figure VI-6 INEPT is applied so that essentially only CH carbon lines are positive. In Figure VI-7 a different combination is applied, illustrating more the methyl groups. This experiment will obviously be of great utility in analyzing complex spectra, where it is normally impossible to achieve useful multiplet resolution in a traditional coupled spectrum.*

DEPT (distortionless enhancement by polarization transfer) also relies on coherent pulsing of proton and carbon spectrometer channels, but multiplet selectivity is achieved by varying a proton pulse width (theta) rather than only delays. This results in spectra with much less phase distortion and apparently improved relative intensities. The relevant pulse sequence is given in Figure VI-8.

The use of DEPT is illustrated on a model compound in Figures VI-9 and VI-10. The values of theta and the spectra which result are shown in Figure VI-9. These are added and subtracted according to the equations given in Figure VI-10, resulting in spectra containing only lines of a single multiplicity.

Although some residuals may result in the edited spectra as a result of imperfections in the spectrometer hardware, the spectra of single multiplicity may be used to obtain quantitative integrals for the various species in the sample. This is best done by subtraction of the latter spectra from the normal spectrum. An example of the spectra needed is shown in Figure VI-11. The top trace is acquired under spectrometer conditions which will guarantee that all

---

*We are indebted to the Bruker company and W.E. Hull for acquiring the INEPT spectra at 125 MHz.

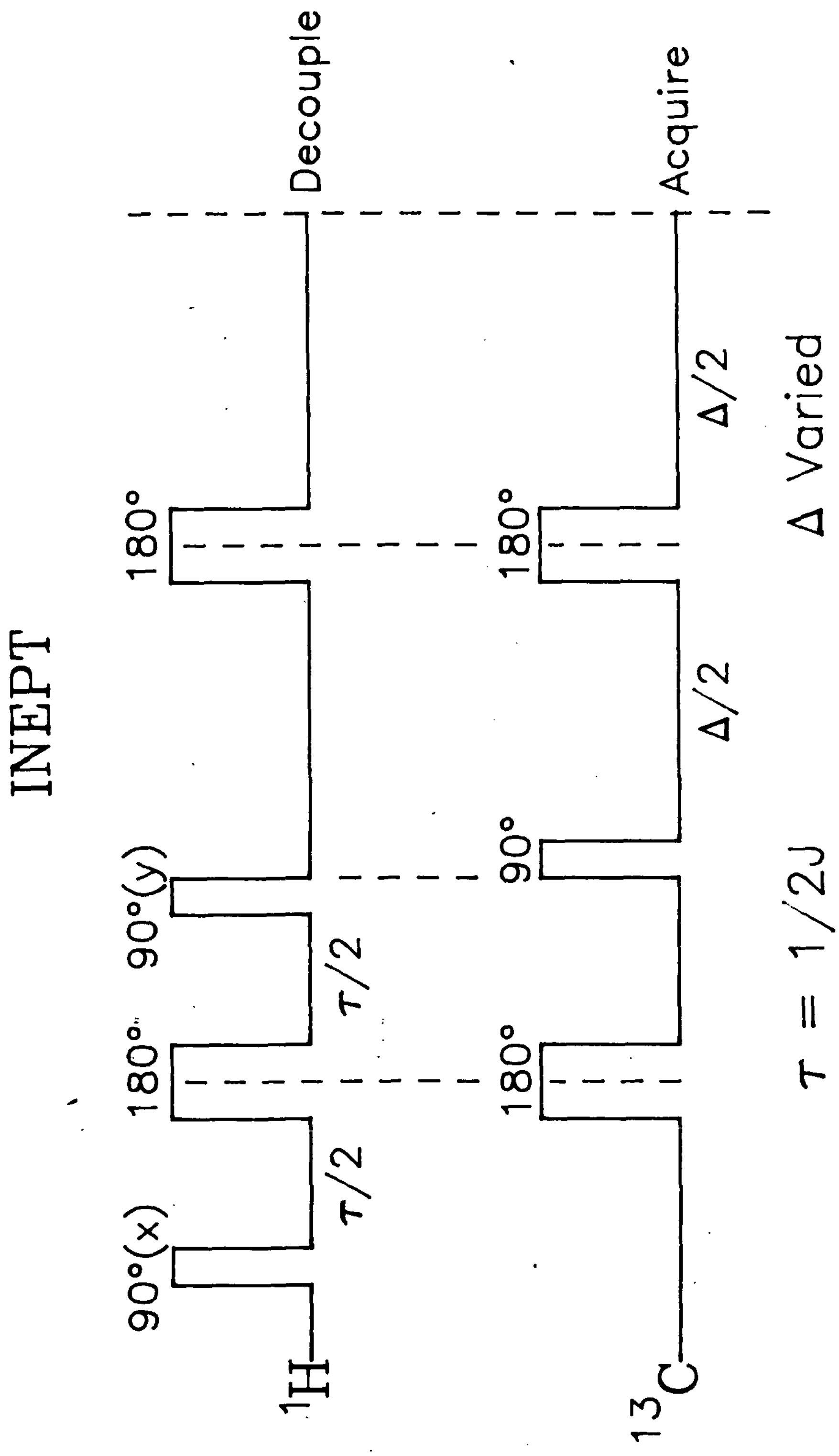


Figure VI-1: The pulse sequence necessary to produce J-refocused ^{13}C NMR spectra, termed INEPT. The value of Δ is varied selectively so as to zero, negate, or enhance lines corresponding to various multiplicities in the coupled spectrum.

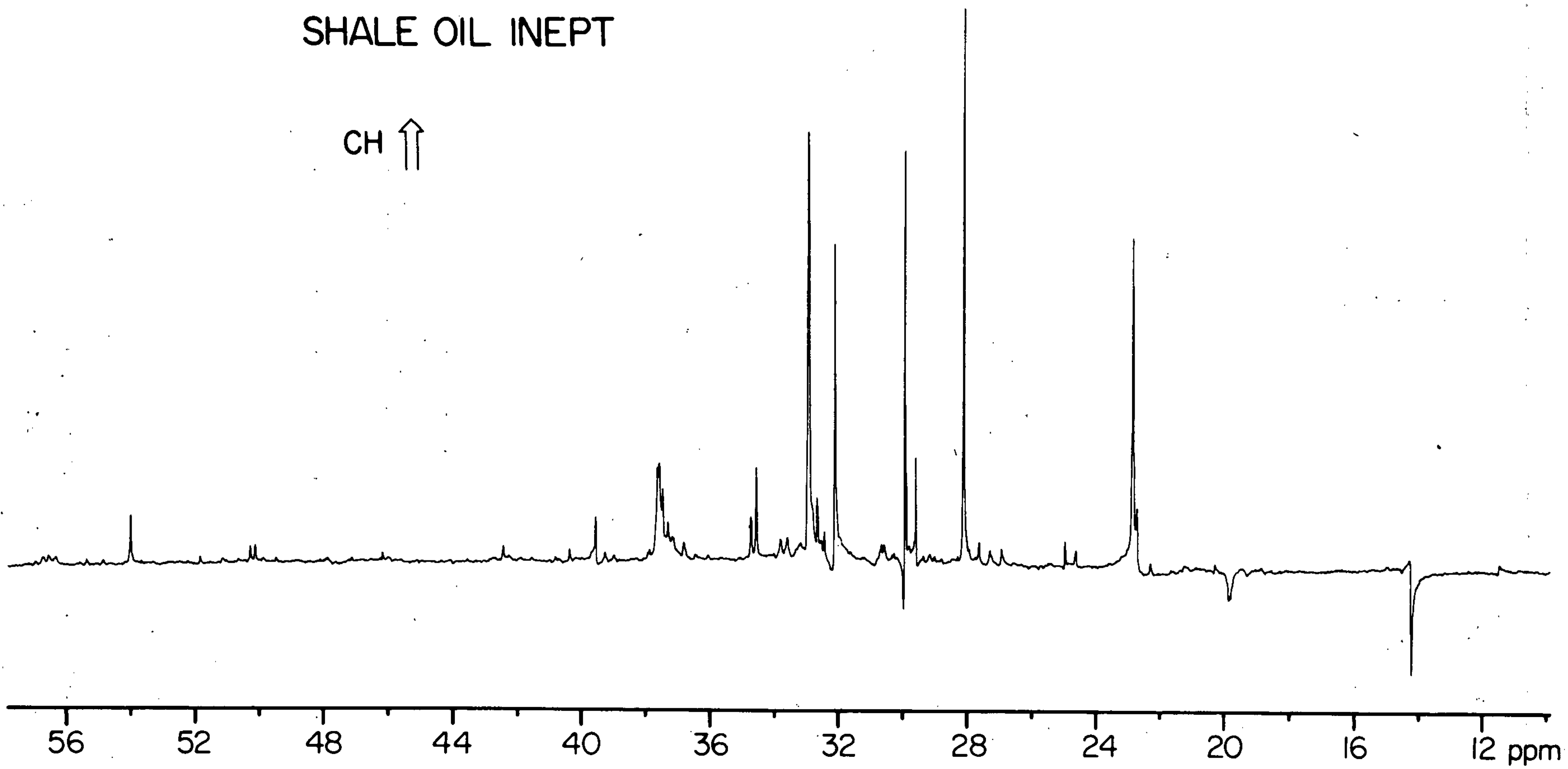


Figure VI-2: The ^{13}C spectrum produced by application of an INEPT pulse sequence to the whole crude shale oil of Figure II-1. The vertical scale is set so that only the strongest lines are observed.

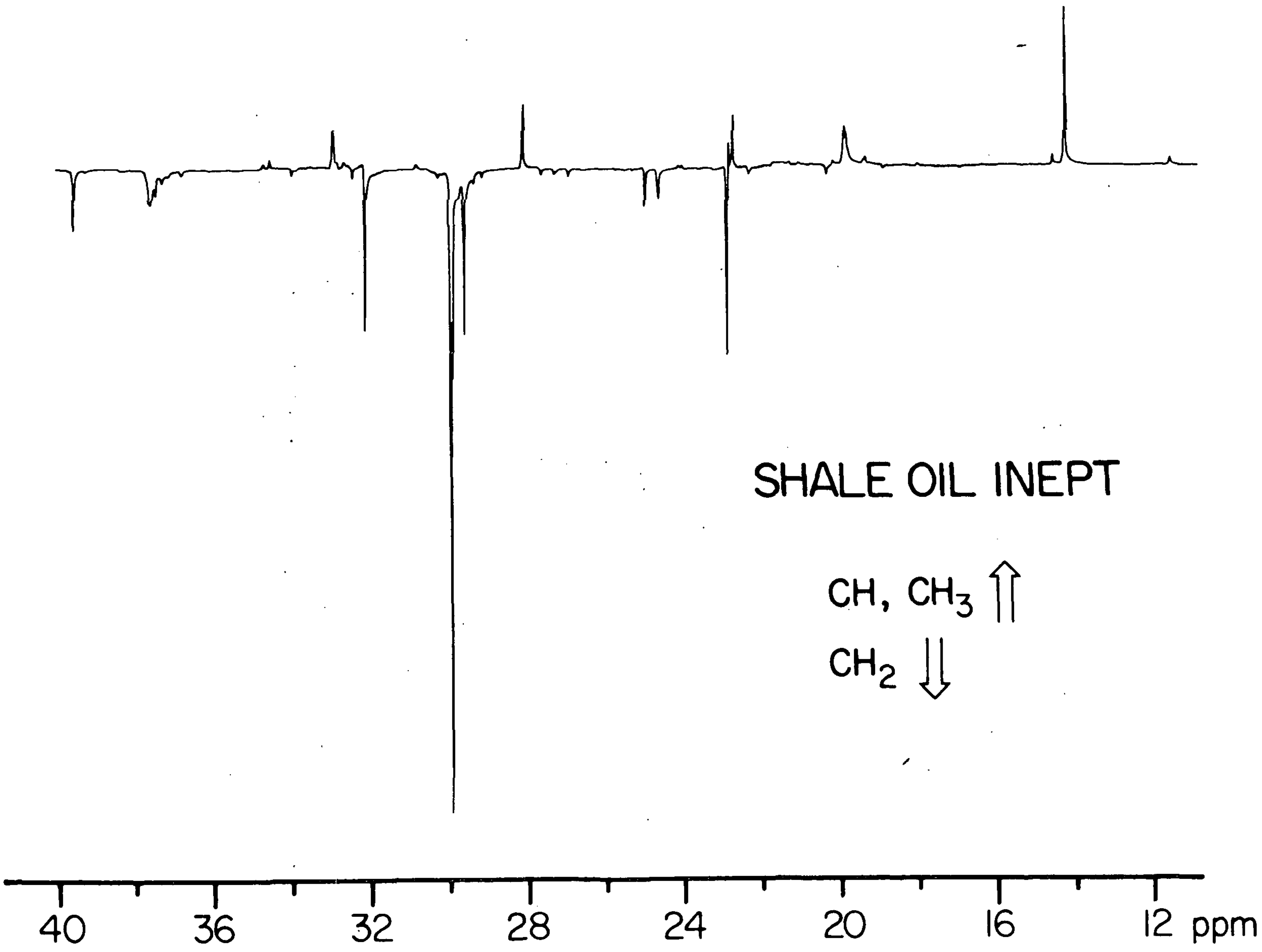


Figure VI-3: A second INEPT ^{13}C spectrum of the shale oil of Figure II-1. Increased vertical scale reveals more detail relative to the CH carbons. Resonance lines from other species are nulled or negative.

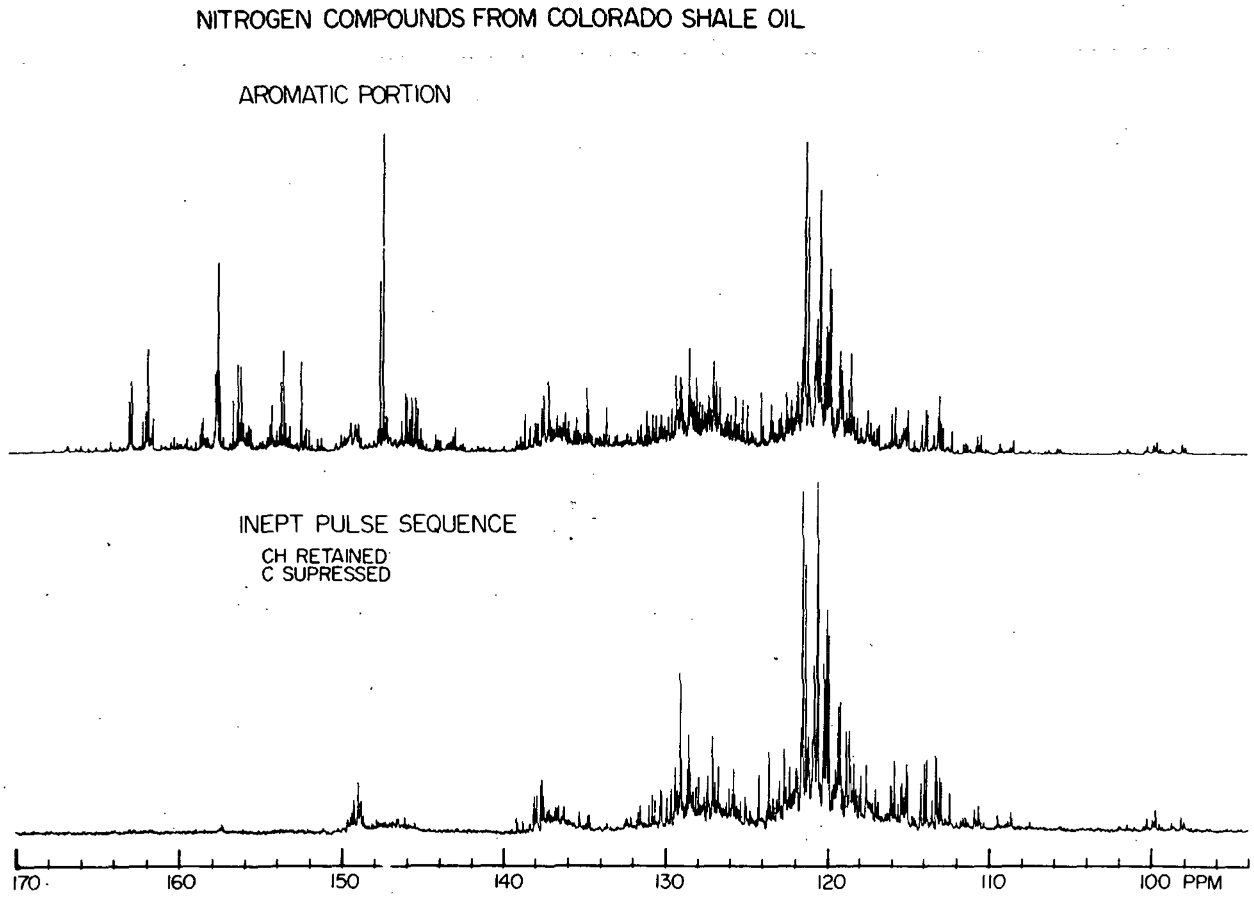


Figure VI-4: Upper trace: the aromatic region of the ^{13}C NMR spectrum of the nitrogen compounds extracted from shale oil (sample I). Lower trace: the unprotonated carbons have been nulled by use of an INEPT pulse sequence.

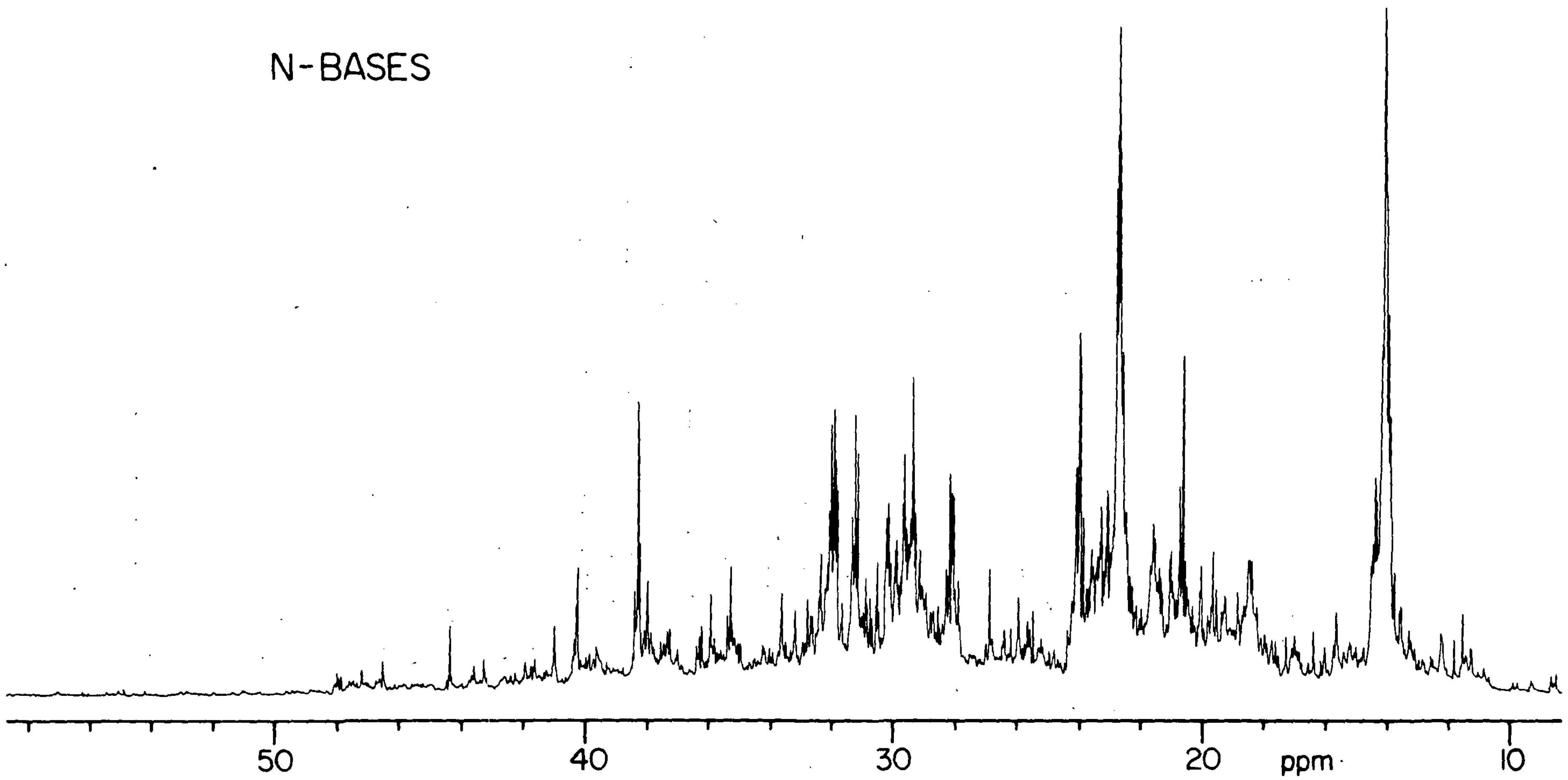


Figure VI-5: The aliphatic portion of the ^{13}C NMR spectrum of the nitrogen compounds extracted from shale oil (sample I).

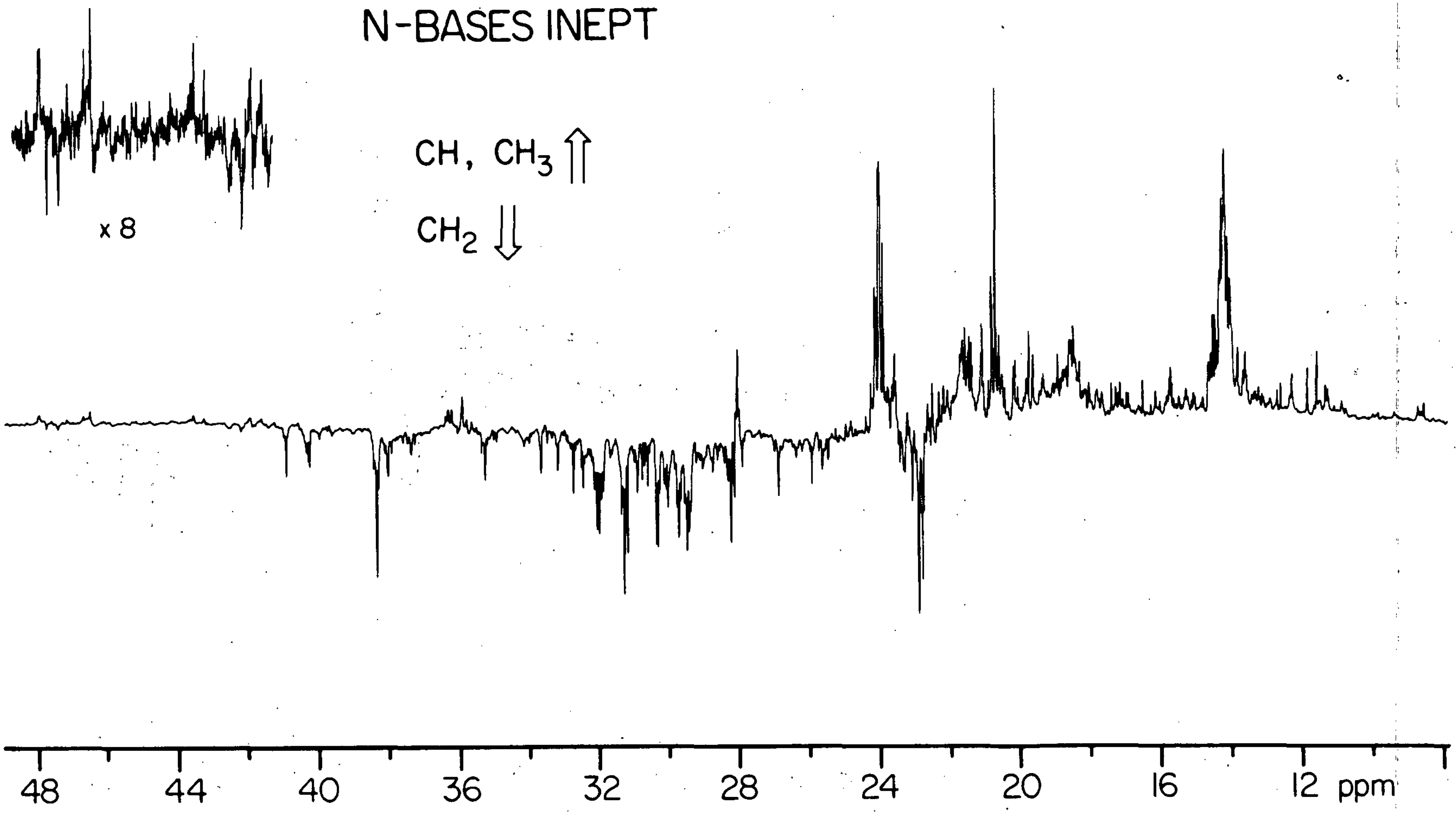


Figure VI-6: The same spectrum as shown in Figure VI-5 after application of an INEPT pulse sequence.

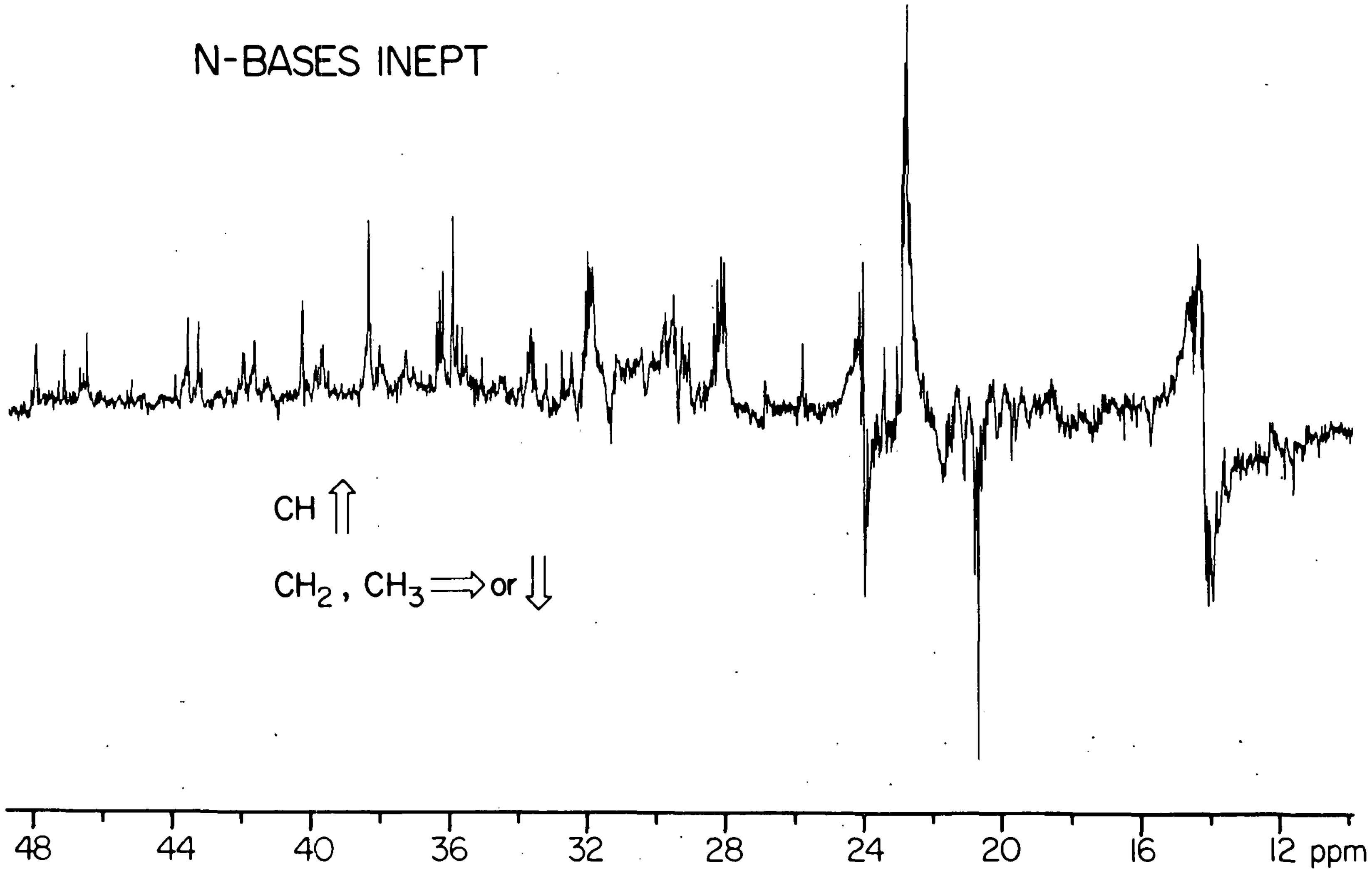


Figure VI-7: The same spectrum as given in Figure VI-6, but using a different set of delays in the INEPT pulse sequence.

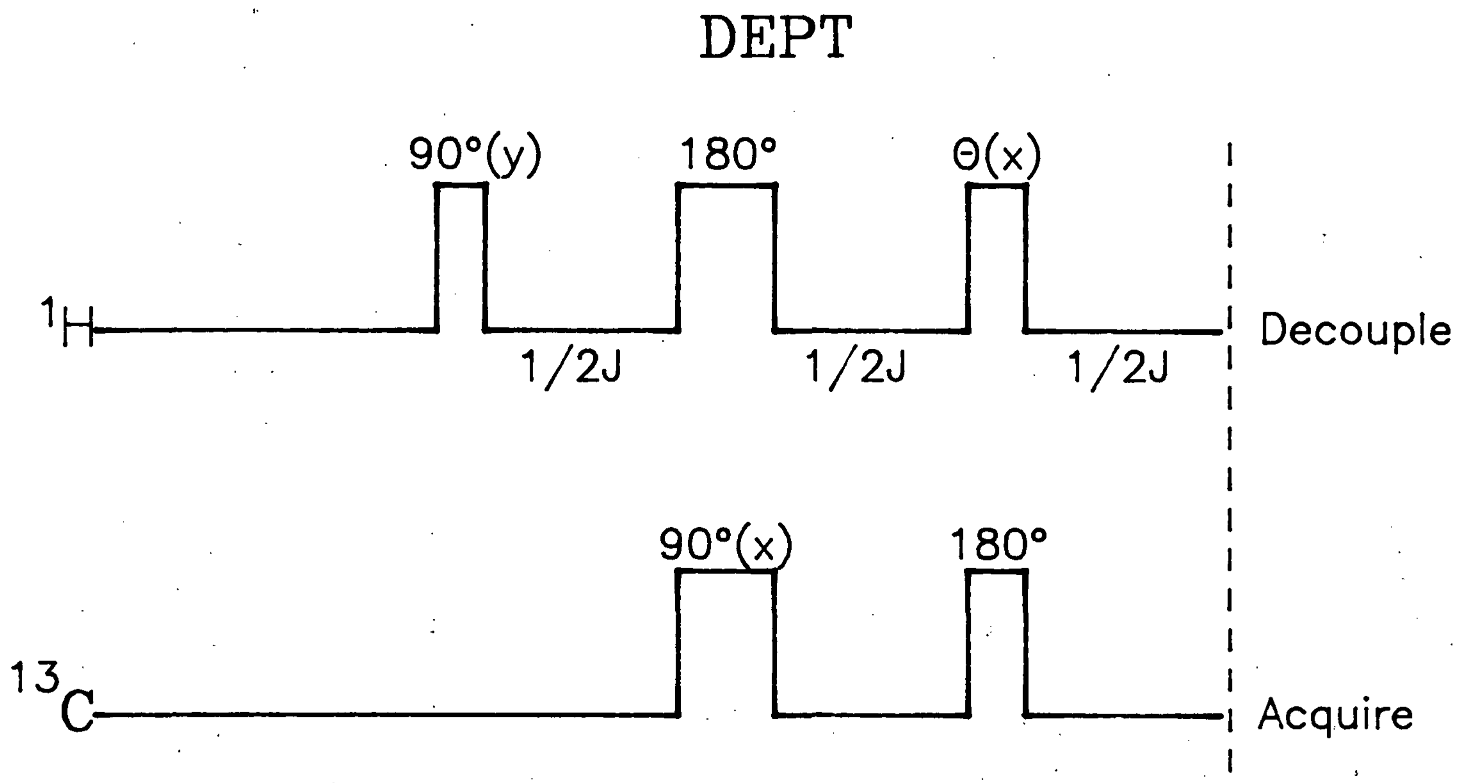


Figure VI-8: This pulse sequence produces DEPT ^{13}C NMR spectra. The value of theta is set to $\pi/4$, $\pi/2$, and $3\pi/4$ so as to enhance, null or negate lines corresponding to various multiplicities in the coupled spectrum.

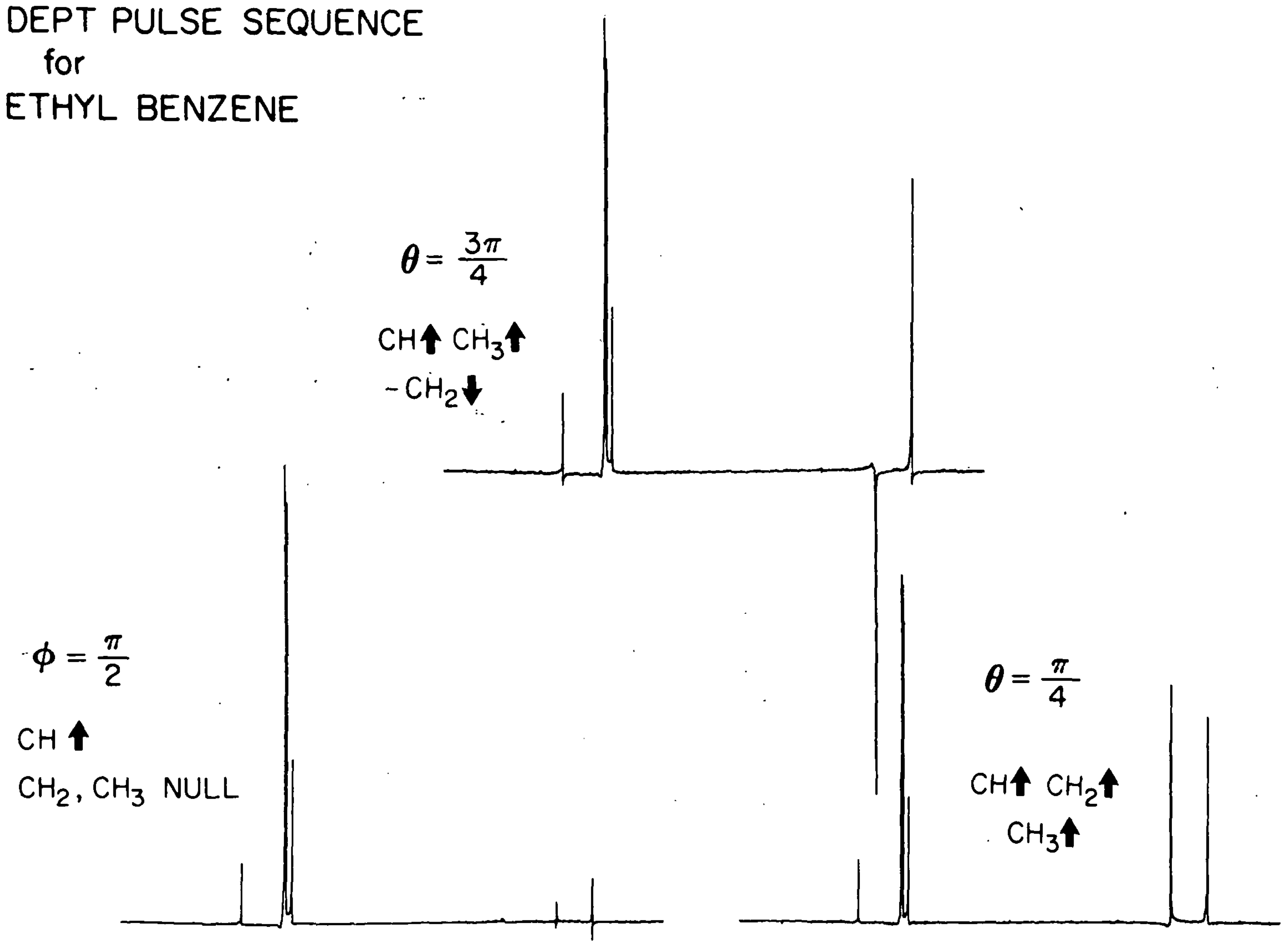


Figure VI-9: The ^{13}C spectra produced by application of a DEPT pulse sequence to ethylbenzene.

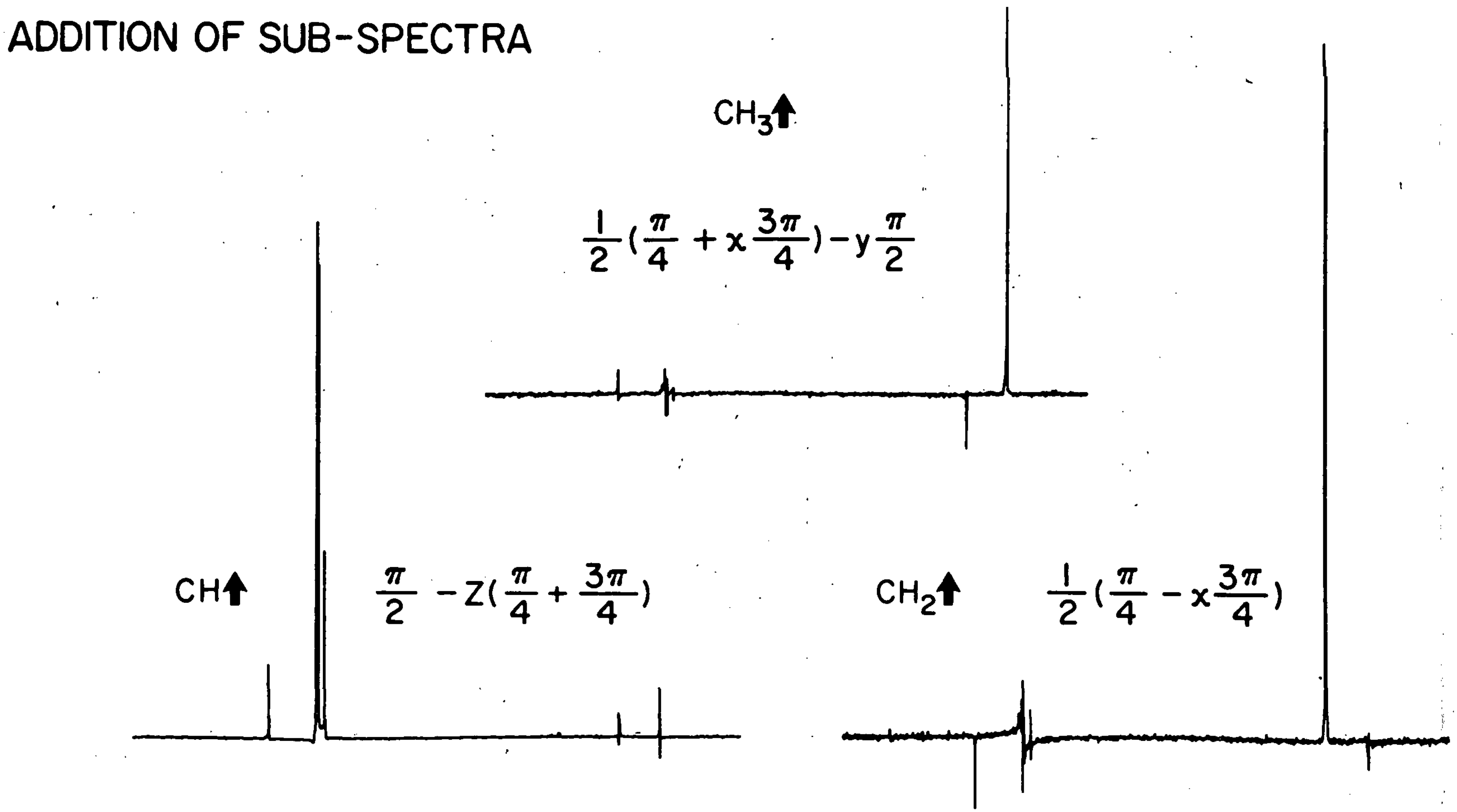


Figure VI-10: Addition and subtraction of the spectra given in Figure VI-9 according to the equations given here results in spectra containing lines of only a single multiplicity.

lines have correct relative intensities. The bottom spectrum has been produced by the DEPT procedure. The normal spectrum should be carefully integrated. Then, the bottom spectrum should be subtracted from the top one and and the result integrated. The difference in the integrals will indicate the amount of methylene carbon present as a fraction of the total. Similar calculations may be done for methyl and methyne, and by difference for unprotonated carbon.

One of the motivations for obtaining quantitative integrals from DEPT or INEPT spectra is the possible use of the data in more sophisticated analyses of hydrocarbon mixtures. We demonstrate here, for example, that it is possible to calculate the carbon/hydrogen (C/H) weight ratio or the fraction of carbon or hydrogen in a fuel mixture by use of NMR integrals derived from DEPT spectra.

The weight of carbon, C_M, of a particular multiplicity (CH_3, CH_2, CH or C) in a given sample is proportional to the NMR integral for that species. The weight of hydrogen in the sample may be delineated similarly. Hence we have

$$\frac{C_M}{C} = \frac{I_M^C}{I_T^C} = R_C \quad \text{and} \quad \frac{H_M}{H} = \frac{I_M^H}{I_T^H} = R_H$$

where I stands for integral and T for total. Now the weight ratio of carbon to hydrogen obtained by combining these equations is

$$\frac{C}{H} = \frac{C_M}{R_C} \cdot \frac{R_H}{H_M} = \frac{R_H}{R_C} \cdot \frac{C_M}{H_M} = \frac{R_H}{R_C} \cdot M$$

The ratio $M = C_M/H_M$ is just the weight ratio of carbon to hydrogen in a given type of group, i.e.

for methyl	M = 3.972
for methylene	M = 5.958
for methyne	M = 11.912

Thus it is possible to calculate the C/H ratio of a sample by knowing only the NMR integral ratios for a given type of carbon.

If aromatic CH integrals are used for the standard, R_H becomes f_a^H, hydrogen aromaticity. It is also now possible to calculate the fraction carbon, F_C, or fraction hydrogen, F_H, in the sample:

$$F_C = C/(C+H) \quad \text{and} \quad F_H = H/(C+H)$$

Since these relationships may be expressed in terms of C/H above, we readily obtain F_C and F_H in terms of the integral ratios:

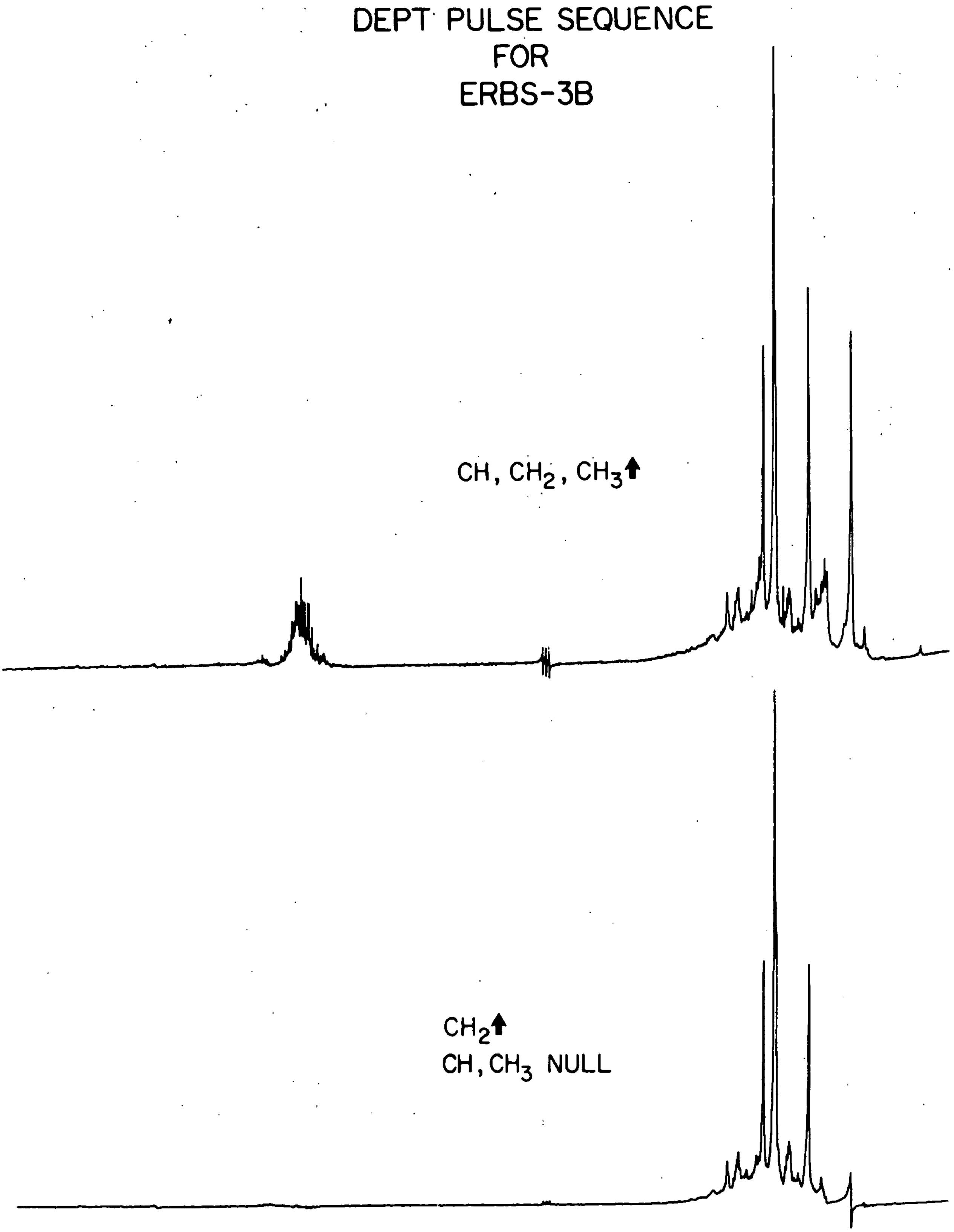


Figure VI-11: Top trace: the normal ^{13}C spectrum for ERBS 3B-12.8. Bottom trace: the CH_2 only DEPT spectrum for the same molecule. The two spectra may be subtracted to determine the amount of methylene carbon in the sample.

$$F_C = MR_H/(MR_H+R_C) \quad \text{and} \quad F_H = R_C/(MR_H+R_C)$$

Of course, the latter calculation will not be correct if the sample contains elements other than C and H, and the method is no more accurate than the integrals used to calculate the values, but it does have the definite advantage that it is not necessary to compare or calibrate to an external standard.

In order to check the method, DEPT integral values were acquired for the model compound ethylbenzene, and the H/C ratio was calculated by use of the above method. The results were within 1% of the theoretical values. Although this is somewhat less accurate than traditional elemental analysis, it is sufficiently accurate to be of great utility and suggests that the DEPT technique has the potential for generating very precise data. Unfortunately a modern spectrometer capable of doing the DEPT experiment was not routinely available during the course of this study; hence only a simple example of the power of the technique is presented.

Refinement and utilization of techniques like DEPT to determine accurately the distribution of carbon in species of the various multiplicities would allow some significant additional refinements of average parameter treatments. These developments are on the immediate horizon, and they will enable us to gain a clearer and more accurate insight into the actual composition of complex hydrocarbon mixtures.

Page intentionally left blank

Page intentionally left blank

VII. CONCLUDING REMARKS

The principle objectives of this study centered on the investigation of the following subjects:

1. model compounds related to fuels
2. products resulting from the refining of shale oil
3. properties of broadened-specification fuels
4. new spectroscopic techniques applicable to complex mixtures

These objectives have been met, and the major conclusions and scientific findings are summarized below.

The model compound studies were concentrated on four saturated, acyclic isoprenoids, farnesane, pristane, phytane, and squalane, which are similar to those found in many geochemical deposits. Such compounds are of interest, because the distribution of stereoisomers in them has been related to maturation of the deposit. Previous characterization of the diastereomers required extensive use of chemical derivatization techniques. This study has demonstrated that it is possible to detect the distribution of diastereomers in such mixtures by use of high field carbon-13 NMR. Farnesane was found to be a 1:1 mixture of isomers, probably produced by hydrogenation, while our pristane sample contained only a single isomer and is undoubtedly a natural product. Phytane was observed to exhibit mixed stereochemistry, having only one conformation represented at two chiral centers, but random stereoconformation at the third. It was likely produced by reduction and hydrogenation of naturally occuring phytol. Squalane was found to have random stereochemistry, probably resulting again from hydrogenation. Some of the carbons in that molecule were influenced by three chiral centers, poducing four resonance environments. Long range steric chemical shifts were noted for carbons as remote as seven bonds from a chiral center, and chemical shift regularities were noted.

In attempting to prepare 100 milligram quantities of fuel fractions by use of HPLC, we found that great difficulty was encountered in liberating the fractions from the eluent. This led us to utilize supercritical fluid chromatography on a modified HPLC instrument, with carbon dioxide as the carrier fluid. Successful separation of fuel samples on a preparative scale required the careful determination of needed chromatograph conditions and the development of some new techniques for sample collection.

The shale oil samples were analyzed by use of NMR. Suitable samples were fractionated by use of SCFC chromatography. One of the most interesting conclusions of this work is that perhaps the quantity of aromatic material present in a fuel sample is more critical in determining its properties than the absolute nature of the aromatic species present, at least insofar as the samples being compared are derived from the same feedstock. A second point of interest is that the long, straight chain aliphatics were observed almost exclusively in the saturates fractions.

Average parameter analysis was refined by grouping the parameters into two groups: 1) those depending only on the quality of the raw data for their accuracy, and 2) those depending upon the prior determination of other parameters. Perhaps the most critical parameter was found to be average length of alkyls, as many other values depended on its determination. The assumptions often utilized in connection with the calculation of average chain length were examined and thought to be inadequate in many cases. A second method for determining that number was developed when criteria relative to the possible number of aromatic rings were violated. The average parameters were utilized to demonstrate the formulation of model mixtures approximating the fractions in order to illustrate graphically the progress of the refining.

The ERBS samples were fractionated by use of HPLC into saturates, one-ring, two-ring, three-ring and polar fractions. The two-ring fraction consisted mostly of mono- and dimethylnaphthalenes with some ethyl substitution, but little other saturated carbon. It was not possible to identify specific compounds in the three-ring fraction, but again the saturated carbon was limited almost exclusively to methyl groups.

The ERBS samples were subjected to SCFC separation and average parameter analysis as above. The analysis revealed that the aromatic fuel fractions resembled more the shale products before final aromatic saturation rather than the finished fuels. Example model mixtures were again developed.

Theoretical considerations were developed to demonstrate the necessity of an aromatic-saturates separation in order that an average parameter analysis produce accurate results. INEPT spectra of some of the shale samples were evaluated relative to the information on multiplicity and composition which they provided. It was also demonstrated that DEPT spectra might be used to extract some quantitative information not available from standard NMR spectra.

Suggestions for future work might include application of the separation and analysis techniques developed in this study to refinery products of traditional crudes, in order to compare the results. Obviously, we have been able only to scratch the surface of the possible applications of SCFC to fuels analysis. Also, the utilization of DEPT for direct determination of the amounts of carbon of various multiplicities suggests the refinement of average parameter analysis far beyond what is now available.

REFERENCES

1. Symposium on Aircraft Research and Technology for Future Fuels, Preprint, NASA Lewis Research Center, Cleveland, Ohio, April 1980.

2. Industry-military Energy Symposium, Preprint, Directorate of Energy Management, Air Logistics Center, Kelly Air Force Base, San Antonio, Texas, October 1980.

3. Shelton, E.M., "Aviation Turbine Fuels, 1978," U.S. Department of Energy, BETC/PPS-79/2, 1979.

4. Dickinson, E., "Structural Comparison of Petroleum Fractions Using Proton and ^{13}C NMR Spectroscopy," Fuel, Vol. 59, 1980, pp. 290-294, for example.

5. Netzel D.A.; McKay, D.R.; Heppner, R.A.; Guffey, F.D.; Cooke, S.D.; Varie, D.L.; Linn, D.E., "^{1}H- and ^{13}C-NMR Studies on Naphtha and Light Distillate Saturate Hydrocarbon Fractions Obtained from in-situ Shale Oil," Fuel, Vol. 60, 1981, pp. 307-320.

6. Joseph, J.T.; Wong, J.L., "Distribution of Aliphatic and Aromatic Carbons in H-Coal Liquids by Quantitative ^{13}C FT-NMR Spectroscopy," Fuel, Vol. 59, 1980, pp. 777-781, for example.

7. Suzuki, T.; Itoh, M.; Takegami, Y.; Watanabe, Y., "Chemical Structure of Tar-sand Bitumens by ^{13}C and ^{1}H NMR Spectroscopic Methods," Fuel, Vol. 61, 1982, pp. 402-410, for example.

8. Deutsch, V.K.; Jancke, H.; Zeigan, D., "Struktur der Alkylsubstituenten in den Aromaten des Rohols," J. Prakt. Chem., Vol. 318, 1976, pp. 177-184.

9. Deutsch, V.K.; Jancke, H.; Zeigan, D., "Struktur der Isoparaffine des Rohols ," J. Prakt. Chem., Vol. 319, 1977, pp. 1-7.

10. Maxwell, J.R.; Cox, R.E.; Ackman, R.G.; Hooper, S.N., "The Diagenesis and Maturation of Phytol. The Stereochemistry of 2,6,10,14-Tetramethylpentadecane from an Ancient Sediment," Adv. in Org. Geochem., 1971, pp. 277-291, and references therein.

11. Patience, R.L.; Rowland, S.J.; Maxwell, J.R., "The Effect of Maturation on the Configuration of Pristane in Sediments and Petroleum," Geochim. Cosmochim. Acta, Vol. 42, 1978, pp. 1871-1875.

12. Patience, R.L.; Yon, D.A.; Ryback, G.; Maxwell, J.R., "Acyclic Isoprenoid Alkanes and Geochemical Maturation," in Advances in Organic Geochemistry. Physics and Chemistry of the Earth, Douglas, A.G. and Maxwell, J.R., Eds., Pergamon Press, New York, N.Y., 1980, pp. 287-293.

13. Morrison, R.T.; Boyd, R.N., Organic Chemistry, Allyn and Bacon, Inc., Boston, Mass., Third Edition , 1973, pp. 130-133.

14. Jennings, W.B., "Chemical Shift Nonequivalence in Prochiral Groups," Chemical Reviews, Vol. 75, 1975, pp. 307-322.

15. Dalling, D.K.; Grant, D.M., "Carbon-13 Magnetic Resonance. IX. The Methylcyclohexanes," J. Am. Chem. Soc., Vol. 89, 1967, pp. 6612-6622.

16. Dalling, D.K.; Grant, D.M.; Paul, E.G., "Carbon-13 Magnetic Resonance. XXIII. The Methyldecalins," J. Am. Chem. Soc., Vol. 95, 1973, pp. 3718-3724.

17. Dalling, D.K.; Grant, D.M., "Carbon-13 Magnetic Resonance. XXIV. The Perhydroanthracenes and Perhydrophenanthrenes," J. Am. Chem. Soc., Vol. 96, 1974, pp. 1827-1834.

18. Anders, D.E.; Robinson, W.E., "Geochemical Aspects of the Saturated Hydrocarbon Constituents of Green River Oil Shale-Colorado No. 1 Core," U.S. Bureau of Mines Report of Investigations No. 7737, 1973, for example.

19. Beierbeck, H.; Saunders, J.K., "Conformational and Configurational Analysis of Hydrocarbon Chains Based on Time-averaged Carbon-13 Chemical Shifts," Can. J. Chem., Vol. 55, 1977, pp. 771-781.

20. Elgert, K.-F.; Ritter, W., "Diastereomere Alkane als Modelle fur die ^{13}C-NMR-Spektroskopie von Polymeren," Makromol. Chem., Vol. 178, 1977, pp. 2857-2866.

21. Klespler, E.; Corwin, A.H.; Turner, D.A., "High Pressure Gas Chromatography above Critical Temperatures," J. Org. Chem., Vol. 27, 1962, pp. 700-701.

22. Gouw, J.T.; Jentoft, R.E., "Supercritical Fluid Chromatography," in Chromatography in Petroleum Analysis, Altgelt K.H. and Gouw, T.H., Eds., Marcel Dekker, Inc., New York, N.Y., 1979, Chap. 13.

23. Peader P.A.; Lee, M.L., "Supercritical Fluid Chromatography: Methods and Principles," J. Liq. Chrom., Vol. 5, 1982, pp. 179-221.

24. Gere, D.R.; Board R.; McManigill, D., "Supercritical Fluid Chromatography with Small Particle Diameter Packed Columns," Anal. Chem., Vol. 54, 1982, pp. 736-740.

25. Antoine, A.C., "Comparison of the Properties of Some Synthetic Crudes with Petroleum Crudes," NASA Technical Memorandum 79220, Lewis Research Center, Cleveland, Ohio, June 1981.

26. Prok, G.M.; Flores, F.J.; Seng, G.T., "Effect of Hydroprocessing Severity on Characteristics of Jet Fuel from TOSCO II and Paraho Distillates," NASA Technical Paper 1768, Lewis Research Center, Cleveland, Ohio, June 1981.

27. Universal Oil Products, "USAF Shale Oil to Fuels," Technical Report AFWAL-TR-81-2116, Wright Aeronautical Laboratories, Wright-Patterson Air Force Base, Ohio, 1980-1982.

28. Amoco Oil Company, "Evaluation of Hydrocracking Catalysts for Conversion of Whole Shale Oil into High Yields of Jet Fuels," Technical Report AFWAL-TR-81-2098, Wright Aeronautical Laboratories, Wright-Patterson Air Force Base, Ohio, 1981-1982.

29. Johnson, C.A.; Moore, H.F.; Sutton, W.A., Ashland Petroleum Company, "Refining of Military Jet Fuels from Shale Oil," Technical Report AFWAL-TR-81-2056, Wright Aeronautical Laboratories, Wright-Patterson Air Force Base, Ohio, 1982.

30. Yokoyama, S.; Uchina, H.; Katoh, T.; Sanada, Y.; Wainai, T., "Combination of ^{13}C- and ^{1}H-NMR Spectroscopy for Structural Analyses of Neutral, Acidic and Basic Heteroatom Compounds in Products from Coal Hydrogenaton," Fuel, Vol. 60, 1981, pp. 255-262.

31. Mashimo, K.; Nakayama, I.; Kiya, K.; Wainai, T., "Determination of Bridgehead Aromatic Carbons in Coal-derived Materials," Fuel, Vol. 61, 1982, pp. 193-195.

32. Takegami, Y.; Watanabe, Y.; Suzuki, T.; Mitsudo, T-a; Itoh, M., "Structural Investigation on Column-chromatographed Vacuum Residues of Various Petroleum Crudes by ^{13}C Nuclear Magnetic Resonance Spectroscopy," Fuel, Vol. 59, 1980, pp. 253-259.

33. Gillet, S.; Rubini, P.; Delpeuch, J.-J.; Escalier, J.-C.; Valentin, P., "Quantitative Carbon-13 and Proton Nuclear Magnetic Resonance Spectroscopy of Crude Oil and Petroleum Products. I. Some Rules for Obtaining a Set of Reliable Structural Parameters," Fuel, Vol. 60, 1981, pp. 221-225.

34. O'Donnell, D.J.; Sigle, S.O.; Berlin, K.D.; Sturm, G.P.; Vogh, J.W., "Characterization of High-boiling Petroleum Distillate Fractions by Proton and ^{13}C Nuclear Magnetic Resonance Spectrometry," Fuel, Vol. 59, 1980, pp. 166-178.

35. Netzel, D.A. and Hunter, P.M., "Hydrocarbon Type Analysis of Jet Fuels by ^{1}H and ^{13}C NMR," Department of Energy/LETC/RI-81-1, 1981.

36. Universal Oil Products, "Calculation of UOP Characterization Factor and Estimation of Molecuar Weight of Petroleum Oils," Technical Report UOP Method 375-59, Des Plaines, Illinois, 1959.

37. Williams, R.B., "Characterization of Hydrooarbons in Petroleum by Nuclear Magnetic Resonance Spectrometry," in <u>Symposium on Composition of Petroleum Oils, Determination and Evaluation</u>, ASTM Special Technical Publication No. 224, 1958, pp. 168-194.

38. Longwell, J.P., Ed., "Jet Aircraft Hydrocarbon Fuels Technology," NASA Technical Report CP-2033, 1977.

39. <u>Coordinating Research Council Annual Report for the Year Ending June 30, 1979</u>, Coordinating Research Council, Inc., Atlanta, Georgia, 1979.

40. Prok, G.M.; Seng G.T., "Initial Characterization of an Experimental Referee Broadened-specification (ERBS) Aviation Turbine Fuel," NASA Technical Memorandum 82833, 1982.

41. Wilson, N.K.; Stothers, J.B., "^{13}C and ^{1}H Spectra of Some Methylnaphthalenes," <u>J. Mag. Res.</u>, Vol. 15, 1974, pp. 31-39.

42. Dalling, D.K.; Ladner, K.H.; Grant D.M.; Woolfenden, W.R., "Carbon-13 Magnetic Resonance. 27. The Dependence of Chemical Shifts on Methyl Rotational Conformations and Dynamics in the Methylated Benzenes and Naphthalenes," <u>J. Am. Chem. Soc.</u>, Vol. 99, 1977, pp. 7142-7150.

43. Caspar, M.L.; Stothers, J.B.; Wilson, N.K., "^{13}C Nuclear Magnetic Resonance Studies of Methylated Anthracenes," <u>Can. J. Chem.</u>, Vol. 53, 1975, pp. 1958-1969.

44. Freeman, R.; Morris, G.A.; Turner, D.L., "Proton-coupled Carbon-13 <u>J</u> Spectra in the Presence of Strong Coupling. I," <u>J. Mag. Res.</u>, Vol. 26, 1977, pp. 373-78.

45. Dalling, D.K.; Haider, G.; Pugmire, R.J.; Shabtai, J.S.; Hull, W.E., "Application of New Carbon-13 NMR Techniques to the Study of Products from Catalytic Hydrodeoxygenation of SRC-II Liquids," <u>Fuel</u>, Vol. 63, 1984, pp. 525-529.

46. Doddrell, D.M.; Pegg, D.T., "Assignment of Proton-decoupled Carbon-13 Spectra of Complex Molecules by Using Polarizaton Transfer Spectroscopy. A Superior Method to Off-resonance Decoupling," <u>J. Am. Chem. Soc.</u>, Vol. 102, 1980, pp. 6388-6390.

47. Doddrell, D.M.; Pegg, D.T.; Bendall, M.R., "Distortionless Enhancement of NMR Signals by Polarization Transfer," <u>J. Mag. Res.</u>, Vol. 48, 1982, pp. 323-327.

1. Report No. NASA CR-174761	2. Government Accession No.	3. Recipient's Catalog No.

4. Title and Subtitle

Carbon-13 and Proton Nuclear Magnetic Resonance Analysis of Shale-derived Refinery Products and Jet Fuels and of Experimental Referee Broadened-specification Jet Fuels

5. Report Date

September 1984

6. Performing Organization Code

7. Author(s)

Don K. Dalling, Brent K. Bailey, Ronald J. Pugmire

8. Performing Organization Report No.

None

10. Work Unit No.

9. Performing Organization Name and Address

University of Utah Research Institute
Research Park
Salt Lake City, Utah 84108

11. Contract or Grant No.

NAG 3-27

13. Type of Report and Period Covered

Contractor Report

12. Sponsoring Agency Name and Address

National Aeronautics and Space Administration
Lewis Research Center
Cleveland, Ohio 44135

14. Sponsoring Agency Code

505-31-42

15. Supplementary Notes

Final Report. Project Manager, Gary T. Seng, Aerothermodynamics and Fuels Division, NASA Lewis Research Center, Cleveland, Ohio 44135.

16. Abstract

A proton and carbon-13 nuclear magnetic resonance (NMR) study was conducted of Ashland shale oil refinery products, experimental referee broadened-specification jet fuels, and of related isoprenoid model compounds. Supercritical fluid chromatography techniques using carbon dioxide were developed on a preparative scale, so that samples could be quantitatively separated into saturates and aromatic fractions for study by NMR. An optimized average parameter treatment was developed, and the NMR results were analyzed in terms of the resulting average parameters; formulation of model mixtures was demonstrated. Application of novel spectroscopic techniques to fuel samples was investigated.

17. Key Words (Suggested by Author(s)) Nuclear magnetic resonance (NMR); Jet fuels; NMR fuels characterization; Shale products; Broadened-specification fuels; Supercritical fluid chromatography; NMR average parameters; NMR isoprenoid studies	18. Distribution Statement Unclassified - unlimited STAR Category 28

19. Security Classif. (of this report) Unclassified	20. Security Classif. (of this page) Unclassified	21. No. of pages 107	22. Price* A06

*For sale by the National Technical Information Service, Springfield, Virginia 22161

National Aeronautics and
Space Administration

Washington, D.C.
20546

Official Business
Penalty for Private Use, $300

SPECIAL FOURTH CLASS MAIL
BOOK

U.S. MAIL

Postage and Fees Paid
National Aeronautics and
Space Administration
NASA-451

NASA

POSTMASTER: If Undeliverable (Section 158
Postal Manual) Do Not Return