A CARBON-13 NMR INVESTIGATION OF THE CHEMICAL COMPOSITION OF COAL DERIVED LIQUIDS

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The recent increased importance of coal as an energy source has dictated that more knowledge be obtained about the basic molecular properties of the solid and its conversion properties. Starting as early as 1966, Carbon-13 NMR spectroscopy has been employed on a limited basis for the analysis of coal derived liquids as well as petroleum samples. Extensive C-13 NMR work has been carried out in our laboratories on Utah coal derived liquid samples which have been subjected to LC and GPC separation techniques. NMR data taken at 25 MHZ and 75 MHZ have been analyzed on the acidic, basic, and neutral portions of the oils in question. These data have demonstrated that valuable chemical information can be readily obtained on aromatic and hydroaromatic ring structures and ring substituents in coal liquids obtained from different sources. The chemical significance of these results will be discussed.

I. Introduction

The recent increased importance of coal as an energy source has dictated that more knowledge be obtained about the basic molecular properties of the solid and its conversion products. In the solid form, coal does not readily lend itself to a detailed molecular characterization. However, recent advances in experimental techniques[1] have been quite encouraging and promise to shed new light on this chemical structural characteristic of solid hydrocarbons.

Starting with the work of Friedel and Retcofsky,[2,3] Carbon-13 nuclear magnetic resonance has been employed on a limited basis for the analysis of coal derived liquids as well as petroleum samples.[2,4] Early works were somewhat hampered in these investigations due to such complicating factors as: 1) instrument sensitivity and techniques; 2) the lack of an extensive reservoir of Carbon-13 magnetic resonance (CMR) data on which to base detailed spectral interpretation; and 3) the extremely complex chemical composition of the materials under investigation. The problems associated with adequate instrumentation for the analysis of complex hydrocarbon investigation have largely been overcome in the past 5-7 years with the advent of fourier transform NMR techniques.[5] Many early workers in the CMR field concentrated their efforts on hydrocarbons and by the early 1970s a fairly extensive body of chemical shift data on fossil fuel derived hydrocarbons was emerging.[6] Advances in instrumentation has significantly aided in this interpretation of the composition of complex hydrocarbon mixtures. Whereas, early studies were concerned with such problems as aromaticity of various coal samples[2,3,4,6,7,8] and average molecular parameters,[9] only limited progress was made in increasing the sophistication of the analytical results obtained by means of CMR. More recent workers focused on analysis of the extracts from coal.[10,11] However, recognition of the necessity to fractionate coal derived liquids in order to enhance sample analysis has provided useful new information regarding the chemical structure of the liquid.[12,13] While LC and GPC separation schemes required to fractionate the coal liquids are well known, they involve significant effort.

This work is the first in a series describing the chemical information derived from the LC and GPC chromatographic separation and CMR analysis of the liquefication products of Hiawatha high volatile bituminous coal.

II. Experimental

A. Liquefication and Separation Procedure

The coal used in this study was Utah high volatile bituminous B rank. The details of the hydrogenation procedure have been given elsewhere.[14] The coal hydrogenation product was initially obtained as a "light liquid" and "heavy liquid" product in the two condenser units of the reactor. The heavy coal hydrogenated product was separated into saturates, monoaromatic, diaromatic, triaromatic, and polyaromatic/polar fractions using gradient elution through dual-packed (silica gel-alumina gel) absorption columns according to the technique described by Hirsch et al.[15] Further separation of these fractions was obtained by means of gel permeation chromatography (GPC) in accordance with the procedure of Haines and Thompson.[16] The separation scheme employed is portrayed in Figure 1.

B. NMR Procedures

Proton spectra for each sample was obtained on a Varian EM-390 spectrometer. Carbon-13 NMR spectra were obtained on Varian XL-100 and SC-300 sepectrometers, operating in the fourier transform mode. At 25 MHZ, an 8K spectra was obtained on each sample using 0.8 sec. acquisition time, a 45° pulse angle and no pulse delay. At 75 MHZ, a 16 K spectra was obtained utilizing 0.9 sec. acquisition time, a 45° pulse angle, and no pulse delay. Deuterochloroform was used as solvent and samples were run in 5 or 10 mm tubes, depending on quantity of sample available. Standard broad-band decoupling was used and no attempts were made to compensate for differences in carbon NOE or T_1 values.

III. Results and Discussion

The distribution of materials derived from gradient elution through silica-alumina gel columns are given in Table 1. The asphaltene and oil samples were further separated by GPC techniques into seven subfractions. The acidic fraction was further separated by both GPC and LC techniques into five GPC and five LC fractions. The CMR data of selected fractions of the saturate, monoaromatic, diaromatic, triaromatic, poly/polar aromatic and asphaltene fractions are shown in Figures 2-10. It was noted that in GPC fraction number one of all aromatic species, the saturates region is dominated by the spectral lines associated with normal paraffin groups. With subsequent fractions one observes a marked decrease in unbranched paraffinic structure with little or no evidence of such side chains in the last fractions (smallest molecular size) eluted from the column. These results can be rationalized by considering the volume occupied by flexible alkyl substituents on the aromatic rings in question, which, on the basis of effective molecular size, would be quickly eluted from the column.

By closely examining the spectra of each GPC fraction and comparing the line positions with those of model compounds, it is possible to derive structural features which can be used to arrive at types of molecular species that may be present. For instance, comparison of Figure 4 with Figure 6, 7, 9 and 10 illustrates that only a restricted number of possible aliphatic and/or cycloaliphatic structures are present in substantial amounts in the smaller molecular weight fractions of the polynuclear aromatic and asphaltene compounds as compared with

the monoaromatic family of compounds. In fact, the banding structure in the aliphatic region of Figures 6, 7, 9, and 10 correspond to the lines predicted for hydroaromatic species that do not contain a large number of alkyl side chains on the cycloaliphatic moeity. With the exception of GPC fractions 1 and 2 of all samples examined, which have a relatively high percentage of n-alkyl side chains, one observes a general preponderance of aliphatic line patterns similar to those in Figures 6, 7, 9, and 10.

The data in Table 2-6 provide a convenient summary of the general structural features of the individual oil fractions examined. No attempt has been made to portray all the structural features that may be present nor to attempt to quantify the results. Rather, structural features are given for the most easily identified molecular species.

It is interesting to note that electronegative functional groups containing oxygen and nitrogen usually shift adjacent carbon atoms sufficiently downfield, compared to carbons which do not bear a substituent, to enable ready identification. Of the 34 GPC fractions of the oil fractions examined in detail, only 3 fractions exhibit evidence of such functional groups. GPC fraction number one in the 3-ring aromatic fraction was the only sample exhibiting carbons contained in or adjacent to an ester functional group; i.e., $R-\overset{O}{\overset{\|}{C}}-O-C-R$. In the case of the polyaromatic/polar fraction, GPC fractions four and seven display resonance lines indicative of the presence of ethers and/or alcohols. The functional groups could not be present in more than a few tenths percent. Hence, the CMR data suggests that the majority of the oxygen and, perhaps the nitrogen compounds as well, are not present in the oils but, rather, have probably concentrated in the other fractions (acids, bases, and asphaltenes). The CMR data does not permit comment on the presence of absence of nitrogen or sulfur species.

With the exception of GPC fractions 1, 2, and 3 of the saturates fraction, which contain almost entirely normal paraffins, the spectral lines are so complex that at 25 MHZ only a small fraction of the chemical information available can be interpreted. An illustration example of the power of carbon-13 NMR techniques to simplify the problem somewhat is illustrated in Figures 11, 12 and 13. In this case the light liquid, which has not been subjected to any further separation, was examined at 75 MHZ (Figure 12) with the corresponding 25 MHZ spectrum (Figure 11) included for purposes of comparison. The increased field of the superconducting spectrometer not only provides a three-fold increase in line dispersion but also greatly increases the sensitivity. Hence, with this higher field one can resolve nearly all of the lines in the spectrum in Figure 11. (It is admitted that the light liquid is less complex than the GPC fractions considered in this paper but the comparison is informative). A 250 Hz plot (Figure 13) of a portion of the aromatic region in Figure 12 demonstrates the wealth of chemical information that is available in this sample. This light liquid sample has been subjected to a GC separation using glass capillary column techniques by Dr. F. J. Yang.[17] Using a flame ionization detector, 306 peaks in the chromatogram were resolved and measured by means of computer techniques.[17,18] However, only 30-40 compounds are present in significant amounts (ca. 1%). Dr. J. N. Shoolery has employed ^{13}C NMR analysis, using microsampling techniques,[19] to identify toluene as the most prominent component in the light liquid.[20] The resonance positions of toluene are marked in Figure 12.

It is interesting to point out, without further comment, that the resonance lines for alkenes are observed in nearly all GPC fractions studied.

The GPC and LC subfractions of the acid fraction were examined in detail. GPC fractions 4 and 5 were not studied due to solubility problems in a solvent suitable for CMR studies. GPC fractions 1-3 exhibited resonance lines in the aromatic region associated with phenolic and carbazolic structures. However, little significant change was observed in either the aromatic or aliphatic regions as a function of molecular size. The five LC fractions examined also exhibited aromatic lines characteristic of phenol and carbozole derivatives. However, the relative changes in resonance line patterns were quite distinct, especially in the saturate region, between the various fractions that were eluted from the column. Perhaps the most significant result is that only in sample LC-3 (the third sample collected from the column) one observes resonance lines from both ester and ether functional groups. Inasmuch as silica-alumina gel columns have functional separation characteristics, it is not surprising that such discrimination is noted.

The basic fraction was subjected to LC separation techniques only and exhibited the resonance lines in the aromatic region characteristic of pyridine type compounds and their derivatives.

The CMR data obtained demonstrates the utility of Carbon-13 NMR techniques in obtaining chemical structural information on coal derived liquids. As with any analytical technique, the detail of the information obtained is dependent, to some extent, on the sophistication of the separations scheme employed in order to reduce the number of compounds or compound types to a manageable level. However, even the most elaborate separation scheme renders individual compound identification very tedious if it must be carried out manually. Fortunately, the advent of sophisticated data processing equipment may soon allow significant progress in this area as archival files and data manipulating sub-routines replace the inadequacies of human data analysis. The status of these techniques will be discussed.

ACKNOWLEDGEMENTS

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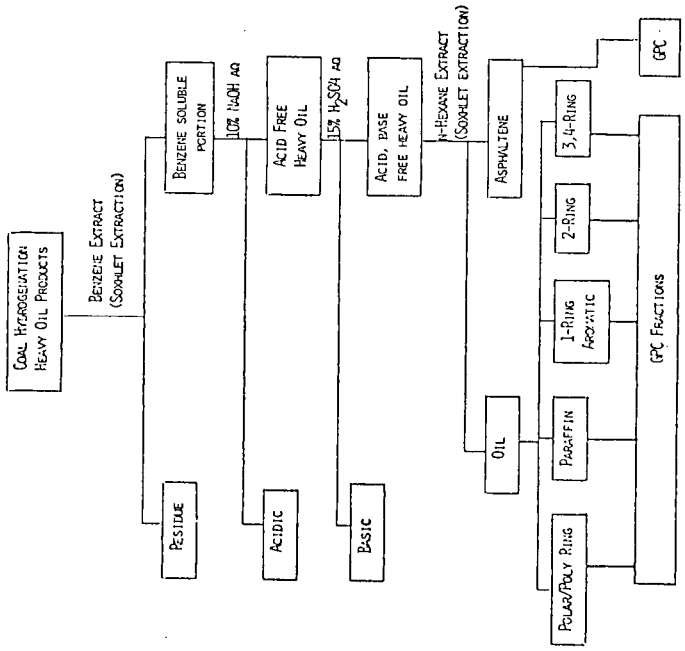
FIGURE 1

SEPARATION SCHEME



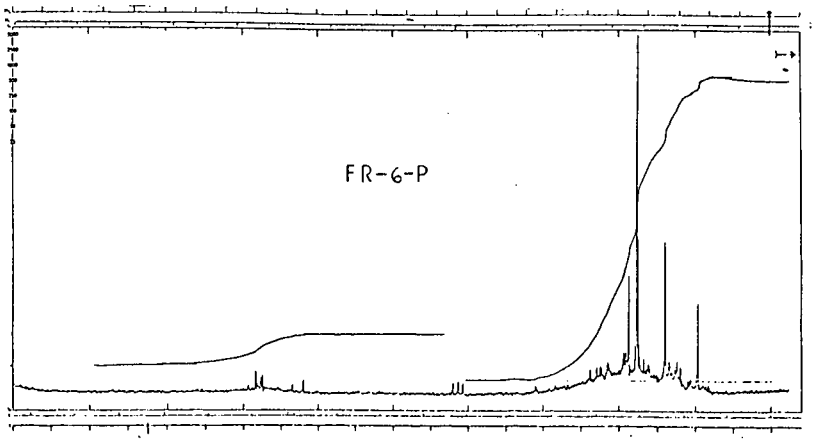


FIGURE 2 GPC subfraction number 6 of the saturates fraction of the heavy oil. UV data indicate that aromatic species are present. However, line positions in the unsaturates regional also indicate the presence of alkenes. Predominant lines are due to normal alkanes. Spectra was taken at 25 MHz.

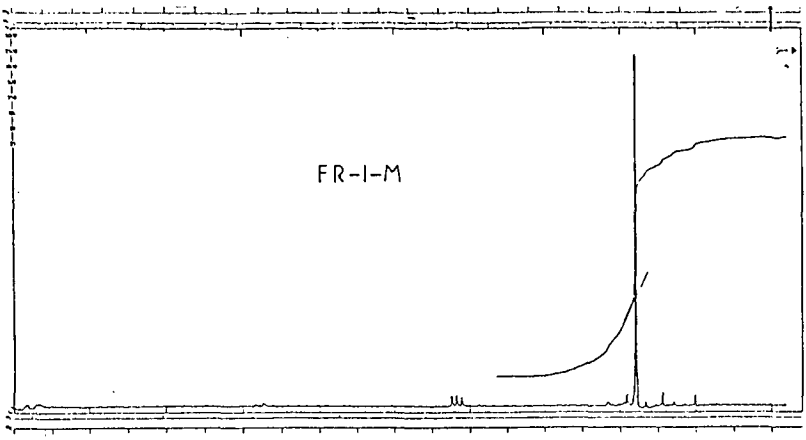


FIGURE 3 GPC subfraction number 1 of the monoaromatic fraction. Little structure is observable except in the aliphatic region where n-alkyl substituents dominate.

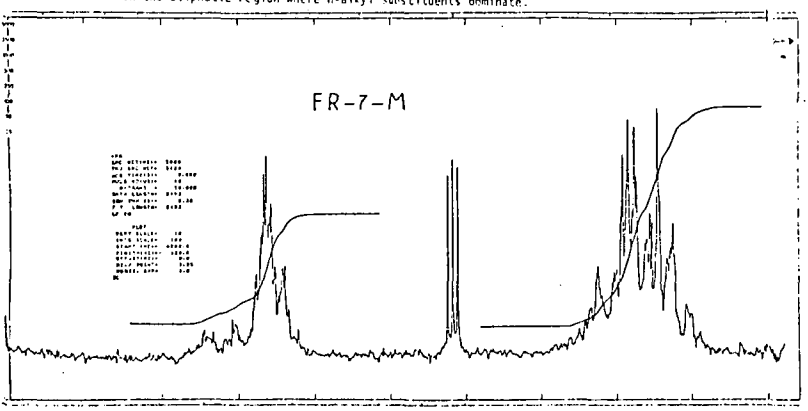


FIGURE 4 GPC subfraction number 7 of the monoaromatic fraction.

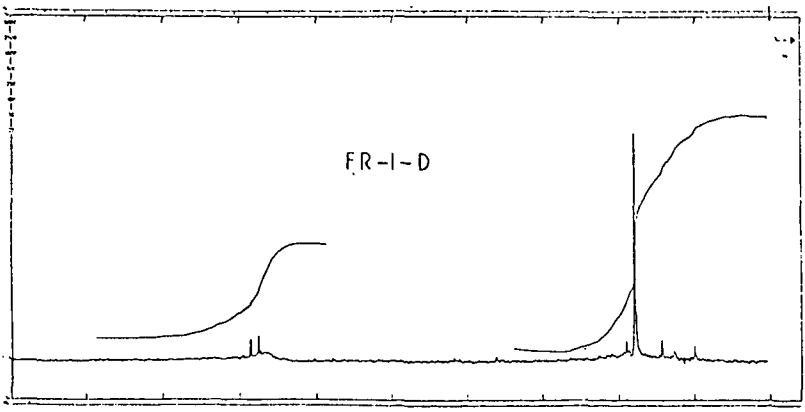


FIGURE 5 GPC subfraction number 1 of the diaromatic fraction. The structural features of the aliphatic region are dominated by n-alkyl substituents.

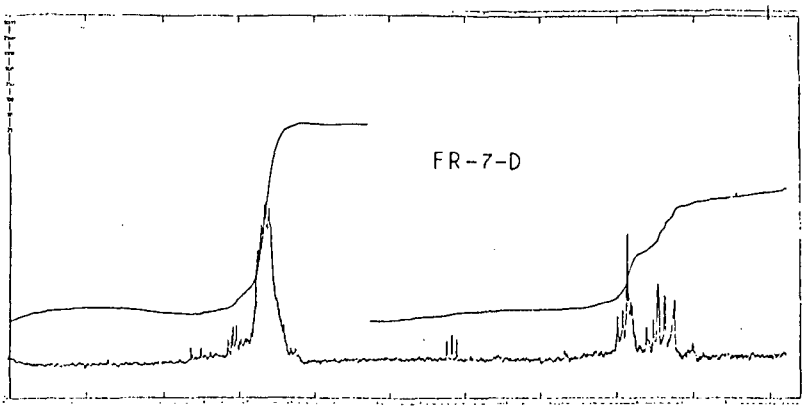


FIGURE 6 GPC subfraction number 7 of the diaromatic fraction. The aliphatic structure displays evidence of hydroaromatic species.

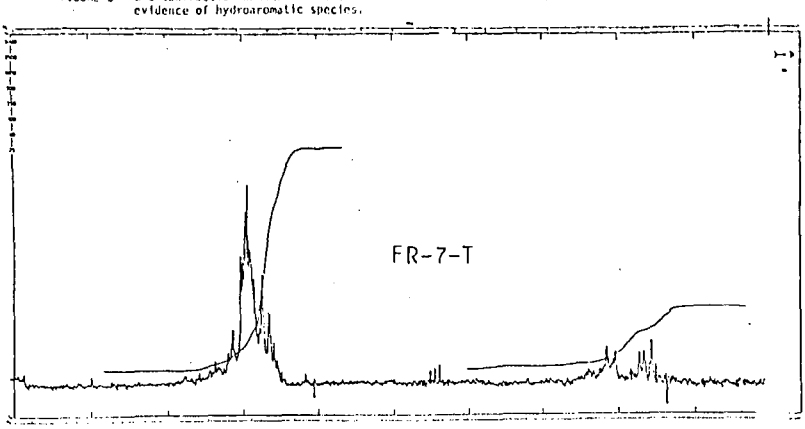


FIGURE 7 GPC subfraction number 7 of the three/four ring aromatic fraction.

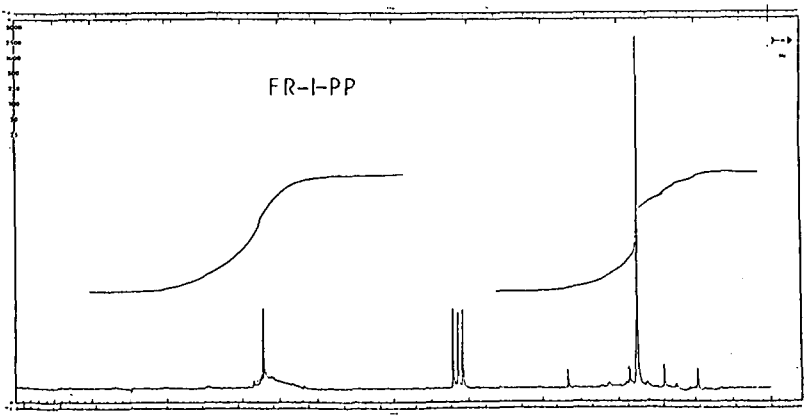


FIGURE 8 GPC subfraction number 1 of the poly/polar aromatic fraction. Note the presence of resonance lines due to n-alkyl substituents.

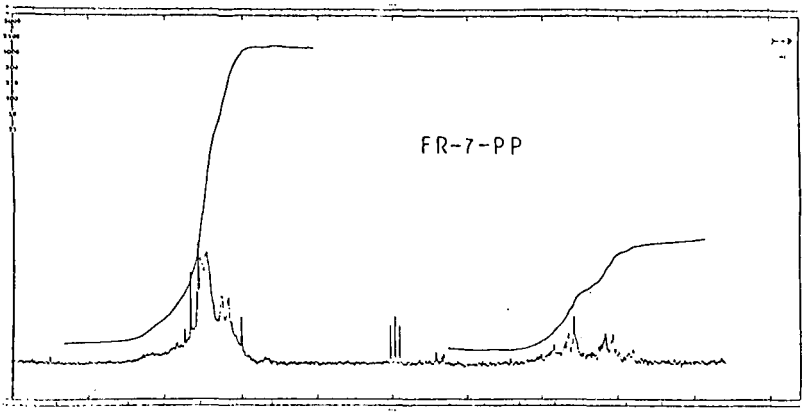


FIGURE 9 GPC subfraction number 7 of the poly/polar aromatic fraction.

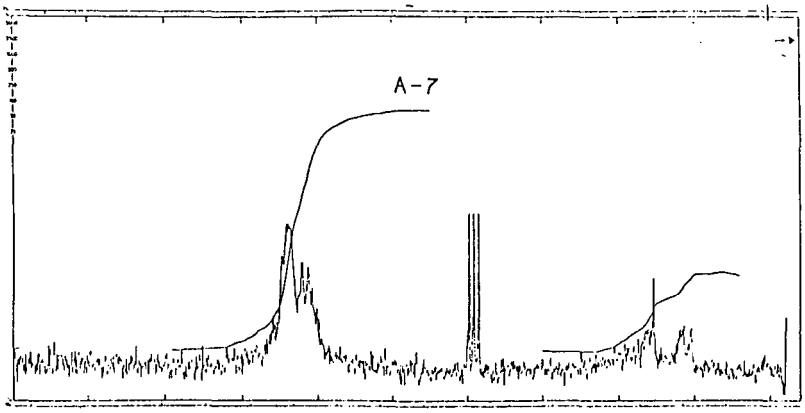


FIGURE 10 GPC subfraction number 7 of the asphaltenes. The signal to noise is too low to permit observation of minor structural features. The aliphatic region is similar to that observed in Figure 6, 7, and 9.

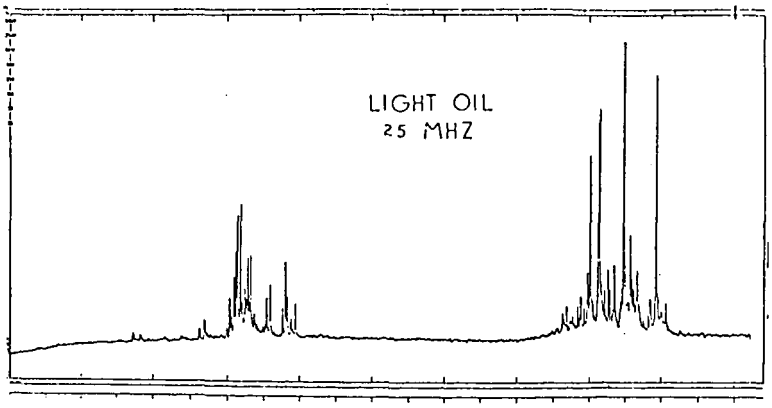


FIGURE 11 CMR spectra of light oil taken at 25 MHz. A D_2O capillary was used as external lock. A total of 35,445 transients were accumulated. Total time required was 8 hours.

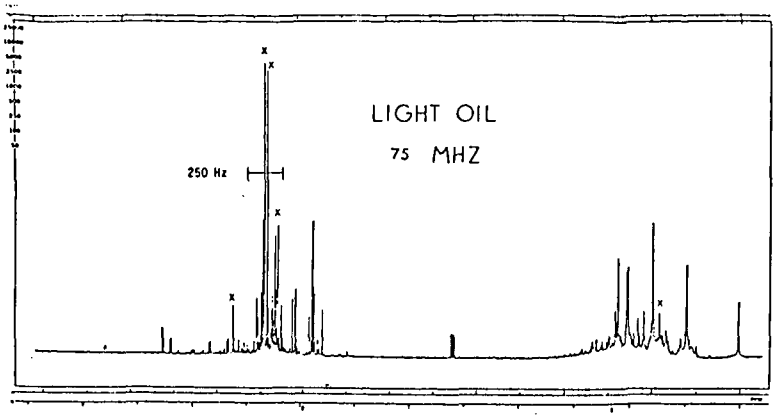


FIGURE 12 CHR spectra of sample shown in Figure 11. Data was taken using DCl_3 as an internal lock. TMS was added as a reference. The lines designated by x correspond to the lines found in toluene. Spectra width was 15 KHz. The spectra was obtained from accumulation of 203 transients requiring approximately 0.1 hour.

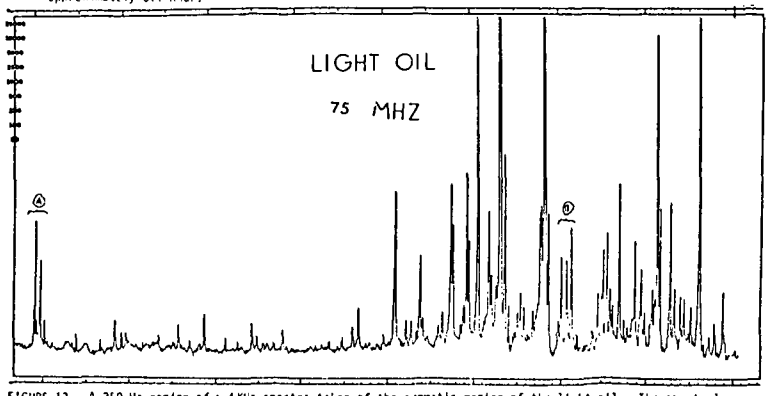


FIGURE 13 A 250 Hz region of a 4KHz spectra taken of the aromatic region of the light oil. The spectral region is that indicated in Figure 12. 1194 transients were obtained with an aquisition time of 4.096 sec. for a total spectrometer time of 1.4 hours.

TABLE 1. DISTRIBUTION OF HEAVY OIL FRACTIONS

SAMPLE: HIAWATHA H.V. BITUMINOUS COAL

YIELD: HEAVY OIL 31.3% W/W COAL

PRODUCTS

	% HEAVY OIL	% COAL
ASPHALTENE	6	1.8
OIL	62.2	19.6
SATURATES	6.29	1.97
ONE-RING AROMATIC	7.76	2.43
TWO-RING AROMATIC	8.05	2.52
THREE-FOUR-RING AROMATIC	8.72	2.73
POLAR/POLY RING AROMATIC	29.65	9.28
ACIDIC	12.9	4.0
BASIC	2.2	0.7
RESIDUE (BENZENE INSOLUBLE)	3.3	1.0
LOSS	12.9	4.0

TABLE 2. SUGGESTED COMPOSITION OF SATURATES FRACTIONS

GPC FRACTION	UNSATURATES: R-C-C-R[1] OR AROMATICS	R-C=C	RC=C-C	⬡	⬡ R	SATURATES: %N-P[2]	N[2]	C R-C-C-C-R	C R-C-C	R R-C-C-C-C R	ISO-PARAFFINS	CYCLIC PARAFFINS	% OF OIL
FR-1-P	X					60	24	X		X		X	0.54
FR-2-P	X SIMILAR TO FR-1-P					85-90	25	MOST OF BRANCHED AND CYCLIC PARAFFIN LINES GONE					1.21
FR-3-P	X SIMILAR TO FR-1-P					85-90	24	MOST OF BRANCHED AND CYCLIC PARAFFIN LINES GONE					1.05
FR-4-P	X SIMILAR TO FR-1-P					64	18				X	X	1.09
FR-5-P		X	X			45-50	14			X	X	X	1.12
FR-6-P	X			X	X	20	14	OTHER THAN N-PARAFFINS, LITTLE DEFINITIVE STRUCTURE PRESENT					1.28
												TOTAL	6.29

[1]These spectral lines correspond with those of monosubstituted benzenes as well as long chain alkenes. UV data exhibits absorption bands characteristic of aromatic rings indicating that the separations procedure does not eliminate all aromatic material from the saturates fraction.

[2]%N-P represents the percent of normal paraffins present in the sample while N represents the number average length of the alkyl chains.

TABLE 3A

SUGGESTED COMPOSITION OF MONOAROMATIC FRACTIONS
UNSATURATES

GPC FRACTION	C ⬡	C ⬡	R R C R ⬡	R ⬡	C-C=C-R	R ⬡	R-C=C-R	⬡⬡	% OF OIL
FR1-M	X								0.93
FR2-M	X								1.02
FR3-M	X	X	X	X	X	X	X		1.12
FR4-M	X	X		X	X				1.12
FR5-M	X	X		X	X				1.04
FR6-M	X	X	X	X		X			1.18
FR7-M	X	X	X	X	X	X	X	X	1.37
								TOTAL	7.79

TABLE 3B

SUGGESTED COMPOSITION OF MONOAROMATIC FRACTIONS
SATURATES

GPC FRACTION	%N-P[1]	N[1]	φ-C	φ-C-C	φ-C-C-R	φ-C-C-R	⬡⬡⬡	CYCLIC PARAFFINS	C R-C-C-C	% OF OIL
FR1-M	~60	~31	X	X	X	X				0.93
FR2-M	A	>10	X		X	X				1.02
FR3-M	15-20	~8	X	X	X	X				1.12
					BROAD BAND RICH IN STRUCTURE					
FR4-M	A	~5	X	BROAD BAND WITH LITTLE STRUCTURE						1.12
FR5-M	A	~5	X	BROAD BAND WITH MUCH BRANCHED AND CYCLIC ALIPHATIC STRUCTURE						1.04
FR6-M	A		X	X			X	X	X	1.18
FR7-M	A		X				X	X	X	1.37
									TOTAL	7.79

[1]Same as N in Table 2 except in the aromatic fractions N is used to designate the n-alkyl substituents.

[2]Not measured.

TABLE 4

SUGGESTED COMPOSITION OF DIAROMATIC FRACTIONS

	Unsaturates						Saturates						
GPC Fraction	R-C=C	C-C=C-C-R	C-C=C-R				% n-P[1]	n[1]	ϕ-C	ϕ-Iso Paraffin	Cyclic Paraffins	ϕ-R-C	% of Oil
FR-1D							25	13				X	0.95
FR-2-D	X	X	X	X	X	X		5	X	X	X	X[2]	0.99
FR-3-D		X	X	X	X	X			X	X	X	X[2]	1.02
FR-4-D		X	X	X	X	X			X	X	X	X[2]	1.12
FR-5-D		X	X	X	X	X			X	X	X	X[2]	1.44
FR-6-D		X	X	X	X	X			X	X	X	X[2]	1.34
FR-7-D		X	X	X	X	X			X	X	X	X[2]	1.25
												TOTAL	8.02

[1]See Footnote 2 in Table 2.

[2]Decreasing amounts as molecular weight decreases.

TABLE 5

SUGGESTED COMPOSITION OF 3-RING AROMATIC FRACTIONS

	Unsaturates					Saturates							
GPC Fraction	R-C=C	C-C=C-R				% n-P[1]	n[1]	O R-C-O-C-R	O R-C-O-C-R	ϕ-C			Iso-Paraffins	% of Oil
FR-1-T	X	---BANDS WITH NO RESOLVABLE STRUCTURE---				16	9	X	X	X			X	1.21
FR-1-T	X	X	X		X						X	X	X	1.27
FR-3-T	X	X	X	X	X					X	X	X	X	1.15
FR-4-T	X	X	X	X	X					X	X	X	X	1.41
FR-5-T	X	X	X	X	X					X	X	X	X	1.37
FR-6-T	X	X	X	X						X	X		X	1.05
FR-7-T	X	X	X	X						X	X	X		1.15
													TOTAL	8.74

[1]See Footnote 2 in Table 2.

TABLE 6

SUGGESTED COMPOSITION OF POLYAROMATIC/POLAR FRACTIONS

	Unsaturates						Saturates							
GPC Fraction	R-C=C	C-C=C-R	C-C=C-R				% n-Par.[1]	n[1]	ϕ-C	ϕ-Iso-Paraffins		ϕ-R-C	R-CH2-OR[2]	% of Oil
FR-1-PP	Broad band of low intensity						25	13	X			X		4.15
FP-2-PP	X	X	X	X	X	X	-	5	X	X	X	X		5.02
FP-3-PP		X	X	X	X	X			X	X	X	X		3.93
FP-4-PP		X	X	X	X	X			X	X	X	X	X	3.50
FP-5-PP		X	X	X	X	X			X	X	X			4.09
FP-6-PP		X	X	X	X	X			X	X	X			4.22
FP-7-PP		X			X	X			X	X	X		X	4.44
													TOTAL	29.55

[1]See Footnote 2 in Table 2.

[2]The resonance lines observed are probably due mainly to ethers but the line positions do not preclude the possibility of secondary or tertiary alcohols.

FIELD DESORPTION MASS SPECTROMETRY - APPLICATION TO THE ELUCIDATION OF THE STRUCTURE OF HUMIC ACID by R. L. Wershaw, U.S. Geological Survey, Denver Federal Center, Denver, CO, 80225, D. F. Barofsky and E. Barofsky, Oregon Graduate Center, Beaverton, Oregon, 97005

Progress in the elucidation of the structure of humic acids has been impeded, in part, by our inability to dissociate humic acid aggregates into analyzable units and, in part, to the nonavailability of adequate analytical tools to monitor the chemical procedures. Field desorption mass spectrometry (FDMS) has two properties that make it ideally suited to the analysis of relatively large molecular aggregates such as humic acids. These are: (1) The FDMS of most compounds exhibit predominantly molecular or pseudomolecular ions and (2) sample volatilization is not required prior to ionization.

Field desorption mass spectrometry allows us to monitor the chemical reactions that we have used to dissociate humic acid fractions by enabling us to observe the dissociated fragments. The most significant result arising out of this work to date, has been the observation of humic acid fragments following either chlorination or permethylation; in untreated samples we get no spectra. The disaggregation on permethylation is attributed to a reduction in hydrogen bonding.

The first part of this paper will present a brief survey of FDMS, that is, its theory, instrumentation, and techniques The second part will present the results of the application of FDMS to the structural elucidation of humic acid and the general applicability of FDMS to similar problems.