

CHARACTERIZATION OF ORGANIC BASES
IN HYDROCRACKED SHALE OIL FUELS

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As part of a continuing in-depth fuel characterization program for fuels produced in the U.S. Navy's shale programs (1,2,3,4), an extensive determination of acid extractable organic nitrogen compounds in Shale-II fuels has been completed. This report provides a description of an improved GC-MS system which simplifies the analysis. In addition, qualitative and some quantitative data on the organic bases in the fuels are presented. Since shale oil contains a significantly higher weight percent of Nitrogen than petroleum and Nitrogen containing compounds at low levels in finished fuels have long been implicated in fuel stability problems (5), we have been looking at samples from the fuel refining stream available from the Shale-II project. Ultimately this chemical composition information will be utilized in attempts to account for fuel stability problems both at high temperatures and at ambient temperatures.

EXPERIMENTAL

The hydrocracked shale oil refining process details used in the Shale-II exercise have been previously described (6). Following hydrocracking and fractionation, the fuels were acid and clay treated. Table I shows the nitrogen content of three fuels from the refinery before final acid/clay treatment. The nitrogen concentration for the fuels, the fuels after extraction and the acid extracts were determined by pyrolysis/combustion at 1000 degrees C and measurement of chemiluminescence from the reaction of NO with ozone (7). The crude shale oil contained 2.1 percent nitrogen (w/w). The relative deviation of the values was +5 percent. The basic nitrogen fraction of the three fuels was obtained by extracting with 1N HCl, neutralizing with aqueous NaOH, and back extracting into ether.

A Hewlett-Packard 5982A GC-MS was modified at the GC-MS interface in order to accommodate a 50m x 0.3mm I.D. flexible fused silica column with a stationary phase coating of SP2100 (relatively non-polar, similar to OV-101). The MS ion source flange was connected to the GC oven interior wall by a heated 1/8" O.D. copper tube. The capillary column was threaded into the heated 1/8" tube from the GC oven, through the tube, into the MS source so that the column outlet was positioned about 1.0 cm behind the electron beam of the ion source. The 1/8" tube was sealed to high vacuum at the MS source flange and in the GC oven at the point where the capillary column entered the tube. Flow rates through the capillary column were measured near atmospheric pressure and related linearly to column head pressure. Flows were measured between 0.5 ml/min and 1.5 ml/min of helium carrier gas. Under vacuum conditions the MS source region normally attains pressures of about 5×10^{-7} torr; at helium flow rates of 1 ml/min into the source region pressures of about 1×10^{-6} torr were attained.

The split ratio of the Hewlett-Packard 18740B capillary injector was set at 80:1 and 0.2 to 0.5 μ l injections of the fuel extracts were made. The carrier gas flow for most sample runs was 1.0 to 1.1 ml/min helium (nominal at atmospheric pressure). The column temperature was held for 2 min at 85 degrees C, programmed at 8 degrees C/min to 220 degrees C and held at the upper temperature for 8 mins. Mass spectra were taken between m/z 50 and m/z 300 at the rate of about 1 spectrum/1.5 sec.

RESULTS AND DISCUSSION

A reconstructed total ion chromatogram for the JP-5 extract is shown in Figure 1. The excellent resolution, column efficiency and minimal tailing of the polar Nitrogen containing components is typical of the chromatograms which can be produced by the all glass system and interface described above. At 14.1 min the column efficiency is 125,000 theoretical plates. The chromatographic advantages of eluting components directly into the high vacuum ionization region are obvious. The absolute sensitivity of the technique is enhanced by the wide bore (0.3 mm ID) of the column which permits up to 1.0 μ l injections of the fuel extracts without signs of column overload. Even at the relatively high source pressures encountered, the mass spectra observed are identical to normal electron impact (70ev) spectra generally taken at 10(exp-7) torr.

The results of the capillary GC-MS analysis of the acid extraction of Shale-II naphtha are shown in Table II. Over thirty nitrogen containing compounds were detected, most of which were $C_nH_{2n-5}N$ type compounds. These pyridines accounted for over 90 percent of the basic nitrogen compounds by weight. The average molecular weight for this naphtha fuel extract was 125. The most frequent isomers encountered contained three or four carbons in side chains.

The JP-5 acid extract results are given in Table III. Over seventy nitrogen containing compounds were identified. As in the naphtha extract, the bulk of the material was composed of $C_nH_{2n-5}N$ type compounds. These pyridines contributed 85 percent of the extracted Nitrogen compounds by weight. The average molecular weight was 172 and most of the compounds contained from five to eight carbons in side chains. A significant amount of $C_nH_{2n-11}N$ (quinolines) and $C_nH_{2n-7}N$ (tetrahydroquinolines) averaging 2 to 3 carbons in side chains were also detected. The hydrotreatment of the crude shale oil in the refinery is the most likely explanation for the presence of tetrahydroquinolines in the jet fuel.

Table IV outlines the findings for DFM (Diesel Fuel Marine). Over one hundred nitrogen containing compounds were detected in this extract. Over 60 percent of them were in the class $C_nH_{2n-9}N$. Seven, ten and twelve carbon side chain isomers predominated, and the average molecular weight was 195. As in the JP-5 sample, a significant amount of $C_nH_{2n-11}N$ and $C_nH_{2n-7}N$ compounds were identified. Also over 20 percent of the nitrogen compounds by weight were of the type $C_nH_{2n-9}N$ (indoles) which were primarily seven and eight carbon side chain isomers. Indole types were not detected in the JP-5 extract.

Although only 0.2% nitrogen remained in the neutral, acid fraction of DFM, GC/MS analysis of a silica gel column fraction eluted by chloroform revealed the presence of both $C_nH_{2n-9}N$ (indoles) and $C_nH_{2n-15}N$ (carbazoles).

CONCLUSIONS

The major compound class isomers found in the acid extract of Shale-II naphtha were 3 to 4 carbon side chain substituted pyridines. In the Shale-II JP-5 sample prior to final refinery acid/clay treatment, the major compound class isomers were 5 to 8 carbon

side chain pyridines, 1 to 3 carbon side chain tetrahydroquinolines and 2 to 3 carbon side chain quinolines. In the DFM extract the major compound class isomers found were 5 to 12 carbon side chain pyridines, 3 to 4 carbon side chain tetrahydroquinolines, 5 to 8 carbon side chain indoles and 3 to 5 carbon side chain quinolines.

The outlined analytical procedure could be improved by the addition of suitable internal standards to facilitate quantitation of particular compounds of interest.

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TABLE I

SHALE II PRE-ACID TREATED FUELS
NITROGEN ELEMENTAL ANALYSIS PPM (W/W)

<u>Sample</u>	<u>Fuel</u>	<u>Ext. Fuel</u>	<u>% N Ext.</u>	<u>Acid Ext.</u>
G-1 (Naphtha)	900	3	99.7	103000
J-7 (JP-5)	2100	85	96.0	62000
D-7 (DFM)	3000	5	99.8	61000

Acid Extract = 1N HCl

TABLE II
SHALE II - NAPHTHA
COMPOUNDS IN ACID EXTRACT BY EI-MS

<u>Compound Class</u>	<u>Number of Carbons in Side Chain</u>	<u>Number of Isomers Detected</u>	<u>Relative Amount of Class</u>
Piperdines ($C_n H_{2n+1} N$)	2	2	7%
	3	3	
Pyridines ($C_n H_{2n-5} N$)	1	1	93%
	2	4	
	3	10	
	4	8	
	5	3	

TABLE III
SHALE II - JET
COMPOUNDS IN ACID EXTRACT BY EI-MS

<u>Compound Class</u>	<u>Number Carbons in Side Chain</u>	<u>Number of Isomers Detected</u>	<u>Relative Amount Of Class</u>		
Pyridines ($C_n H_{2n-5} N$)	3	1	85%		
	4	4			
	5	9			
	6	10			
	7	8			
	8	11			
	9	3			
	10	3			
	Tetrahydroquinolines ($C_n H_{2n-7} N$)	1		3	10%
		2		5	
3		4			
4		1			
5		2			
Quinolines ($C_n H_{2n-11} N$)	1	1	5%		
	2	4			
	3	3			
	4	2			
	5	1			

TABLE IV
 SHALE II - DFM
 COMPOUNDS IN ACID EXTRACT BY EI-MS

<u>Compound Class</u>	<u>Number of Carbons in Side Chain</u>	<u>Number of Isomers Detected</u>	<u>Relative Amount Of Class</u>
Pyridines (C _n H _{2n-5} N)	3	1	64%
	4	3	
	5	7	
	6	6	
	7	14	
	8	5	
	9	6	
	10	9	
	11	3	
	12	13	
Tetrahydro-quinolines (C _n H _{2n-7} N)	2	5	8%
	3	2	
	4	4	
	5	0	
	6	2	
Indoles (C _n H _{2n-9} N)	4	2	21%
	5	2	
	6	3	
	7	8	
	8	9	
Quinolines (C _n H _{2n-11} N)	2	1	7%
	3	2	
	4	2	
	5	2	
	6	1	

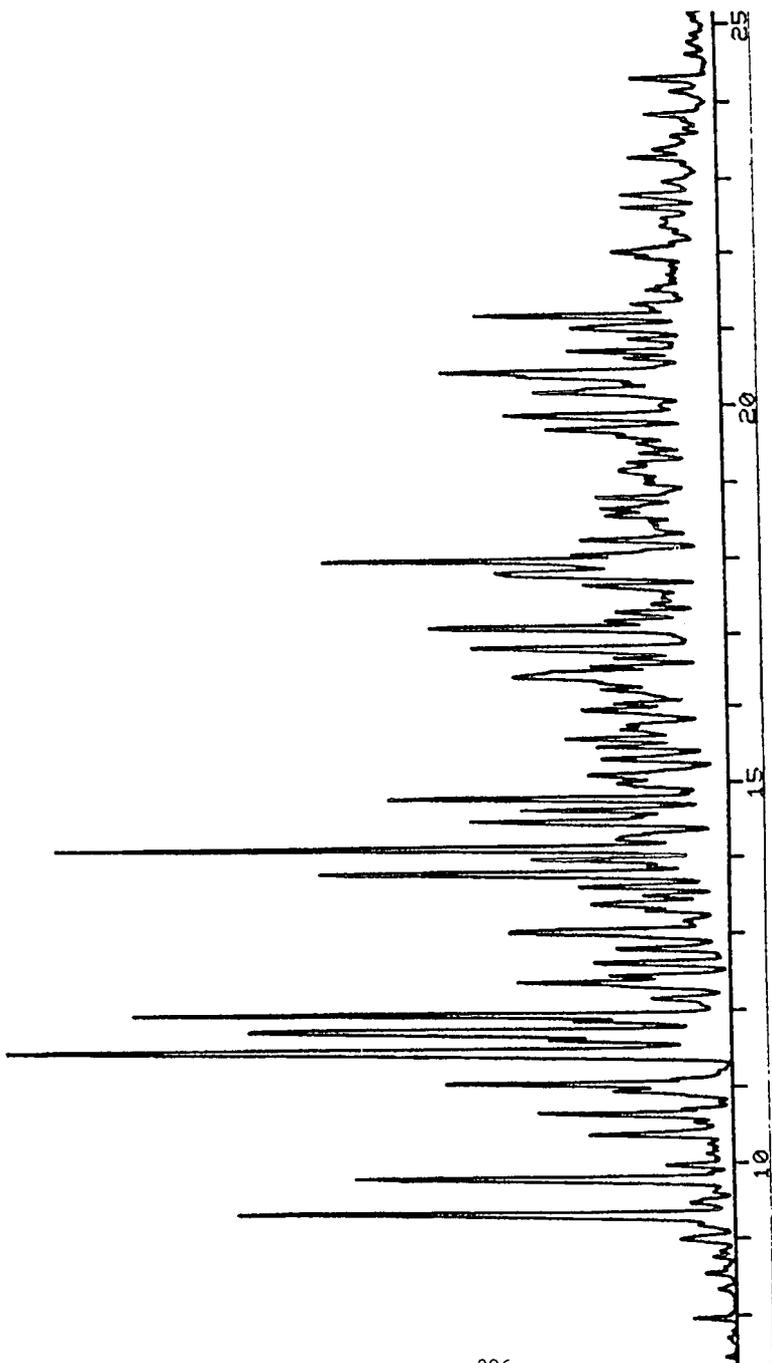


FIGURE 1. Reconstructed total ion chromatogram of J-7 (JP-5) acid extract. Retention times are in minutes.