

CHARACTERIZATION OF COAL LIQUEFACTION PRODUCTS BY  
HIGH RESOLUTION-LOW VOLTAGE MASS SPECTROMETRY

By

Thomas Aczel, J. Q. Foster, J. H. Karchmer  
Esso Research and Engineering Company, Baytown, Texas

## INTRODUCTION

High resolution mass spectroscopy is one of the most promising tools for the characterization of very complex materials. Since commercial instruments became available in the early nineteen sixties, the technique has been applied with considerable success to the analysis of materials derived both from petroleum and coal (1, 2, 3, 4).

This paper deals with the application of a particular approach, high resolution-low voltage mass spectrometry, coupled with computerized data acquisition and reduction, to the analysis of liquid and solid materials derived from coal liquefaction processes. These processes are of considerable industrial interest at the present; and the particular analytical approach used permits one to obtain routine quantitative or at least semiquantitative data on the hundreds of components present in each sample. Pilot plant or bench scale experiments can be thus supported with detailed analytical data.

## EXPERIMENTAL

The high resolution-low voltage technique used, as well as the computerized data acquisition and reduction system, has been described elsewhere (5, 6, 7). In brief, mass spectra are obtained on an AEI model MS 9 instrument at a resolving power of approximately 1/10,000, and at low ionizing voltages, approximately 12 volts. This resolving power is sufficient to separate all significant mass multiplets up to about m/e 400, with exception of the  $^{13}\text{CH-N}$  doublet, the separation of which requires additional calculations. At the same time, the use of low ionizing voltages reduces the spectra to essentially parent peaks and their  $^{13}\text{C}$  isotopes, so that interferences between sample components are practically eliminated, and data can be obtained both on the compound type and carbon number distribution. Quantitative information is obtained by using pure compound or extrapolated calibration coefficients. The data acquisition system consists of an IBM Model 1802 computer, which converts the analog signals from the mass spectrometer to digital data and records these on magnetic tape. Subsequent calculations, including the recognition of peaks, calculation of peak areas, precise masses, formulas and, finally, the complete quantitative analysis, are carried out on an IBM Model 360/50 computer. At present, the quantitative analysis provides data routinely for up to 58 compound types and up to 2900 components, in less than three hours, including instrument time and interpretation. These types include hydrocarbons with formulas  $\text{C}_n\text{H}_{2n}$  to  $\text{C}_n\text{H}_{2n-44}$ , oxygenated compounds from  $\text{C}_n\text{H}_{2n-20}$  to  $\text{C}_n\text{H}_{2n-360}$ , and sulfur compounds from  $\text{C}_n\text{H}_{2n-2\text{S}}$  to  $\text{C}_n\text{H}_{2n-34\text{S}}$ . Semiquantitative information on additional compound types, such as those containing N, or containing more than one heteroatom per molecule, or possessing a higher condensation than outlined above, can be obtained in a short additional time. The analysis is normalized to the volatile portion of each sample, determined by weighing the sample and any observed residue.

## DISCUSSION

Application of the high resolution-low voltage method to coal liquefaction products yields a very detailed characterization. Isomeric hydrocarbon types, possessing the same general formula, but different aromatic nuclei, can be separated and determined at least semiquantitatively. The behavior of the components during processing can be closely followed. The analysis includes data on aromatic and heteroaromatic components ranging from ppm to several percent in concentration and from 78 to 500+ in molecular weight. A large number of components and compound types can be determined rapidly in each sample. The degree of sophistication attained is best illustrated with practical examples.

The ability of distinguishing isomeric hydrocarbon types is based on the observed fact that the concentrations of the aromatic nuclei are higher than those of the alkyl-substituted members in any homologous series. Thus maxima in the carbon number distribution in any series correspond in most cases to the appearance of an individual nucleus. A number of these nuclei are naphthenoaromatic compounds. Examination of samples hydrogenated to different extents can thus corroborate the presence of naphthenoaromatic nuclei, as the concentration of these increases with the extent of the hydrogenation. The data reported below will serve to illustrate the procedure.

Carbon Number Distribution in the  $C_nH_{2n-10}$  Series, Weight Percent

<u>Formula</u>	<u>Mildly Hydrogenated Material</u>	<u>Severely Hydrogenated Material</u>
$C_9H_8$	0.062	0.056
$C_{10}H_{10}$	0.220	0.408
$C_{11}H_{12}$	0.168	0.162
$C_{12}H_{14}$	0.444	0.926
$C_{13}H_{16}$	0.552	1.175
$C_{14}H_{18}$	0.702	1.493
$C_{15}H_{20}$	0.278	0.624
$C_{16}H_{22}$	0.314	0.443
$C_{17}H_{24}$	0.122	0.252
$C_{18}H_{26}$	0.006	0.088

The only reasonable structure for a  $C_9H_8$  hydrocarbon is indene.  $C_{10}H_{10}$  could be methyl-indene or dihydronaphthalene. As the total  $C_{10}$  concentration is higher than the  $C_9$  concentration, dihydronaphthalene is believed to be the major component. This assumption is corroborated by the fact that this difference in concentration is enhanced in the more severely hydrogenated material, and dihydronaphthalene is an obvious hydrogenation product from naphthalene. Analogously, increases in concentration at  $C_{12}$ ,  $C_{13}$ ,  $C_{14}$ , and  $C_{16}$ , all enhanced in the severely hydrogenated material, indicate the presence of additional nuclei, respectively identified as tetrahydroacenaphthene, benzohydrindane, octahydroanthracene and dodecahydropyrene. Data from other series of the same general formula are treated similarly. Only maxima or increases in concentration which appear at the same carbon number and series in a large number of samples are accepted as a genuine indication of more than one compound type in a given series.

As mentioned above, the concentration of alkyl-substituted components is considerably lower than that of the respective nuclei. This can be observed best in series and carbon number intervals where only one compound type is present, as shown below.

Carbon Number Distribution in the  $C_nH_{2n-8}$  Series, Weight Percent

<u>Formula</u>	<u>Mildly Hydrogenated Material</u>	<u>Severely Hydrogenated Material</u>
$C_{10}H_{12}$	5.804	9.180
$C_{11}H_{14}$	2.977	5.291
$C_{12}H_{16}$	1.805	2.671
$C_{13}H_{18}$	1.043	1.291

The decrease in concentration with increasing carbon number is approximately twofold. This rate of decrease has also been observed for other series, and in a large number of samples. We were able thus to develop a method to estimate the concentration of each isomeric compound type in a given series. The procedure, illustrated below, starts with extrapolating the concentrations of the homologs of the compound type with the lowest molecular weight nucleus. The concentration of the nucleus of the next compound type is obtained by subtracting the extrapolated concentration of the homolog of the first compound type at the carbon number involved from the concentration observed for the series. Concentrations of the homologs of the second compound type are then extrapolated; and the procedure continues similarly for all other compound types. The extrapolation is used, of course, only in carbon number intervals where more than one type is conceivably present. In addition, the method is applicable only to samples with boiling range wide enough to contain all isomers involved in the separation.

Separation of Isomeric Compound Types in the  $C_nH_{2n-14}$  Series, Weight Percent

<u>Formula</u>	<u>Total <math>C_nH_{2n-14}</math> Series</u>	<u>Acenaphthenes</u>	<u>Tetrahydro-anthracenes</u>	<u>Octahydro-pyrenes</u>
$C_{12}H_{10}$	2.954 <sup>(1,2)</sup>	2.954 <sup>(2)</sup>	-	-
$C_{13}H_{12}$	1.894 <sup>(2)</sup>	1.894 <sup>(2)</sup>	-	-
$C_{14}H_{14}$	2.536 <sup>(1,2)</sup>	0.947 <sup>(3)</sup>	1.589 <sup>(4)</sup>	-
$C_{14}H_{16}$	1.105 <sup>(2)</sup>	0.474 <sup>(3)</sup>	0.631 <sup>(4)</sup>	-
$C_{16}H_{18}$	1.146 <sup>(1)</sup>	0.237 <sup>(3)</sup>	0.316 <sup>(3)</sup>	0.593 <sup>(4)</sup>
$C_{17}H_{20}$	0.631 <sup>(2)</sup>	0.118 <sup>(3)</sup>	0.158 <sup>(3)</sup>	0.355 <sup>(4)</sup>
$C_{18}H_{22}$	0.316 <sup>(2)</sup>	0.059 <sup>(3)</sup>	0.079 <sup>(3)</sup>	0.178 <sup>(4)</sup>

- (1) Maxima in carbon number distribution, indicating the appearance of respectively, acenaphthene, tetrahydroanthracene and octahydro-pyrene.
- (2) Raw concentrations.
- (3) Concentrations obtained by extrapolation.
- (4) Concentrations obtained by subtraction.

The information thus obtained on the concentration of the individual compound types can be used to follow their behavior upon hydrogenation. Typical data obtained are shown below.

Ring Systems	Weight Percent	
	Mildly Hydrogenated Material	Severely Hydrogenated Material
<u>Naphthalene System</u>		
Naphthalenes, $C_nH_{2n-12}$	14.2	7.9
Dihydronaphthalenes, $C_nH_{2n-10}$	0.5	0.7
Tetralins, $C_nH_{2n-8}$	11.5	18.4
Octahydronaphthalenes, $C_nH_{2n-4}$	0.3	0.4
Decalins, $C_nH_{2n-2}$	<u>2.0</u>	<u>2.6</u>
Total	28.5	30.0
<u>Anthracene System</u>		
Anthracenes, $C_nH_{2n-18}$	7.2	5.4
Tetrahydroanthracenes, $C_nH_{2n-14}$	3.0	3.8
Hexahydroanthracenes, $C_nH_{2n-12}$	1.3	1.5
Octahydroanthracenes, $C_nH_{2n-10}$	0.7	1.5
Decahydroanthracenes, $C_nH_{2n-8}$	<u>0.6</u>	<u>1.2</u>
Total	12.8	13.4
<u>Acenaphthene System</u>		
Acenaphthylenes, $C_nH_{2n-16}$	0.1	0.0
Acenaphthenes, $C_nH_{2n-14}$	6.6	5.3
Tetrahydroacenaphthenes, $C_nH_{2n-10}$	<u>0.7</u>	<u>1.7</u>
Total	7.4	7.0
<u>Fluorene System</u>		
Fluorenes	<u>5.0</u>	<u>5.0</u>
Total	5.0	5.0

Another aspect of the characterization of coal liquefaction products is the determination of components containing heteroatoms. Most of these can be directly identified from the computer output of the high resolution-low voltage spectra as illustrated below for typical mass multiplets.

Computer Identification of FormulasMultiplets at m/e 310 and 330

<u>Intensity, % I</u>	<u>Measured Mass</u>	<u>Error, mmu</u>	<u>Formula</u>
0.0016	310.0857	+0.7	C <sub>19</sub> H <sub>18</sub> S <sub>2</sub>
0.0332	310.1346	-1.2	C <sub>23</sub> H <sub>18</sub> <sup>0</sup>
0.5825	310.1736	+1.5	C <sub>24</sub> H <sub>22</sub>
0.0075	310.2276	-2.0	C <sub>22</sub> H <sub>30</sub> <sup>0</sup>
0.0435	310.2675	+1.5	C <sub>23</sub> H <sub>34</sub>
0.0017	330.1360	-4.8	C <sub>26</sub> H <sub>18</sub>
0.0064	330.1605	-1.5	C <sub>23</sub> H <sub>22</sub> O <sub>2</sub>
0.0131	330.1963	-2.1	C <sub>24</sub> H <sub>26</sub> <sup>0</sup>
0.1219	330.2360	+1.3	C <sub>25</sub> H <sub>30</sub>
0.0051	330.3291	+0.5	C <sub>24</sub> H <sub>42</sub>

The resolving power of our instrument, however, is insufficient to separate the <sup>13</sup>CH-N doublet above m/e 120-130. Components containing one N atom are therefore detected using isotope correction techniques. The presence of N compounds of odd molecular weights is indicated by residual peakheights after isotope correction and shift in the measured mass from the value of the <sup>13</sup>C isotope to that of the N compound, as shown in the example reported below.

<u>Measured Mass</u>	<u>Formula</u>	<u>Error, mmu</u>	<u>Intensity, % I</u>
180.093	C <sub>14</sub> H <sub>12</sub>	-0.6	1.903
181.090	-	-	0.845

  

<u>Formula</u>	<u>Theoretical Mass</u>	<u>Theoretical Intensity, % I</u>
<sup>13</sup> CC <sub>13</sub> H <sub>12</sub>	181.096	0.290
C <sub>13</sub> H <sub>11</sub> N	181.089	0.555*

• Residual after isotope correction.

Theoretical mass for unresolved doublet:

$$\frac{(181.096 \times 0.290) + (181.089 \times 0.555)}{0.845} = 181.091$$

Error of mass calculation for unresolved doublet: -1.0 mmu (-0.4 with respect to 180.093).

The techniques discussed above result in a thorough characterization of coal liquefaction products. The wealth of data obtained is illustrated by the list of compound types detected in one individual sample, reported below.

Series	Model Structure	Series	Model Structure
$C_n H_{2n}$	Cyclohexanes	$C_n H_{2n-20}$	Naphthenoanthracenes
$C_n H_{2n-2}$	Decalins	$C_n H_{2n-20}$	Tetrahydrochrysenes
$C_n H_{2n-2}$	Hydrindans	$C_n H_{2n-22}$	Pyrenes
$C_n H_{2n-4}$	Hydrindenes	$C_n H_{2n-22}$	Hexahydrobenzopyrenes
$C_n H_{2n-4}$	Octahydronaphthalenes	$C_n H_{2n-24}$	Chrysenes
$C_n H_{2n-4}$	Perhydroanthracenes	$C_n H_{2n-24}$	Tetrahydrobenzopyrenes
$C_n H_{2n-6}$	Benzenes	$C_n H_{2n-26}$	Cholanthrenes
$C_n H_{2n-8}$	Indanes	$C_n H_{2n-28}$	Benzopyrenes
$C_n H_{2n-8}$	Tetralins	$C_n H_{2n-30}$	Picenes
$C_n H_{2n-10}$	Indenes	$C_n H_{2n-32}$	Anthanthrenes
$C_n H_{2n-10}$	Dihydronaphthalenes	$C_n H_{2n-34}$	Dibenzopyrenes
$C_n H_{2n-10}$	Tetrahydroacenaphthenes	$C_n H_{2n-36}$	Coronenes
$C_n H_{2n-10}$	Benzhydrindanes	$C_n H_{2n-38}$	Benzanthanthrenes
$C_n H_{2n-10}$	Octahydroanthracenes	$C_n H_{2n-4}^S$	Thiophenes
$C_n H_{2n-10}$	Dodecahydropyrenes	$C_n H_{2n-10}^S$	Benzothiophenes
$C_n H_{2n-12}$	Naphthalenes	$C_n H_{2n-12}^S$	Naphthenobenzothiophenes
$C_n H_{2n-14}$	Acenaphthenes	$C_n H_{2n-14}^S$	Indenothiophenes
$C_n H_{2n-14}$	Tetrahydroanthracenes	$C_n H_{2n-16}^S$	Dibenzothiophenes
$C_n H_{2n-16}$	Acenaphthylenes	$C_n H_{2n-18}^S$	Acenaphthenothiophenes
$C_n H_{2n-16}$	Fluorenes	$C_n H_{2n-20}^S$	Fluorenothiophenes
$C_n H_{2n-16}$	Dihydroanthracenes	$C_n H_{2n-2}^O$	Dihydrofurans
$C_n H_{2n-16}$	Hexahydropyrenes	$C_n H_{2n-4}^O$	Furans
$C_n H_{2n-18}$	Anthracenes	$C_n H_{2n-6}^O$	Phenols
$C_n H_{2n-18}$	Tetrahydropyrenes	$C_n H_{2n-8}^O$	Naphthenophenols
$C_n H_{2n-18}$	Hexahydrochrysenes	$C_n H_{2n-10}^O$	Benzofurans
$C_n H_{2n-18}$	Decahydrobenzopyrenes	$C_n H_{2n-12}^O$	Naphthols
		$C_n H_{2n-14}^O$	Naphthenonaphthols
		$C_n H_{2n-16}^O$	Dibenzofurans
		$C_n H_{2n-18}^O$	Hydroxyanthracenes
		$C_n H_{2n-20}^O$	Hydroxynaphthenoanthracenes
		$C_n H_{2n-22}^O$	Hydroxypyrenes

$C_n H_{2n-24} O$	Hydroxychrysenes	$C_n H_{2n-6} O_2$	Dihydroxybenzenes
$C_n H_{2n-26} O$	Hydroxycholanthrenes	$C_n H_{2n-8} O_2$	Dihydroxyindanes
$C_n H_{2n-28} O$	Hydroxybenzopyrenes	$C_n H_{2n-10} O_2$	Hydroxybenzofurans
$C_n H_{2n-30} O$	Hydroxypicenes	$C_n H_{2n-12} O_2$	Dihydroxytetralins
$C_n H_{2n-32} O$	Hydroxyanthanthrenes	$C_n H_{2n-14} O_2$	Hydroxyindenofurans
$C_n H_{2n-38} O$	Hydroxybenzanthanthrenes	$C_n H_{2n-16} O_2$	Hydroxydibenzofurans
$C_n H_{2n-5} N$	Pyridines	$C_n H_{2n-18} O_2$	Dihydroxyanthracenes
$C_n H_{2n-7} N$	Naphthenopyridines	$C_n H_{2n-20} O_2$	Dihydroxynaphthoanthracenes
$C_n H_{2n-9} N$	Indoles	$C_n H_{2n-22} O_2$	Dihydroxypyrenes
$C_n H_{2n-11} N$	Quinolines	$C_n H_{2n-24} O_2$	Dihydroxychrysenes
$C_n H_{2n-13} N$	Naphthoquinolines	$C_n H_{2n-26} O_2$	Dihydroxycholanthrenes
$C_n H_{2n-15} N$	Carbazoles	$C_n H_{2n-8} SO$	Hydroxycyclopentenothiophenes
$C_n H_{2n-17} N$	Acridines	$C_n H_{2n-10} SO$	Hydroxybenzothiophenes
$C_n H_{2n-19} N$	Naphthenobenzquinolines	$C_n H_{2n-12} SO$	Hydroxynaphthenobenzothiophenes
$C_n H_{2n-21} N$	Benzocarbazoles	$C_n H_{2n-16} SO$	Hydroxydibenzothiophenes
$C_n H_{2n-23} N$	Benzacridines	$C_n H_{2n-18} SO$	Hydroxynaphthenonaphthothiophenes
$C_n H_{2n-25} N$	Naphthenobenzacridines	$C_n H_{2n-20} SO$	Hydroxyfluorenoothiophenes
$C_n H_{2n-27} N$	-	$C_n H_{2n-16} O_3$	Dihydroxydibenzofurans
$C_n H_{2n-29} N$	-	$C_n H_{2n-10} SO_2$	Dihydroxybenzothiophenes
$C_n H_{2n-31} N$	-	$C_n H_{2n-16} SO_2$	Dihydroxydibenzothiophenes
		$C_n H_{2n-18} SO_2$	Dihydroxynaphthenonaphthothiophenes
		$C_n H_{2n-20} SO_2$	Dihydroxyfluorenoothiophenes

The model structures listed above were deduced by observing the molecular weight of the first member for each compound type in a large number of samples. This observed molecular weight was in most cases identical to that of the model structures proposed. As isomeric compound types of the same nuclear molecular weight, such as anthracenes and phenanthrenes, cannot be separated by mass spectrometric means, these structures should be considered only indicative.

Additional compound types have been of course detected in other samples. The most interesting among these were compounds as condensed as  $C_n H_{2n-48}$ ,  $C_n H_{2n-42} O$ ,  $C_n H_{2n-34} O_2$ ,  $C_n H_{2n-32} SO$ , and several compound types containing NO, and S<sub>2</sub> groups.

The presence of O, O<sub>2</sub> groups, most probably in the hydroxyl form, is considered quite revealing, particularly in view of the fact that these hydroxyl groups are located on hydrocarbons containing up to 8 aromatic rings. The detection of these very condensed heterocompounds in coal liquefaction products corroborates the views on coal structure, reported by Hill (8). According to this and other authors, coal is viewed as a polymer composed of polyaromatic nuclei linked by -O- and -S- bridges.

It is reasonable to expect that these linkages break upon hydrogenation, thus giving rise to the polyaromatic phenols detected in our analyses.

Another interesting insight in the structure of coal is provided by the analysis of the heavier fractions (700°F.+) of hydrogenated material. As shown by the example reported below, these materials contain considerable amounts of polynuclear aromatics, associated with as many as a total of fifteen to twenty C atoms in side chains. It is conceivable, of course, that naphthenoaromatic nuclei are also present. It is believed that these side chains are short, with one or two C atoms per side chain, although due to the insolubility of this type of material in any solvent, this assumption could not be confirmed by NMR techniques. These short side chains could be derived from hydrocracking of naphthenoaromatic compounds or from hydrogenation of methylene linkages in the original coal structure.

Analysis of a Heavy Hydrogenated Fraction

<u>Compound Type</u>	<u>Weight Percent</u>	<u>Avg. MW</u>	<u>Compound Type</u>	<u>Weight Percent</u>	<u>Avg. MW</u>
$C_n H_{2n-0}$	0.033	308	$C_n H_{2n-36}$	0.147	379
$C_n H_{2n-2}$	0.077	129	$C_n H_{2n-38}$	0.072	386
$C_n H_{2n-4}$	0.254	185	$C_n H_{2n-40}$	0.013	410
$C_n H_{2n-6}$	0.298	102	$C_n H_{2n-42}$	0.015	415
$C_n H_{2n-8}$	0.792	153	$C_n H_{2n-44}$	0.002	400
$C_n H_{2n-10}$	1.675	195	$C_n H_{2n-4}^S$	0.004	126
$C_n H_{2n-12}$	1.425	228	$C_n H_{2n-16}^S$	0.003	226
$C_n H_{2n-14}$	2.196	236	$C_n H_{2n-18}^S$	0.002	231
$C_n H_{2n-16}$	4.312	248	$C_n H_{2n-20}^S$	0.005	252
$C_n H_{2n-18}$	5.743	270	$C_n H_{2n-10}^O$	0.006	203
$C_n H_{2n-20}$	6.931	286	$C_n H_{2n-12}^O$	0.010	215
$C_n H_{2n-22}$	7.628	282	$C_n H_{2n-14}^O$	0.013	178
$C_n H_{2n-24}$	6.066	302	$C_n H_{2n-16}^O$	0.066	228
$C_n H_{2n-26}$	4.407	322	$C_n H_{2n-18}^O$	0.163	240
$C_n H_{2n-28}$	2.794	327	$C_n H_{2n-20}^O$	0.062	248
$C_n H_{2n-30}$	1.393	340	$C_n H_{2n-22}^O$	0.093	264
$C_n H_{2n-32}$	1.095	341	$C_n H_{2n-24}^O$	0.122	294
$C_n H_{2n-34}$	0.378	365			

$C_n H_{2n-26}^O$	0.125	302	$C_n H_{2n-32}^O$	0.012	356
$C_n H_{2n-28}^O$	0.056	317	$C_n H_{2n-34}^O$	0.004	357
$C_n H_{2n-30}^O$	0.015	328			
Nonvolatile residue 51.50					

Note: This is the routine format, which does not include  $O_2$  or N compounds, and does not separate isomeric hydrocarbons.

Carbon Number Distribution in a Heavy Hydrogenated Fraction

<u>Carbon Number</u>	<u><math>C_n H_{2n-22}</math></u>	<u><math>C_n H_{2n-28}</math></u>	<u><math>C_n H_{2n-32}</math></u>	<u><math>C_n H_{2n-38}</math></u>
16	0.740	-	-	-
17	0.447	-	-	-
18	0.333	-	-	-
19	0.311	-	-	-
20	0.582	0.128	-	-
21	0.760	0.220	-	-
22	0.750	0.218	0.100	-
23	0.685	0.220	0.102	-
24	0.690	0.255	0.074	-
25	0.500	0.295	0.094	-
26	0.475	0.300	0.104	0.007
27	0.370	0.305	0.110	0.005
28	0.330	0.220	0.092	0.006
29	0.243	0.184	0.094	0.012
30	0.165	0.152	0.111	0.006
31	0.135	0.080	0.051	0.006
32	0.040	0.084	0.046	0.007
33	0.044	0.074	0.030	0.008
34	0.028	0.044	0.017	0.012
35	-	0.015	-	0.003
Total	7.628	2.794	1.025	0.072

CONCLUSION

High resolution-low voltage mass spectrometry is thus a very powerful tool for the characterization of coal liquefaction products and for yielding rapid and detailed data useful for process development studies. The method can also be applied to the volatile portions of powdered coal and coal extracts. The data obtained on a great many samples analyzed permitted us to gain some insight into the structure of coal.

ACKNOWLEDGEMENT

The authors wish to thank Mr. G. R. Taylor and Mr. J. L. Taylor who obtained the experimental mass spectral data.

## LITERATURE CITED

1. Lumpkin, H. E., *Anal. Chem.* 36, 2399 (1964).
2. Sharkey, A. G., Jr., Shultz, J. L., Kessler, T., "Procedures of the 15th Annual Conference on Mass Spectrometry and Allied Topics, May 1967, pp. 443-446. ASTM E-14; Denver, Colorado.
3. Kessler, T., Raymond, R. I., Sharkey, A. G., Jr., "Procedures of the 16th Annual Conference on Mass Spectrometry and Allied Topics, May 1968, pp. 356-358. ASTM E-14, Pittsburgh, Pennsylvania.
4. Shultz, J. L., Kessler, T., Friedel, R. A., Sharkey, A. G., Jr., *Ibidem*, pp. 359-361. LJ
5. Johnson, B. H., Aczél, Thomas, *Anal. Chem.* 39, 682, 1967.
6. Aczél, Thomas, Johnson, B. H. Preprints of papers, Division of Petroleum Chemistry, 153rd National Meeting of the American Chemical Society, Miami Beach, Florida, April 1967.
7. Aczél, Thomas, Allan, D. E., Harding, J. H., Knipp, E. A., "Procedures of the 16th Annual conference on Mass Spectrometry and Allied Topics, May 1968, pp. 366, 367. ASTM E-14, Pittsburgh, Pennsylvania.
8. Hill, G. R., Lyon, Lloyd B., *Ind. & Eng. Chem.* 54, 37 (1962).